The Investigation of Electronic Interactions in some Polyhalogenoaromatic Compounds using Electric Dipole Moment and NMR Studies

by

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TO MY PARENTS

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Abstract

The electric dipole moment of several polyfluoro-, polyfluoronitro- and polychlorofluoro-benzenes have been determined at 25°C in dilute solution in cyclohexane. The dipole moments of a range of polybromo- and polybromonitro-benzenes have been determined in *p*-xylene at 25°C The departures from additivity in the moments are discussed in terms of variations in atom polarisation, changing mesomeric effects or steric distortion; no evidence is found for these explanations. The assignment of an empirically calculated value to the C-NO_2 and C-halogen bond moments in various environments gives excellent correlation between the observed and calculated moments. This is explained in terms of an induced moment in the π-electron system caused by the primary group moment. The relative importance of the mesomeric and π-inductive effects of the nitro- and halogen-groups in conjugated systems are considered.

The influence of a substituent on the chemical shift of a magnetic nucleus is described. The substituent constant parameters are determined in terms of chemical shifts in ppm of the observed nuclei (^{1}H, ^{13}C, ^{19}F) at the *ortho*-, *meta*- and *para*- positions to the substituent in monosubstituted benzenes. The extent of correlation between the observed and calculated chemical shifts in the above range of compounds have been examined. The latter shifts are the sum of the appropriate substituent constants. No considerable agreement has been observed between these chemical shifts and their corresponding calculated values. The deviations are larger for the polysubstituted benzenes. No single explanation could be given for the origin of the effects causing the non-additivity of these chemical shifts.

The F-H coupling constants of the polychlorofluorobenzenes have been determined for the three spin systems of ABX type. The H-H and C-H coupling constants in polybromo- and polybromonitro-benzenes have been determined for several first order spectra.

The products of the reaction of sodium borohydride as a reducing agent in dimethyl sulfoxide, as solvent, over the range of polybromobenzenes have been examined. The mechanism of the reaction could be a nucleophilic attack of borohydride ion on the least electro-negative bromine atom of the ring.

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D.3 RESULTS AND DISCUSSION OF THE DIPOLE MOMENT INVESTIGATION

I. Dipole Moment Studies

D.1 Introduction

1. Nature of the Dipole Moment and Critical Observation on the Vectorial Additivity Scheme

It was first suggested by J.J. Thomson(1) as early as 1923 that the dipole moment of a polyatomic molecule $\vec{\mu}$ can be considered as the resultant of the vectorial combination of the moments belonging to the individual bonds and groups in that molecule. For example, in a molecule containing n bonds of different types,

$$\vec{\mu} = \sum_{i=1}^{n} \vec{\mu}_i \qquad (1)$$

where $\vec{\mu}_i$ is the moment characterising the i-th bond.

Thus, if the geometry of the molecule is known or can be assumed, calculation of the dipole moment is carried out by the usual rules of vectorial combination of the vectors of the bond moments. The moment of the bond present in a diatomic molecule can be taken as equal to the dipole moment of the molecule in question, but such bond moment values, if present in other molecules, are evidently of little use in computing the dipole moments of the other molecules. Determination of the absolute magnitude and direction of the bond moments is an extremely difficult task, the solution of which depends not only on the effective charge localised on the atoms forming the bond, but also on such contributions as the hybridisation state of the individual atoms, homopolar dipoles and the dipoles due to the presence of unshared pairs of electrons in hybrid orbitals. Therefore, an accurate calculation of the influence of all the factors mentioned is difficult at the present time and theoretical claculations of dipole moments of individual bonds are, in the main, of purely qualitative value.

In many cases, in the calculation of molecular dipole moments it is more convenient to use not bond moments but moments of individual groups of atoms. For example, the replacement of one of the hydrogen atoms in benzene by any atom or group such as the nitro-group will result in a finite dipole moment in the molecule, the magnitude of which should be equal to the vector sum of the moments of the bonds C-N, $N \rightarrow O$ and $N=O$ introduced and that of the hydrogen atom in the position para to it. Since calculation of the moment of C-H bond is a complex problem in which the choice of its direction and magnitude depends on whether it is linked to a carbon atom of sp^3 or sp^2 hybridisation state, it has a considerable effect on the values of the bond moments calculated from the dipole moments of organic compounds. Therefore its omission in this explicit form is very convenient.

Experimental evidence, such as X-ray and electron-diffraction measurements(2) together with zero molecular dipole moments of benzene, p-dihalogeno- and p-dinitro-benzenes confirm the planar hexagonal structure of the benzene ring and that the group moments of C-halogen, C-NO_2 and C-H must lie in the plane of the ring and act in exactly the opposite directions to each other. Therefore the dipole moments of disubstituted benzenes may be calculated by the vector law using:

for ortho-substituents. $\mu = \sqrt{\mu_1^2 + \mu_2^2 + \mu_1 \mu_2}$

for meta-substituents $\mu = \sqrt{\mu_1^2 + \mu_2^2 - \mu_1 \mu_2}$

for para-substituents $\mu = \mu_1 - \mu_2$

where μ_1 and μ_2 are the group moments of the two substituents.

Although the vector summation of the group moments present in a molecule gives a rough estimate of the value of the molecular moment, for many cases the agreement between the calculated and experimentally observed values is poor. Since the magnitudes of group moments are calculated from the dipole moments of molecules with only one polar group they consequently do not take into account the possibility of the mutual influence of the atoms and groups in more complex molecules. For instance, comparison of the dipole moment of aromatic compounds with those of their aliphatic analogues suggests that different group moments have to be assigned in the two cases (the situation is even more difficult when considering molecules such as polysubstituted benzenes). In this connection it is not sufficient to assume, as would seem quite reasonable, that, owing to the different states of hybridisation of the carbon orbitals in the two cases, the H-C bond moments differ in the two series. A single example will illustrate this; the moment of methyl chloride and chlorobenzene being 1.86 and 1.58 D, respectively, it follows that if we suppose the H-C bond moment (or hydrogen "group moment") in methyl chloride to be 0.40 D, a H-C bond moment of 0.10 D in benzene will account for the observed value of chlorobenzene. Hence we should expect the moment of nitromethane to be 0.30 D greater than that for nitrobenzene, since the observed value for p-chloronitrobenzene shows that the direction of the C-Cl and C-NO_2 moments are the same. Instead of being 4.31 D as anticipated, nitromethane has a moment of only about 3.20 D in benzene solution.

In order to explain these, and many similar, apparent anomalies which arise when the vector theory is applied, it is necessary to consider the various mechanisms by which the introduction of substituent groups may cause a displacement of electrons in the remainder of the molecule. Such effects can broadly be subdivided into electronic and steric components. In recent years a considerable amount of effort(3) has been made to explain and predict the effect of substituents on various physical properties. Since the range of compounds for which the effect of substituents are examined in the present work are polyhalogeno- and polyhalogenonitrobenzenes, our attention is devoted to describing mainly electronic and steric effects in benzene derivatives.

A. Types of Electronic Substituent Effects

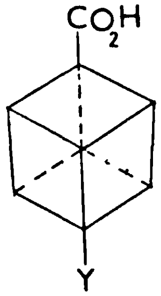
(a) Effects in saturated organic systems

When a substituent is attached to a σ-bonded system, its electronic effect on some property measured elsewhere in the molecule is usually referred to as a polar or inductive effect. The substituent generally has an electro-negativity different from the hydrogen atom that is replaced and mainly this is the site of the bond dipole moment.

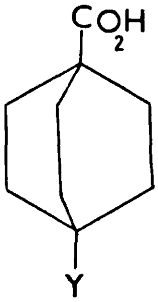
There are two important means of transmitting this effect to a site elsewhere in the molecule. The first is a progressive, but diminishing, relay of the effect along chains of carbon atoms.

$$\overset{\delta-}{Y}\text{—}\overset{\delta+}{CH_2}\text{—}\overset{\delta\delta+}{CH_2}\text{—}\overset{\delta\delta\delta+}{CH_2}\text{—}$$

The magnitude of which (symbolised I_σ) depends on the numbers of paths available and thus should be more effectively transmitted to the probe site in the cubane structure (IA) than in the 2,2,2-bicyclooctane structure (IB) even though the geometric relation of the probes to the substituents are almost identical.

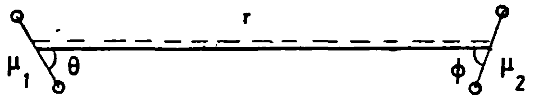


(IA)



(IB)

The other likely mode for transmission is a direct, through space, electrostatic effect as shown below.



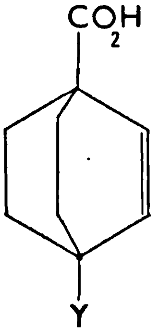
For two dipoles, if separated by the distance r, large compared to the lengths of the two dipoles, the magnitude of the effect in terms of potential energy of interaction will be expressed as,

$$E = \frac{2\mu_1\mu_2 \cos\theta \cos\Phi}{D\, r^3} \qquad (2)$$

where μ_1 and μ_2 are dipole moments of the two bonds, θ and Φ are the angles they make with the line joining the middle of the two dipoles and D the effective permittivity of the medium. The calculation of this interaction energy is quite inaccurate since much of the so-called field effect (symbolised F) is caused by lines of force within the solute cavity and thus D is generally much lower than the solvent permittivity and furthermore, molecular dipoles are not ordinary point charges separated by a given distance.

The two effects can be experimentally distinguished to a fair degree, although at the limit, lines of force close to the bonds, or polarisation through space or σ-bonds, merge into a common mechanism. There is evidence that in most reactions polar effects of substituents are largely field effects rather than inductive effects. Baker, Parish and Stock(4) compared the acidities of some of the derivatives of compounds of type (IA) and (IB), where the distance between the substituent and carboxy group is identical to within 0.1Å as is the orientation of the C-Y bonds with respect to the carboxy groups. On the other hand, there are three three-bond pathways for transmitting the inductive effect of the substituent to the carboxy group in the bicyclooctanecarboxylic acids but six (overlapping) three bond pathways in the cubane carboxylic acids. Thus to a first approximation, if only the field effect is operating, substituent effects should be of the same magnitude in each of the two series of acids, but if only the inductive effect is operating substituent effects should be twice as large in the cubane carboxylic acids as in the bicyclooctane carboxylic acids. Since it is found that the substituent effect on acidity is almost the same in both series, the field effect is the dominant factor.

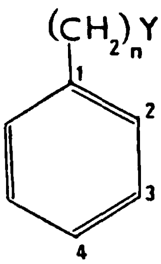
Now the inclusion of a more polarisable bond like a π-bond for instance will enhance the transmission by any through-bond relay, but, for example, in a molecule like 2,2,2-bicyclooctene (II) which is very similar to (IB), the experimental evidence(4) suggests a predominant field effect.



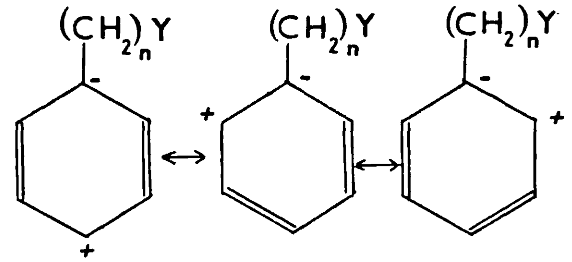
(II)

(b) Effects in π-systems

A polar substituent can have two types of effects in a π-system. First, induction of charge differences on the underlying σ-framework (I_σ effect) may change the π-electron distribution (π_σ effect). Thus for example in compound (III) a substituent more electro-negative than hydrogen can in principle induce a fractional positive charge in the σ-framework at C-1 and this may in turn induce a redistribution of π-electron density in the sense represented by the canonical forms (IIIA).



(III)



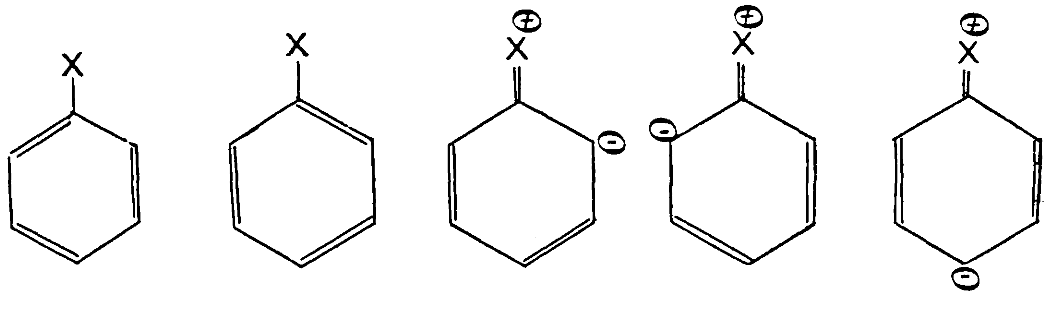
(IIIA)

Since the σ-induced disturbance of π-system diminishes rapidly, so it is disregarded where $n > 1$. But the field effect of the substituent may polarise the π-system directly (π_F effect) and this is felt most at the position closest to the substituent and depends on the geometry of the dipole.

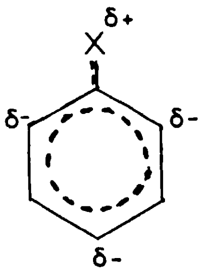
(c) Substituents attached directly to an unsaturated system

The effects discussed above can still exist here, although clearly it may be harder and less realistic to try to separate them as factors from the overall substituent effect. The possibility of large variations in charge transfer between the π-system and suitable orbitals of the substituent, the so-called resonance effect (R), is clearly very important in these systems.

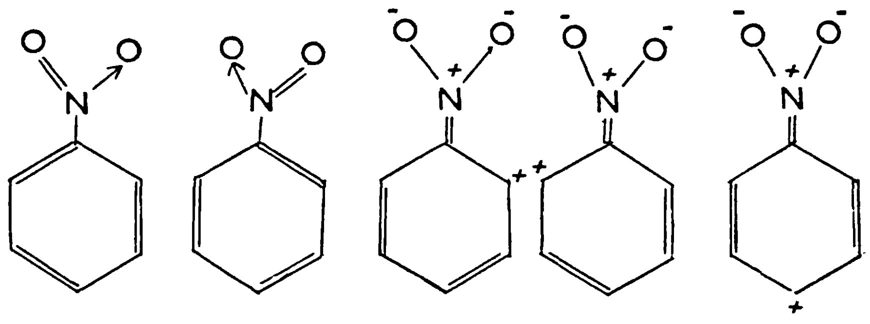
In substituted benzenes when the atom adjacent to the ring carries unshared electron pairs, the interaction of substituent orbitals of suitable symmetry with the π-orbitals of the ring can lead to contributions to the state of the molecule from structures in which these pairs are shared with the carbon atom of the ring, since this atom satisfies the necessary condition of being linked to another atom by a multiple bond and this leads to adjustments in the disposition of the other electrons, so the overall structure has contributions from the five structures.



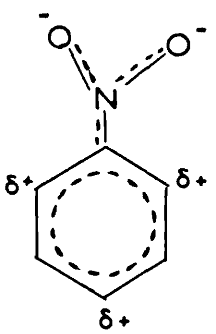
The result is that there are fractional negative charges on the ortho- and para- carbon atoms of the ring as indicated in the configuration below (symbolised +M effect).



On the other hand, when the substituent contains, adjacent to the ring, an atom which has no lone pair, but which is linked to another atom by double or triple bond, the opposite form of mesomeric effect (symbolised - M effect) is possible. The state of the molecule is then represented by the five structures, for nitrobenzene for example,



in which the three atomic orbitals of nitrogen in a trigonal (sp^2) hybridisation state will overlap with orbitals of the carbon atom and the two oxygen atoms respectively to form σ-bonds and as a result the three atoms linked to the nitrogen atom are coplanar with it and the remaining p-orbital, which is doubly occupied, is directed along an axis at right angles to this plane. This p-orbital and the singly occupied p-orbitals of the two oxygen atoms interact to give a mesomeric conjugated system. There will be therefore fractional positive charges at the positions ortho and para to the substituent groups, as shown in the configuration below.



The mesomeric interaction of a substituent with the benzene nucleus must correspond to the appearance of an additional moment directed from the substituent to the nucleus for + M substituents and in the opposite direction for − M substituents. Since the polarity of the C-X bond is generally such that the carbon atom acts as the positive pole, the mesomeric interaction leads to a reduction in the dipole moment of a substituted benzene as compared with a substituted alkane in the case of + M substituents and an increase in the case of − M substituents.

Sutton(5) proposed to call the difference in the values of the dipole moments of the corresponding saturated and benzene derivatives the mesomeric moment μ_M. He expressed the total moment of a compound as the vector sum of a group moment μ_g (the moment of the substituent), a moment μ_i induced in the carbon chain by the group moment and the mesomeric moment μ_M. By comparing the moments of aromatic compounds with those of the respective t-butyl compounds; where the μ_i's would be approximately the same, he calculated μ_M for a number of groups as the difference between the moments of corresponding t-butyl and aryl derivatives. For atoms or linear groups, μ_M is simply $\mu_{\text{aromatic}} - \mu_{\text{aliphatic}}$, whereas for bent groups, corrections have been made for the angle between the resultant and the C_1-C_4 axis. But induction in conjugated systems is rather different from that in saturated compounds. An additional term arises on account of the highly polarisable character of the π-electron system, and the inductive effect cannot be separated completely from the mesomeric effect: the mesomeric moment, therefore represents the sum of these effects.

A rather more exact treatment of this problem was attempted by Groves and Sugden$^{(6)}$, who evaluated the inductive effect in the aliphatic and aromatic compounds and thence derived the contribution to the moment from the mesomeric effect in the latter. This, however, led to the different values of resonance moments and to the opposite order for the halogens.

Mesomeric Moments in Benzene Derivatives

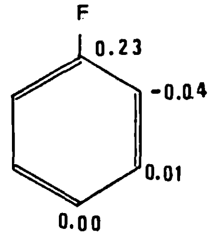
	OH	F	Cl	Br	I	OCH_3	CN	$COCH_3$	NO_2
Sutton$^{(5)}$	0.6	0.30	0.31	0.27	0.22	0.8	$^{-}0.79$	$^{-}1.43$	$^{-}0.96$
Groves and Sugden$^{(6)}$	1.12	1.00	0.97	0.89	0.87	0.40	$^{-}0.05$	$^{-}0.17$	$^{-}0.29$

It is doubtful that iodine has a larger positive μ_M than OCH_3, which raises a question about the reliability of those values too. But, the initial order assigned to the mesomeric moments of the halogens, chlorine with greater mesomeric moment than fluorine is in general inconsistent with chemical evidence. For instance the acid strengths of the p-halogenophenols and anilinium cations increase in the order $F < H < Cl < Br < I$, the mesomeric effect being so great in the case of the fluoro-compound as to reverse the inductive effect at the para position$^{(7)}$.

If there is an electron-accepting group in the para (or ortho) position to an electron-donating substituent in the benzene nucleus, a polar conjugation effect may be observed, which consists of the displacement of electrons from the electron-donating to the electron-accepting substituent through the phenylene system. This displacement of electrons may lead to the appearance of an additional moment, the vector of which will coincide with the direction of the vector of the mesomeric moments of the substituents. Consequently, the observed value of the dipole moments of molecules of this type may exceed the values calculated from the sum of the moments of the polar groups. It has been proposed to call the vectorial difference between the experimental and calculated dipole moments the interaction moment(8):

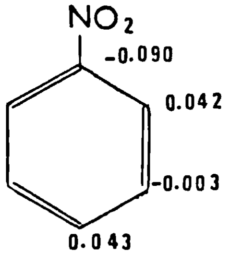
$$\overrightarrow{\mu}_{\text{int.}} = \overrightarrow{\mu}_{\text{exp.}} - \overrightarrow{\mu}_{\text{cal.}} \qquad (3)$$

The polar nature of a substituent or substituent-carbon bond can polarise a π-system without charge transfer. This has generally been referred to as π-inductive effect, the sum of π_F and π_σ effects, and in fact can be readily seen in calculation of its magnitude on fluorobenzene(9). Although these charge displacements are small and have the direction of an electron release: (the ortho-carbon has an electron excess of 0.003 electrons, the meta of 0.010 and the para-carbon of 0.007 electrons), they should be compounded with those from the electrostatic influence of fluorine acting in the opposite sense, and are probably swamped by them. ESCA(10) results on fluorobenzene however, based on the inductive (-I) and resonance (+M) effects, indicate that the overall charge on the ring is slightly positive relative to benzene (-I > +M).

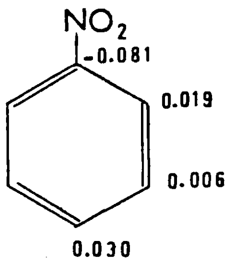


The actual mechanism of this additional redistribution within orbital theory has been described(11) as a mixing of π and π^* orbitals in the unsaturated system brought about through interaction with the substituent. The effect has been considered(12) in the past to be more important than resonance in connection with the ultraviolet spectra of many mono-substituted benzenes, but direct physical evidence for its existence in the ground state in such molecules is apparently not available.

There is little possibility of separating π_F and π_σ effects in directly substituted systems since they both affect mainly C-1 and give rise, for example, in substituted benzenes to a redistribution of electron population in the sense of (III A) page (7). Theoretical calculations for highly polar substituents indicate that the total π-inductive effect is significant: the figures below(13) give the ab initio calculated changes in the π-system for nitrobenzene both in the planar form and when resonance is eliminated by having the substituent orbitals orthogonal to the π-orbitals of the ring. Clearly the π-inductive effect is much more significant here than the π transfer (0.031 electron) that can occur in the planar form.



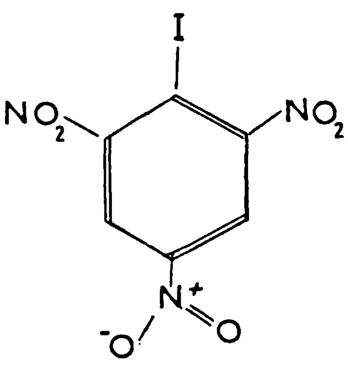
Planar

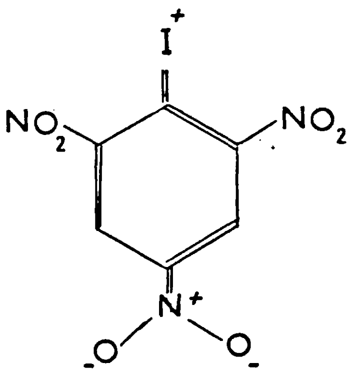


Orthogonal

B. Steric Effects of Substitutents in Benzene Derivatives

The introduction of voluminous groups into the ortho- position of a substituted benzene nucleus inhibits the conjugation of a substituent with the nucleus only in those cases where the effective volume of the substituent is sufficiently large to make a planar configuration of the molecule impossible and to turn the substituent relative to the plane of the nucleus by a sufficiently large angle. A good illustration is provided by picryl iodide. Diffraction studies$^{(14)}$ reveal that the p-nitro group is coplanar with the ring whereas the o-nitro groups are not.





This lack of coplanarity is due to the presence of the large iodine atom. As a result the C-N bond distance for the o-NO$_2$ groups is close to the aliphatic C-N length and there is a considerable double-bond character for the para C-N bond.

In o-dihalobenzenes, it has been suggested(15) that the deviation between the observed and calculated moments might be accounted for, in part, by widening of the angle between the two dipole axes by steric repulsion between the two groups. However, the results of electron-diffraction measurements(16) subsequently indicated no measurable angle widening in o-dichlorobenzene and a widening of only about 10° in o-diiodobenzene(17), while a widening of about 30° was necessary to account for the observed lowering. Spectroscopic investigations indicate(16) that the chlorine atoms in o-dichlorobenzene and the bromine atoms in o-dibromobenzene are pushed out of the plane of the ring by 18°, one above the ring, one below. The situation is further complicated by mutual distortion (polarisation) of the electron clouds associated with the two substituents.

2. Electric Dipole Moments of Polyhalogenobenzenes and Polyhalogenonitrobenzenes

Background

In early studies of the dipole moments of halogenobenzenes, investigators explained the deviations between the observed and calculated moments of polysubstitution in the benzene ring in terms of variations in atom polarisation, changes in mesomeric and inductive effects and steric distortion. The definitions of some of these terms have been given earlier in the introduction. A full discussion of their suggestions is given below.

Smallwood and Herzfeld(18) have measured the dipole moments of several polyhalogenobenzenes and polyhalogenonitrobenzenes, showing that the calculated moment of compounds of the type o-$C_6H_4X_2$ where X = halogens, -CH_3 and -NO_2 group by vectorial addition are from 10 to 30% higher than their experimental values. They suggested that since these molecules are not rigid and since each group is subjected to an electric force exerted by the other, dipole moments will be induced in each group in such a direction as to lessen the resultant moment. The inclusion of induced dipoles in the calculated magnitude of the dipole moments substantially improved agreements with their experimental values.

The dipole moments of several polyhalo aromatic compounds have been discussed in detail by Smyth and Lewis(19) who interpreted their results in terms of inductive and resonance effects. The effect of induction between groups is taken care of by using the moment of a di-, tri- or tetra-substituted molecule as a single vector. They suggested that only the inductive effect was required to explain the variation in moment where polysubstitution into the benzene ring by methyl groups and chlorine atoms is concerned. They found in their observations a fairly accurate agreement between the observed and calculated values of moments of meta-disubstituted benzenes, suggesting that, since the effect of mutual induction is small, therefore any increase of moment caused by decrease in double bond character must be small.

Littlejohn and Smith(20) have attempted to calculate the amount of reduction in moment due to mutual induction in both ortho- and meta-disubstituted halogenobenzenes and halogenonitrobenzenes. But they found that such mutual induction can account for only a small fraction of the differences observed between the moments of mono- and meta-disubstituted benzenes and also in ortho-disubstituted benzenes their calculated reductions were smaller than those observed by a factor of three. Mutual repulsion of the groups were suggested to be responsible partly for the reduction in the moments of the *ortho*-compounds, but in *meta*-disubstituted benzenes an increase of about 2½° in the angle between the dipoles would be necessary to account for the observed values of their dipole moments. The mesomeric effect of each group in the presence of the other would cause the moment of the *meta*-dihalogenobenzenes to be greater than those of the corresponding monohalogenobenzenes, which they found to be smaller than the moment of monohalogenobenzenes. Therefore, they concluded that although the total displacement of the electrons in the ring brought about by the inductive effect of the substituents is greater in the *meta*-disubstituted benzenes than in the mono-substituted benzenes, the effect attributable to each substituent is less in the former than in the latter. Hence, they suggested that in calculating "theoretical" values of the dipole moments of derivatives of *m*-dinitro- or *m*-dihalogeno-benzenes it seems most logical to assume the effective group moments to be equal to the moment of the corresponding disubstituted compound, although a slightly lower figure might be correct. So far as the *para*-disubstituted compounds are concerned they observed that *p*-chloro- and *p*-bromo-nitrobenzene moments exceed the calculated values by 0.12 D and 0.16D respectively. Such differences as have been mentioned earlier have usually been ascribed(19) to the mutual enhancement of the mesomeric effects of *o*-, *p*- and *m*-directing groups when they occupy positions *para* to one another. Later, Littlejohn and Smith(20) found that the moment of 3,5-dichloronitrobenzene also exceeds the calculated value by 0.12D. Knowing that in this molecule the mesomeric effects of the nitro-group and of the chlorine atoms cannot mutually enhance one another, they suggested that such differences might be due to the electron withdrawal effect of the nitro-group reducing the electron density of the ring through its strong inductive and mesomeric effect, causing the displacement of the ring electrons by the inductive effects of the halogen atoms to be much less than in the halogenobenzenes, so that the effective group moments of chlorine and bromine atoms are reduced to about 1.46 and 1.40 D, respectively. They added, in support of their argument that although the mesomeric moment of fluorine atom is greater than that of the other halogen atoms, the moment of p-fluoronitrobenzene exceeds the calculated value by only 0.11D.

Observed and Calculated Dipole Moments of nitro-compounds(20)

	$\mu_{(obs)}$ D	(a) $\mu_{(cal)}$ D	(b) $\mu_{(cal)}$ D	differences* D
p-Chloronitrobenzene	2.57	2.43	2.45	+0.12
p-Bromonitrobenzene	2.65	2.45	2.49	+0.16
p-Fluoronitrobenzene	2.62	2.53	2.51	+0.11
3,5-Dichloronitrobenzene	2.66	2.52	2.54	+0.12

(a) μ calculated neglecting induction.

(b) μ calculated with allowance for induction which is calculated considering the molecule as an aggregate of polarisable units.

* difference between the observed and calculated moments.

For the ortho-substituted nitrobenzenes, there is another factor which must come into play. As mentioned before, it is the coplanarity of the nitro-group with the benzene ring. Littlejohn and Smith(20) tried to calculate the effective moment of the nitro-group in some polysubstituted nitrobenzene compounds. Although the evidence obtained by Allen and Sutton(16) from electron-diffraction measurements suggests that C-Cl bonds in such compounds as o-dichlorobenzene and hexachlorobenzene are deflected by at least 18° out of the plane of the ring. Littlejohn and Smith(20) found that if the C-halogen and C-N bonds are each deflected to such an extent, thensymmetrical trihalogenotrinitrobenzenes should have dipole moments of the order of 1.5D, corresponding to an orientation polarisation at 20°C about $47 cm^3$. They suggested that even if the molecules were distributed between various structures with out-of-plane deflection of the groups such that adjacent groups are not always on opposite sides of the plane of the ring, the mean orientation polarisation would still be expected to be quite appreciable. They therefore concluded that, in polyhalogenonitrobenzenes and polyhalogenopolynitrobenzenes any bond deflection occurs in the plane of the ring and not at right angles to it. For o-chloro- and o-bromo-nitrobenzene, an increase in the angle between the axes of the C-N bond and C-halogen bonds would decrease the dipole moment of the molecule. In the 2,4,6-trisubstituted nitrobenzenes the nitro-group would not undergo in-plane displacement, so it would be expected that the C-X bond, where X=Cl, Br, $-CH_3$ and $-NO_2$ groups in the trisubstituted nitrobenzenes, might undergo greater deflection than the C-X bonds in o-substituted nitrobenzenes, but the angle between the C-N and C-X bond axes would be less than in the latter compound. Hence the steric obstruction to coplanarity of the nitro-groups with the ring might be expected to be greater in trisubstituted nitrobenzenes than in o-monosubstituted nitrobenzene.

Huang and Ng(21) have compared the steric effects of chloro-, bromo- and methyl-groups on the repression of $Ar^{+}=NO_2^{-}$ resonance by comparing the calculated molar Kerr constants, for planar configuration and when the nitro-group plane is perpendicular to the plane of the benzene ring, with the observed values in these compounds. Their calculations led to the conclusion that in 2,5-dihalogenonitrobenzene, there is a greater steric effect expected from an ortho-bromo-substituent than from an ortho-chloro one and in both compounds suppression of $Ar^{+}{=}NO_2^{-}$ resonance is apparently still incomplete. For 2,4,6-tribromonitrobenzene, following the same method of calculation and comparison with the corresponding experimentally determined value, they reached the conclusion that the plane of the nitro-group is almost perpendicular to that of the benzene ring, confirming the earlier suggestions of Littlejohn and Smith(20) from the dipole moment evidence, that repression of the mesomeric effect of the nitro-group is almost complete in 2,4,6-tribromonitrobenzene.

Considering the polyfluoronitrobenzene moments Huang(22) suggested that a simple way of seeing the effect of replacing the four hydrogens in the 2,3,5,6-position by fluorine atoms in _para_-substituted fluorobenzenes and in mono-substituted benzenes is to compare the moments of the derivatives of penta- and 2,3,5,6-tetra-fluorobenzenes with those of fluorobenzene and benzene respectively. In doing so, he concluded for the case when the substituent is the nitro-group, that the difference between the moment of pentafluoronitrobenzene with _p_-fluoronitrobenzene and 2,3,5,6-tetrafluoronitrobenzene with nitrobenzene is due to the presence of three factors: (a) steric inhibition of resonance between the nitro-group and the aromatic ring; (b) a competitive mechanism whereby the fluorine atoms decrease the charge density in both the π - and σ -framework of the ring system so effectively that the mesomeric effect of the nitro-group is repressed and (c) mutual induction (electrostatic field effect) between the nitro-group (which has high moment) and _o_-fluoro atoms. He suggested that half of the difference is due to the effect of (a) and the other half to a combined effect of (b) and (c).

As far as the interaction of halogens with pentafluorophenyl groups is concerned, Huang(22) suggested that the increase in the moment from fluorine to iodine as a substituent is either due to the magnitude of the atom polarisation which is inversely proportional to the out-of-plane bending frequency of the para-C-F and halogen bonds and this one due to an increase in mass of the halogen will be smaller for iodine than fluorine, therefore the atom polarisation would increase in the order I > Cl > Br > F, causing an increase in the moment from chloro- to bromo- and iodo-pentafluorobenzene. However, judging by the magnitude of the atomic polarisation of hexachlorobenzene(23) it is not certain that the whole of the apparent moment observed can be attributable to this cause. Arguing, again, that it might also be due to the polarisability of the halogen which increases from chlorine through bromine to iodine, so too would the effective moment of the carbon-halogen bond be increasingly reduced. In monohalogenobenzenes it has been suggested that(24) the high polarity of the carbon-halogen bond (with the halogen atom negative) would favour the transfer or back-donation of halogen lone-pair electrons to the benzene ring. But, in the pentafluorophenyl compounds, however, the relatively high electro-negativity of the C_6F_5 group would lower the polarity of the ring substituent σ -bond so that the tendency of the halogen to donate its lone-pair will be correspondingly reduced.

In a recent paper, Sandall et al(25) have determined the dipole moments of polychlorobenzenes and toluenes and suggested that departure of the moments from additivity resulted from inductive effects between ortho-substituted (and to a lesser extent meta-substituted) chlorine atoms which lessen the apparent C-Cl bond moment. They found no evidence for suggesting that the departures from additivity were due to variations in atom polarisation, mesomeric effects or steric distortion.

D.2 Experimental Procedure of Determination of Dipole Moments

1. Methods of Determining Dipole Moments

The practical determination of dipole moments by measuring the permittivity of solutions is based on the existence of an orientation effect for polar molecules in an applied electric field. The calculated magnitudes of dipole moments may be regarded as reliable only where intermolecular interactions are excluded and the molecule can freely orient itself in the applied field. For this reason the most reliable data on dipole moments are obtained from studies in the gas phase at very low pressures when the distance between any two molecules is so large that electrostatic interaction between them can be assumed to be non-existent. The method of determination possesses some disadvantages of a practical nature such as the comparative complexity of the apparatus used, its laboriousness, and the impossibility in many cases of converting the substance from the condensed phase into the vapor phase without decomposition. A full description of its application is outside the scope of the present work.

The second method, which is the method used in this work, is based on measurements of the permittivity of dilute solutions of polar substances in non-polar solvents.

(i) Determination of the Dipole Moment in Dilute Solutions

The calculation of molecular polarisation and dipole moment, by the application of the Clausius-Mosotti and Debye equations to a single polar solution in a non-polar solvent, requires the determination of the permittivities, densities and refractive indices of a series of solutions of graded concentration.

For a solution sufficiently dilute for the solute molecules to be without influence on each other, Debye expressed the molar polarisation of the solution, $P_{1,2}$ as:

$$P_{1,2} = P_1X_1 + P_2X_2 = \frac{\epsilon_{1,2} - 1}{\epsilon_{1,2} + 2}(M_1X_1 + M_2X_2)\frac{1}{d_{1,2}} \qquad (4)$$

where P_1 = molar polarisation of solvent

P_2 = molar polarisation of solute

$\epsilon_{1,2}$ = permittivity of the solution

$\frac{1}{d_{1,2}}$ = specific volume of the solution

X_1, X_2 = mole fractions of the solvent and solute respectively

M_1, M_2 = molecular weights of solvent and solute respectively

Since the polarisation of the solution $P_{1,2}$ is determined directly from the experimental values of the permittivity and the density and the mole fractions X_1 and X_2 are given, it is easy to calculate the values of the molar polarisation of the solute, P_2, from formula (5), on the assumption that the polarisation P_1 is taken as equal to the polarisation of the pure solvent.

$$P_2 = \frac{P_{1,2} - P_1}{X_2} + P_1 \qquad (5)$$

The results obtained are used to plot a curve of P_2 as a function of the concentration. To exclude the effect of residual interaction between the molecules of the solute, P_2 is extrapolated to zero concentration (X_2=0) and the value of the molar polarisation at infinite dilution, $P_{2\infty}$ is found:

$$P_{2\infty} = \lim_{x_2 \to 0} P_2 = \lim_{x_2 \to 0} \left(\frac{P_{1,2} - P_1}{X_2} + P_1 \right) \qquad (6)$$

Knowing the value of $P_{2\infty}$ the dipole moment, μ, of the solute may then be obtained from the Debye equation:

$$P_{2\infty} = \frac{4}{3} \pi N \alpha_d + \frac{4}{3} \pi N \frac{\mu^2}{3KT} \qquad (7)$$

where α_d = distortion polarisation of the solute,

N = Avogadro Number

K = Boltzmann Constant

if the value of α_d is known. The term $\frac{4}{3} \pi N \alpha_d$ is known as the distortion polarisation, P_D, the sum of the electron polarisation, P_E and atom polarisation, P_A. Usually P_D is computed as R_2 from measurements of refractive index, applied to the Lorentz-Lorenz formula describing the optical behaviour of a substance:

For a dilute solution it is,

$$R_{1,2} = R_1 X_1 + R_2 X_2 = \frac{n_D^2 - 1}{n_D^2 + 2} (M_1 X_1 + M_2 X_2) \frac{1}{d_{1,2}} \qquad (8)$$

where n_D = refractive index of the solution for the sodium D line

$R_{1,2}, R_1, R_2$ = molar refractions of the solution, solvent and solute

Alternatively R_2 may be calculated as the sum ofthe bond refractions of the solute. Hence:

$$\frac{4\pi N\mu^2}{9KT} = P_{2\infty} - R_2 \qquad (9)$$

and therefore,

$$\mu = 0{\cdot}012812\sqrt{(P_{2\infty} - R_2)T} \qquad (10)$$

The extrapolation of the polarisation P_2 to infinite dilution is not accurate because of the curvilinear nature of the function $P_2=f(X_2)$. In view of this, attempts have been made to decrease the errors by using extrapolation formulae.

Halverstadt and Kumlar(26) have used a linear dependence of the dielectric constant and the specific volume v of the solution on the weight function of the solute:

$$\epsilon_{1,2} = \epsilon_1 + \alpha W_2 \qquad (11)$$

$$v_{1,2} = v_1 + \beta W_2 \qquad (12)$$

Where ϵ_1, v_1 are the permittivity and specific volume of the pure solvent,

α, β are constants.

From the Clausius-Mosotti equation in the form:

$$P_{1,2} = \frac{\epsilon_{1,2} - 1}{\epsilon_{1,2} + 2} v_{1,2} \qquad (13)$$

Where $P_{1,2}$ = specific polarisation of the solution, it follows from (11), (12), (13) that:

$$P_{2\infty} = \frac{3\,\alpha\,v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{\epsilon_1 - 1}{\epsilon_1 + 2} \qquad (14)$$

Where $P_{2\infty}$ is the specific polarisation of the solute at infinite dilution, the specific refraction may be calculated from the equation:

$$r_2 = \frac{3\,\gamma\,v_1}{(n_1^2 + 2)^2} + (v_1 + \beta)\frac{n_1^2 - 1}{n_1^2 + 2} \qquad (15)$$

which is analogous to equation (14) with ϵ replaced by n^2 and α by γ, the slope of the plot of $n^2_{1,2}$ against W_2 which is normally linear. The dipole moment may then be calculated from the equation.

While experimental results confirm that usually $v_{1,2}$ is linear with W_2 it is often the case that the $\epsilon_{1,2} - W_2$ plot is curved, even in solutions sufficiently dilute to preclude the possibility of self-association of the solute. Smith and Cleverdon(27) pointed out that in such a case it is better to assume that the variation of the dielectric constant with weight fraction follows the form:

$$\epsilon_{1,2} = \epsilon_1 + \alpha W_2 + \grave{\alpha} W_2^2 \qquad (16)$$

where α has the same significance as before, i.e. the value of $\frac{\partial \epsilon}{\partial W}$ at zero concentration.

(ii) Determination of Molecular Refraction

The molecular refractions were calculated by addition of individual bond refractions for the yellow sodium line (5893 Å) (n_D), which are given in the literature(28). Accuracy of molecular refraction values calculated by the method above, were checked by measuring the molecular polarisation of p-difluoro-, p-dichloro- and p-dibromo-benzene. Because of the absence of a permanent dipole in these molecules, the total polarisation (P_{Tot}) is equal to the sum of electronic and atomic polarisation.

According to our experimental data, the molecular refraction calculated for p-difluorobenzene was 15% and that of p-dichlorobenzene 5% lower than their corresponding molecular polarisation. This lowering can be attributed to the fact that in molecular refraction calculations the atomic polarisation of molecules are not completely accounted for. Therefore, 15% of the calculated values of the molecular refractions in the case of polyfluoro- and polyfluoronitro-benzenes and 5% of the calculated values of the molecular refractions in the case of polychlorofluorobenzenes were considered as their corresponding atomic polarisation in order to obtain the dipole moments. For p-dibromobenzene, the molecular refraction calculated by the above method was found to be equal to its total polarisation. This means that the atom polarisation is negligible for the range of polybromobenzenes and molecular refractions (calculated considering the bond refractions) are sufficient to account for the distortion polarisation (which is the sum of the electronic and the atomic polarisation).

2. Practical Determination of Dipole Moments in Dilute Solutions

(a) Apparatus

The permittivities of the solutions were determined using the Dipolemeter, Type DM01, manufactured by the Wissens-chaftlich-Technische Werkstätten GMbH. This is a heterodyne beat apparatus, internally thermostated, in which the arithmetical difference in the frequency of two oscillators is detected as a trace on a cathode ray tube. The oscillations are brought into superposition and after amplification the resulting beats are made visible on the C.R.O., enabling observations to be made within fractions of a beat frequency of one Hz.

The dielectric measuring cell containing the experimental solution and the measuring condenser, which is connected in parallel, are part of one oscillating circuit. By tuning the measuring condenser the two capacities can be so adjusted that the resulting frequency is equal to that of a standard oscillator.

Internal standard condensers permit control of the calibration independently of the measuring condenser. A precision dial with 4,500 divisions enables the position of the measuring condenser to be read with the required accuracy.

For liquids a measuring frequency of 1800 KHz is used and the indicating and measuring sensitivities are 1×10^{-6} and 4×10^{-4} respectively. The range is from 1.0 to 3.0 permittivity units using the cell type DFL1. This cell is equipped for thermostatic control ($\pm 0.02^{\circ}$). Its capacity is 20 ml and the interior plates are gold coated.

The instrument was calibrated by determining the scale reading of the measuring condenser for three pure solvents of known permittivity. A linear relationship between permittivity and scale reading was observed, and hence the slope of the line was determined and used for subsequent evaluation of the permittivity. The calibration was checked periodically and remained unaltered.

Solvent	Scale Reading (S)	ϵ* 25.0
Benzene	3786.0	2.2725
Cyclohexane	3146.5	2.015
Carbontetrachloride	3673.2	2.2274
_p_-Xylene	3743.4	2.2630

*Mean literature value

Hence for benzene and cyclohexane:

$$\frac{\Delta\epsilon}{\Delta S} = 4.027 \times 10^{-4}$$

and for cyclohexane and carbon tetrachloride:

$$\frac{\Delta\epsilon}{\Delta S} = 4.033 \times 10^{-4}$$

Mean Value $\frac{\Delta\epsilon}{\Delta S} = 4.03 \times 10^{-4}$

and hence

$$\epsilon_x = 2.015 - 4.03 \times 10^{-4} (3146.5 - S_X) \qquad (17)$$

or for solutes in _p_-xylene as solvent

$$\epsilon_x = 2.2630 - 4.03 \times 10^{-4} (3743.4 - S_X) \qquad (18)$$

Where ϵ_x , S_X are the permittivity and scale reading for the unknown solution.

Densities of solutions were measured using a Warden's pyknometer, the volume of which was determined at 25.0°C using boiled out, de-ionised water, the specific volume of the pure solvent was determined for each series of measurements and the value obtained compared with that in the literature.

(b) Experimental Procedure

Four to six solutions of accurately known weight fraction, ranging from 0.001 to 0.2 in the solvent were prepared. For polyfluorobenzenes, polyfluoronitrobenzenes and polyfluorochlorobenzenes the solvent used was cyclohexane. Since polybromobenzenes and polybromonitrobenzenes are not very soluble in cyclohexane, p-xylene was used as solvent. Before use the dipolemeter was switched on and allowed to stand for two hours to attain its working termpature of 40°C. The cell was connected via a pump to a waterbath maintained at 25.0 ± 0.02°C. Before each measurement the cell was rinsed with dry ether and purged of ether vapour with a current of nitrogen gas. The solution under test was then introduced into the cell, care being taken to avoid the formation of bubbles. After equilibrium, the constant scale reading of the measuring condenser was observed. The readings are subject to a small error due to non-linearity of the measuring condenser-permittivity relationship. This was eliminated by using a calibration graph supplied with the instrument. The permittivity was then calculated from (17) or (18) according to the solvent used. Permittivities and specific volumes are found to be linear with weight fraction of the solutes over the concentration ranges studied.

The following Tables list experimental data for 64 compounds and the parameters derived from this data, as defined in parts (i) and (ii) of this section.

1. Fluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.63	2.0221	1.2914
8.78	2.0327	1.2899
12.27	2.0401	1.2889
12.62	2.0410	1.2888
18.59	2.0525	1.2873
27.69	2.0718	1.2847

$\alpha = 2.05 \pm 0.01$, $\beta = {}^{-}0.273 \pm 0.003$

$P_{2\infty} = 72.06\ \mathrm{cm}^3$, $P_d = 29.84\ \mathrm{cm}^3$

$\mu = 1.44 \pm 0.01$ D

2. *o*-Difluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.20	2.0387	1.2902
10.13	2.0619	1.2881
12.46	2.0730	1.2871
16.08	2.0901	1.2858
18.56	2.1021	1.2848
22.96	2.1226	1.2829

$\alpha = 4.70 \pm 0.02$, $\beta = {}^{-}0.404 \pm 0.004$

$P_{2\infty} = 154.45\ \mathrm{cm}^3$, $P_d = 29.57\ \mathrm{cm}^3$

$\mu = 2.47 \pm 0.03$ D

3. *m*-Difluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
8.92	2.0293	1.2887
12.75	2.0360	1.2873
17.95	2.0441	1.2854
21.62	2.0505	1.2839
25.31	2.0570	1.2824

$\alpha = 1.65 \pm 0.01$, $\beta = {}^{-}0.384 \pm 0.003$

$P_{2\infty} = 71.41\ \mathrm{cm}^3$, $P_d = 29.57\ \mathrm{cm}^3$

$\mu = 1.43 \pm 0.01$ D

4. *p*-Difluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.26	2.2603	1.1625
9.54	2.2612	1.1610
10.88	2.2612	1.1607
14.09	2.2620	1.1597
18.40	2.2628	1.1586

$\alpha = 0.025 \pm 0.08$, $\beta = {}^{-}0.278 \pm 0.003$

$P_{2\infty} = 30.46\ \mathrm{cm}^3$, $P_d = 25.71\ \mathrm{cm}^3$

5. 1.2,4-Trifluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.67	2.0196	1.2917
9.51	2.0273	1.2878
11.63	2.0303	1.2869
14.50	2.0341	1.2854
19.53	2.0406	1.2844
22.20	2.0442	1.2816

$\alpha = 1.320 \pm 0.006$, $\beta = {}^{-}0.47 \pm 0.04$

$P_{2\infty} = 69.34 \text{ cm}^3$, $P_d = 29.29 \text{ cm}^3$

$\mu = 1.40 \pm 0.02$ D

6. 1,2,3,4-Tetrafluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.02	2.0244	1.2913
8.52	2.0418	1.2881
12.90	2.0563	1.2857
14.70	2.0623	1.2847
23.80	2.0915	1.2800
26.80	2.1025	1.2782

$\alpha = 3.26 \pm 0.02$, $\beta = {}^{-}0.53 \pm 0.01$

$P_{2\infty} = 146.50 \text{ cm}^3$, $P_d = 29.03 \text{ cm}^3$

$\mu = 2.40 \pm 0.01$ D

7. 1,2,3,5-Tetrafluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2942
5.26	2.0197	1.2910
7.90	2.0226	1.2896
11.10	2.0262	1.2874
13.90	2.0293	1.2860
16.70	2.0325	1.2844
23.90	2.0404	1.2798

$\alpha = 1.08 \pm 0.02$, $\beta = {}^{-}0.54 \pm 0.03$

$P_{2\infty} = 67.48 \text{ cm}^3$, $P_d = 29.03 \text{ cm}^3$

$\mu = 1.37 \pm 0.02$ D

8. Pentafluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.70	2.0183	1.2902
8.19	2.0223	1.2879
11.04	2.0250	1.2862
12.93	2.0268	1.2851
19.96	2.0335	1.2813
20.32	2.0338	1.2809

$\alpha = 0.93 \pm 0.01$, $\beta = {}^{-}0.55 \pm 0.01$

$P_{2\infty} = 69.09 \text{ cm}^3$, $P_d = 28.76 \text{ cm}^3$

$\mu = 1.40 \pm 0.01$ D

9. Nitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.77	2.0580	1.2905
8.56	2.1116	1.2884
10.78	2.1384	1.2874
14.37	2.1790	1.2858
20.49	2.2502	1.2830
23.83	2.2909	1.2817

$\alpha = 11.56 \pm 0.06$, $\beta = {}^{-}0.444 \pm 0.003$

$P_{2\infty} = 368.31$ cm^3, $P_d = 31.86$ cm^3

$\mu = 4.06 \pm 0.01$ D

10. *o*-Fluoronitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
0.312	2.0192	1.2921
0.563	2.0225	1.2920
0.871	2.0265	1.2917
1.09	2.0296	1.2914
1.14	2.0302	1.2915
1.83	2.0393	1.2913

$\alpha = 13.29 \pm 0.06$, $\beta = {}^{-}0.57 \pm 0.08$

$P_{2\infty} = 476.38$ cm^3, $P_d = 36.37$ cm^3

$\mu = 4.64 \pm 0.03$ D

11. *m*-Fluoronitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.79	2.0575	1.2894
10.81	2.0918	1.2867
19.33	2.1570	1.2822
21.43	2.1749	1.2815
23.33	2.1884	1.2805
25.96	2.2095	1.2791

$\alpha = 7.49 \pm 0.01$, $\beta = {}^{-}0.506 \pm 0.006$

$P_{2\infty} = 281.99$ cm^3, $P_d = 36.37$ cm^3

$\mu = 3.47 \pm 0.01$ D

12. *p*-Fluoronitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.25	2.0191	1.2912
2.70	2.0237	1.2906
12.60	2.0677	1.2856
15.90	2.0803	1.2838
20.90	2.1024	1.2814
23.90	2.1148	1.2798

$\alpha = 4.23 \pm 0.04$, $\beta = {}^{-}0.511 \pm 0.005$

$P_{2\infty} = 171.28$ cm^3, $P_d = 36.37$cm^3

$\mu = 2.57 \pm 0.02$ D

13. 2,4-Difluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2921
6.60	2.0537	1.2887
12.79	2.0896	1.2852
16.22	2.1108	1.2833
19.40	2.1344	1.2816
25.04	2.1642	1.2783

$\alpha = 6.02 \pm 0.10$, $\beta = {}^{-}0.56 \pm 0.01$

$P_{2\infty} = 259.90\ \text{cm}^3$, $P_d = 36.09\ \text{cm}^3$

$\mu = 3.31 \pm 0.03$ D

14. 3,4-Difluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.55	2.0251	1.2926
9.19	2.0413	1.2872
10.76	2.0466	1.2861
11.96	2.0501	1.2856
16.91	2.0643	1.2830
19.69	2.0729	1.2813

$\alpha = 2.94 \pm 0.02$, $\beta = {}^{-}0.61 \pm 0.05$

$P_{2\infty} = 139.84\ \text{cm}^3$, $P_d = 36.09\ \text{cm}^3$

$\mu = 2.25 \pm 0.03$ D

15. 2,6-Difluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.63	2.0322	1.2912
2.85	2.0512	1.2904
3.57	2.0614	1.2899
6.12	2.0981	1.2881
7.46	2.1203	1.2873
7.66	2.1239	1.2871

$\alpha = 14.47 \pm 0.35$, $\beta = {}^{-}0.67 \pm 0.01$

$P_{2\infty} = 578.29\ \text{cm}^3$, $P_d = 36.09\ \text{cm}^3$

$\mu = 5.15 \pm 0.06$ D

16. 2,4,6-Trifluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.13	2.0331	1.2902
7.95	2.0611	1.2874
10.40	2.0760	1.2861
13.62	2.0947	1.2844
15.70	2.1076	1.2843
20.30	2.1350	1.2804

$\alpha = 5.91 \pm 0.03$, $\beta = {}^{-}0.55 \pm 0.03$

$P_{2\infty} = 284.77\ \text{cm}^3$, $P_d = 35.82\ \text{cm}^3$

$\mu = 3.49 \pm 0.02$ D

17. 2,3,4-Trifluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.65	2.0218	1.2910
1.99	2.0233	1.2909
2.03	2.0235	1.2909
2.19	2.0243	1.2908
2.30	2.0239	1.2907
3.06	2.0279	1.2902

$\alpha = 4.16 \pm 0.01$, $\beta = {}^{-}0.65 \pm 0.03$

$P_{2\infty} = 205.81\ \text{cm}^3$, $P_d = 35.82\ \text{cm}^3$

$\mu = 2.90 \pm 0.01$ D

18. 2,4,5-Trifluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
4.51	2.0285	1.2892
5.61	2.0316	1.2884
11.09	2.0522	1.2843
12.64	2.0595	1.2828

$\alpha = 3.53 \pm 0.16$, $\beta = {}^{-}0.74 \pm 0.02$

$P_{2\infty} = 174.96\ \text{cm}^3$, $P_d = 35.82\ \text{cm}^3$

$\mu = 2.61 \pm 0.07$ D

19. 2,3,4,5-Tetrafluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.20	2.0200	1.2903
9.77	2.0304	1.2921
12.20	2.0346	1.2846
15.97	2.0406	1.2823
21.58	2.0494	1.2787
28.69	2.0607	1.2743

$\alpha = 1.60 \pm 0.01$, $\beta = {}^{-}0.66 \pm 0.10$

$P_{2\infty} = 106.20\ \text{cm}^3$, $P_d = 35.55\ \text{cm}^3$

$\mu = 1.86 \pm 0.06$ D

20. 2,3,4,6-Tetrafluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.57	2.0226	1.2910
3.81	2.0299	1.2898
4.63	2.0341	1.2891
5.92	2.0393	1.2883
5.96	2.0398	1.2881
6.84	2.0438	1.2875

$\alpha = 4.10 \pm 0.11$, $\beta = {}^{-}0.67 \pm 0.02$

$P_{2\infty} = 222.94\ \text{cm}^3$, $P_d = 35.55\ \text{cm}^3$

$\mu = 3.03 \pm 0.05$ D

21. Pentafluoronitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.40	2.0236	1.2887
6.33	2.0249	1.2882
11.03	2.0319	1.2853
12.51	2.0346	1.2843
22.66	2.0504	1.2779
23.45	2.0520	1.2772

$\alpha = 1.57 \pm 0.01$, $\beta = {}^{-}0.635 \pm 0.004$

$P_{2\infty} = 115.81\ \mathrm{cm}^3$, $P_d = 35.28\ \mathrm{cm}^3$

$\mu = 1.98 \pm 0.01$ D

22. Chlorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
6.24	2.0278	1.2901
8.56	2.0333	1.2890
10.84	2.0376	1.2882
12.08	2.0408	1.2877
15.27	2.0470	1.2866
25.33	2.0680	1.2830

$\alpha = 2.10 \pm 0.02$, $\beta = {}^{-}0.37 \pm 0.01$

$P_{2\infty} = 83.04\ \mathrm{cm}^3$ $P_d = 32.57\ \mathrm{cm}^3$

$\mu = 1.57 \pm 0.01$ D

23. *o*-Chlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
4.07	2.0308	1.2903
9.66	2.0531	1.2879
12.58	2.0634	1.2867
16.41	2.0794	1.2850
18.86	2.0890	1.2839
22.59	2.1012	1.2822

$\alpha = 3.86 \pm 0.04$, $\beta = {}^{-}0.439 \pm 0.003$

$P_{2\infty} = 149.28\ \mathrm{cm}^3$, $P_d = 32.32\ \mathrm{cm}^3$

$\mu = 2.39 \pm 0.02$ D

24. *m*-Chlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
6.45	2.0250	1.2895
8.35	2.0285	1.2885
10.70	2.0320	1.2876
14.17	2.0378	1.2860
15.91	2.0404	1.2852
26.84	2.0583	1.2804

$\alpha = 1.61 \pm 0.01$, $\beta = {}^{-}0.441 \pm 0.003$

$P_{2\infty} = 78.61\ \mathrm{cm}^3$, $P_d = 32.32\ \mathrm{cm}^3$

$\mu = 1.50 \pm 0.01$ D

25. *p*-Chlorofluorobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.89	2.0160	1.2895
7.83	2.0162	1.2886
13.09	2.0171	1.2865
15.06	2.0175	1.2855
18.56	2.0181	1.2838
26.77	2.0195	1.2802

$\alpha = 0.169 \pm 0.003$, $\beta = {}^{-}0.45 \pm 0.01$

$P_{2\infty} = 33.09\ \text{cm}^3$, $P_d = 32.32\ \text{cm}^3$

$\mu = 0.194 \pm 0.03$ D

26. 2,3-Dichlorofluorobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.27	2.0323	1.2892
8.22	2.0424	1.2875
9.41	2.0437	1.2868
15.72	2.0677	1.2833
19.54	2.0784	1.2810

$\alpha = 3.28 \pm 0.08$, $\beta = {}^{-}0.57 \pm 0.003$

$P_{2\infty} = 160.23\ \text{cm}^3$, $P_d = 37.40\ \text{cm}^3$

$\mu = 2.45 \pm 0.03$ D

27. 2,4-Dichlorofluorobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.28	2.0200	1.2893
8.65	2.0239	1.2874
11.16	2.0260	1.2862
15.47	2.0307	1.2835
17.51	2.0325	1.2825
20.40	2.0358	1.2809

$\alpha = 1.02 \pm 0.01$, $\beta = {}^{-}0.56 \pm 0.01$

$P_{2\infty} = 71.01\ \text{cm}^3$, $P_d = 37.40\ \text{cm}^3$

$\mu = 1.28 \pm 0.02$ D

28. 2,5-Dichlorofluorobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.30	2.0213	1.2891
8.46	2.0256	1.2869
9.42	2.0269	1.2863
10.99	2.0294	1.2850

$\alpha = 1.30 \pm 0.04$, $\beta = {}^{-}0.65 \pm 0.02$

$P_{2\infty} = 78.37\ \text{cm}^3$, $P_d = 37.40\ \text{cm}^3$

$\mu = 1.42 \pm 0.04$ D

29. 2,6-Dichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.75	2.0214	1.2912
2.56	2.0250	1.2909
2.87	2.0263	1.2907
5.96	2.0375	1.2890
7.06	2.0420	1.2885

$\alpha = 3.81 \pm 0.05, \ \beta = {}^{-}0.53 \pm 0.01$

$P_{2\infty} = 182.97 \text{ cm}^3, \ P_d = 37.40 \text{ cm}^3$

$\mu = 2.67 \pm 0.02$ D

30. 3,4-Dichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
6.06	2.0203	1.2890
11.37	2.0256	1.2859
13.33	2.0275	1.2848
16.06	2.0300	1.2832
20.37	2.0341	1.2809
21.94	2.0357	1.2799

$\alpha = 0.95 \pm 0.01, \ \beta = {}^{-}0.562 \pm 0.004$

$P_{2\infty} = 68.15 \text{ cm}^3, \ P_d = 37.40 \text{ cm}^3$

$\mu = 1.23 \pm 0.01$ D

31. 3,5-Dichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
4.83	2.0159	1.2897
7.70	2.0165	1.2882
11.57	2.0174	1.2860
14.01	2.0180	1.2847
19.32	2.0192	1.2818
20.19	2.0194	1.2814

$\alpha = 0.222 \pm 0.004, \ \beta = {}^{-}0.539 \pm 0.003$

$P_{2\infty} = 40.23 \text{ cm}^3, \ P_d = 37.40 \text{ cm}^3$

$\mu = 0.372 \pm 0.002$ D

32. 2,3,6-Trichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
4.74	2.0239	1.2891
9.13	2.0322	1.2862
11.98	2.0383	1.2844
14.31	2.0422	1.2829
16.70	2.0470	1.2814

$\alpha = 1.92 \pm 0.02, \ \beta = {}^{-}0.648 \pm 0.003$

$P_{2\infty} = 124.60 \text{ cm}^3, \ P_d = 42.47 \text{ cm}^3$

$\mu = 2.00 \pm 0.02$ D

33. 3,4,5-Trichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.70	2.0169	1.2899
6.20	2.0181	1.2883
10.76	2.0205	1.2853
12.43	2.0214	1.2845
16.56	2.0237	1.2818
19.29	2.0251	1.2786

$\alpha = 0.526 \pm 0.005$, $\beta = {}^{-}0.68 \pm 0.03$

$P_{2\infty} = 56.11\ \text{cm}^3$, $P_d = 42.47\ \text{cm}^3$

$\mu = 0.82 \pm 0.02$ D

34. 2,4,5-Trichlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
3.29	2.0154	1.2903
7.96	2.0162	1.2872
12.83	2.0170	1.2845
16.10	2.0179	1.2822
21.05	2.0188	1.2792

$\alpha = 0.184 \pm 0.09$, $\beta = {}^{-}0.62 \pm 0.01$

$P_{2\infty} = 42.73\ \text{cm}^3$, $P_d = 42.47\ \text{cm}^3$

$\mu = 0.11 \pm 0.01$ D

35. 2,3,5,6-Tetrachlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
1.91	2.0165	1.2911
2.16	2.0169	1.2910
3.89	2.0179	1.2897
5.39	2.0192	1.2885
6.63	2.0198	1.2878
7.13	2.0202	1.2875

$\alpha = 0.72 \pm 0.02$, $\beta = {}^{-}0.68 \pm 0.02$

$P_{2\infty} = 76.73\ \text{cm}^3$, $P_d = 47.55\ \text{cm}^3$

$\mu = 1.19 \pm 0.05$ D

36. 2,3,4,6-Tetrachlorofluorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
2.98	2.0192	1.2895
3.79	2.0203	1.2888
3.84	2.0204	1.2887
5.70	2.0230	1.2871
8.57	2.0270	1.2845

$\alpha = 1.400 \pm 0.003$, $\beta = {}^{-}0.897 \pm 0.004$

$P_{2\infty} = 102.16\ \text{cm}^3$, $P_d = 47.55\ \text{cm}^3$

$\mu = 1.63 \pm 0.01$ D

37. *p*-Dichlorobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.0150	1.2922
5.24	2.0163	1.2897
7.06	2.0168	1.2886
9.54	2.0173	1.2875
14.74	2.0187	1.2850
16.04	2.0192	1.2842
23.47	2.0209	1.2807

$\alpha = 0.254 \pm 0.004, \beta = {}^{-}0.491 \pm 0.005$

$P_{2\infty} = 38.75\ \mathrm{cm}^3,\ R_D = 35.85\ \mathrm{cm}^3$

38. Bromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1634
3.36	2.2708	1.1619
7.12	2.2766	1.1602
9.85	2.2771	1.1586
13.08	2.2863	1.1572
13.67	2.2877	1.1568
20.51	2.2990	1.1535

$\alpha = 1.72 \pm 0.01,\ \beta = {}^{-}0.49 \pm 0.01$

$P_{2\infty} = 83.18\ \mathrm{cm}^3,\ R_D = 33.90\ \mathrm{cm}^3$

$\mu = 1.55 \pm 0.01$ D

39. *o*-Dibromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1634
3.91	2.2720	1.1611
6.12	2.2760	1.1596
9.28	2.2830	1.1575
11.45	2.2880	1.1561
15.75	2.2940	1.1532
18.35	2.3030	1.1515

$\alpha = 2.09 \pm 0.08,\ \beta = {}^{-}0.654 \pm 0.006$

$P_{2\infty} = 130.34\ \mathrm{cm}^3,\ R_D = 41.61\ \mathrm{cm}^3,$

$\mu = 2.08 \pm 0.04$ D

40. *m*-Dibromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.85	2.2680	1.1611
6.86	2.2710	1.1592
8.23	2.2720	1.1581
11.61	2.2760	1.1562
15.11	2.2800	1.1537
17.98	2.2830	1.1519

$\alpha = 1.10 \pm 0.02,\ \beta = {}^{-}0.64 \pm 0.01$

$P_{2\infty} = 86.45\ \mathrm{cm}^3,\ R_D = 41.61\ \mathrm{cm}^3$

$\mu = 1.48 \pm 0.02$ D

41. p-Dibromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.83	2.2639	1.1606
11.30	2.2649	1.1564
12.09	2.2646	1.1558
18.47	2.2653	1.1514
18.60	2.2653	1.1516

$\alpha = 0.12 \pm 0.01$, $\beta = {}^{-}0.66 \pm 0.01$

$P_{2\infty} = 40.66\ \text{cm}^3$, $R_D = 41.61\ \text{cm}^3$

42. 1,2,3-Tribromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.68	2.2687	1.1610
7.19	2.2745	1.1584
11.41	2.2815	1.1552
13.38	2.2845	1.1539
14.18	2.2863	1.1529

$\alpha = 1.64 \pm 0.01$, $\beta = {}^{-}0.75 \pm 0.01$

$P_{2\infty} = 137.85\ \text{cm}^3$, $R_D = 49.33\ \text{cm}^3$

$\mu = 2.08 \pm 0.02$ D

43. 1.2,4-Tribromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
2.96	2.2652	1.1616
6.81	2.2692	1.1588
10.03	2.2711	1.1564
14.71	2.2749	1.1530
17.76	2.2769	1.1507
21.96	2.2792	1.1478

$\alpha = 0.75 \pm 0.03$, $\beta = {}^{-}0.728 \pm 0.003$

$P_{2\infty} = 86.04\ \text{cm}^3$, $R_D = 49.33\ \text{cm}^3$

$\mu = 1.34 \pm 0.04$ D

44. 1,2,3,4-Tetrabromobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
2.90	2.2653	1.1607
4.41	2.2665	1.1597
8.16	2.2692	1.1567
10.22	2.2711	1.1550
13.94	2.2744	1.1521

$\alpha = 0.81 \pm 0.02$, $\beta = {}^{-}0.82 \pm 0.02$

$P_{2\infty} = 101.43\ \text{cm}^3$, $R_D = 57.04\ \text{cm}^3$

$\mu = 1.47 \pm 0.06$ D

45. 1,2,3,5-Tetrabromobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.13	2.2638	1.1609
4.32	2.2645	1.1600
9.96	2.2660	1.1557
12.04	2.2668	1.1541

$\alpha = 0.31 \pm 0.01, \beta = {}^{-}0.79 \pm 0.01$

$P_{2\infty} = 67.08\ \mathrm{cm}^3,\ R_D = 57.04\ \mathrm{cm}^3$

$\mu = 0.70 \pm 0.16$ D

46. Pentabromobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
0.58	2.2634	1.1632
1.01	2.2633	1.1627
2.30	2.2643	1.1610
3.86	2.2651	1.1599
7.39	2.2658	1.1573

$\alpha = 0.39 \pm 0.05, \beta = {}^{-}0.87 \pm 0.05$

$P_{2\infty} = 76.59\ \mathrm{cm}^3,\ R_D = 64.75\ \mathrm{cm}^3$

$\mu = 0.76 \pm 0.01$ D

47. o-Bromonitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.67	2.2967	1.1617
6.02	2.3193	1.1602
10.80	2.3635	1.1575
15.06	2.4082	1.1549
15.08	2.4061	1.1549
17.93	2.4339	1.1533

$\alpha = 9.59 \pm 0.08, \beta = {}^{-}0.585 \pm 0.004$

$P_{2\infty} = 406.77\ \mathrm{cm}^3,\ R_D = 39.57\ \mathrm{cm}^3$

$\mu = 4.24 \pm 0.02$ D

48. m-Bromonitrobenzene

$10^3 w_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.64	2.2859	1.1616
6.50	2.3023	1.1601
11.50	2.3338	1.1571
12.85	2.3431	1.1561
17.13	2.3702	1.1536
19.79	2.3878	1.1521

$\alpha = 6.29 \pm 0.05, \beta = {}^{-}0.59 \pm 0.01$

$P_{2\infty} = 278.41\ \mathrm{cm}^3,\ R_D = 39.57\ \mathrm{cm}^3$

$\mu = 3.42 \pm 0.01$ D

49. p-Bromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.92	2.2774	1.1614
6.61	2.2856	1.1598
10.61	2.3031	1.1574
14.31	2.3172	1.1553
16.39	2.3257	1.1539
17.82	2.3314	1.1531

$\alpha = 3.87 \pm 0.06$, $\beta = {}^{-}0.595 \pm 0.003$

$P_{2\infty} = 184.21\ \mathrm{cm}^3$, $R_D = 39.57\ \mathrm{cm}^3$

$\mu = 2.66 \pm 0.02$ D

50. 2,3-Dibromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
1.57	2.2709	1.1627
2.98	2.2788	1.1614
3.84	2.2841	1.1608
4.02	2.2848	1.1607
5.62	2.2944	1.1593
6.04	2.2972	1.1590

$\alpha = 5.68 \pm 0.09$, $\beta = {}^{-}0.79 \pm 0.02$

$P_{2\infty} = 337.72\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 3.77 \pm 0.04$ D

51. 2,4-Dibromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.65	2.2773	1.1606
7.40	2.2868	1.1586
9.94	2.2952	1.1568
14.60	2.3123	1.1535
17.16	2.3209	1.1518
20.12	2.3310	1.1497

$\alpha = 3.42 \pm 0.04$, $\beta = {}^{-}0.699 \pm 0.003$

$P_{2\infty} = 223.30\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 2.93 \pm 0.02$ D

52. 2,5-Dibromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
5.51	2.2885	1.1597
7.20	2.2945	1.1587
13.15	2.3223	1.1545
14.42	2.3289	1.1535
16.87	2.3405	1.1518

$\alpha = 4.58 \pm 0.05$, $\beta = {}^{-}0.70 \pm 0.01$

$P_{2\infty} = 285.83\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 3.41 \pm 0.02$ D

53. 2,6-Dibromonitrobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
1.49	2.2736	1.1627
2.62	2.2846	1.1616
4.05	2.2938	1.1608
4.31	2.2962	1.1605
7.17	2.3208	1.1582

$\alpha = 8.03 \pm 0.02$, $\beta = {}^{-}0.77 \pm 0.02$

$P_{2\infty} = 466.24\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 4.53 \pm 0.01$ D

54. 3,5-Dibromonitrobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
3.37	2.2717	1.1614
6.80	2.2806	1.1589
10.29	2.2895	1.1565
17.06	2.3077	1.1518
17.41	2.3087	1.1514
17.96	2.3101	1.1511

$\alpha = 2.63 \pm 0.01$, $\beta = {}^{-}0.703 \pm 0.003$

$P_{2\infty} = 180.32\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 2.55 \pm 0.01$ D

55. 3,4-Dibromonitrobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.78	2.2752	1.1604
7.69	2.2828	1.1582
12.28	2.2944	1.1551
16.10	2.3044	1.1523
17.96	2.3100	1.1509
18.73	2.3116	1.1504

$\alpha = 2.60 \pm 0.02$, $\beta = {}^{-}0.712 \pm 0.004$

$P_{2\infty} = 177.95\ \mathrm{cm}^3$, $R_D = 47.29\ \mathrm{cm}^3$

$\mu = 2.53 \pm 0.01$ D

56. 2,3,4-Tribromonitrobenzene

$10^3 W_2$	ϵ_{12}	v_{12}
0	2.2630	1.1637
2.48	2.2696	1.1615
3.30	2.2726	1.1605
5.98	2.2807	1.1579

$\alpha = 2.97 \pm 0.01$, $\beta = {}^{-}0.97 \pm 0.03$

$P_{2\infty} = 226.05\ \mathrm{cm}^3$, $R_D = 55.00\ \mathrm{cm}^3$

$\mu = 2.89 \pm 0.02$ D

57. 2,4,5-Tribromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.76	2.2734	1.1600
7.89	2.2793	1.1577
13.14	2.2906	1.1538
17.15	2.2990	1.1506
18.34	2.3020	1.1495

$\alpha = 2.11 \pm 0.02$, $\beta = {}^{-}0.77 \pm 0.01$

$P_{2\infty} = 187.91\ \text{cm}^3$, $R_D = 55.00\ \text{cm}^3$

$\mu = 2.55 \pm 0.01$ D

58. 3,4,5-Tribromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.61	2.2699	1.1602
8.05	2.2746	1.1576
11.10	2.2790	1.1553
14.79	2.2848	1.1522
17.11	2.2884	1.1507
22.30	2.2963	1.1466

$\alpha = 1.49 \pm 0.01$, $\beta = {}^{-}0.768 \pm 0.005$

$P_{2\infty} = 145.25\ \text{cm}^3$, $R_D = 55.00\ \text{cm}^3$

$\mu = 2.10 \pm 0.01$ D

59. 2,3,5-Tribromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.70	2.2697	1.1600
7.17	2.2735	1.1581
8.82	2.2760	1.1568
14.52	2.2843	1.1524
18.31	2.2899	1.1495

$\alpha = 1.47 \pm 0.01$, $\beta = {}^{-}0.775 \pm 0.002$

$P_{2\infty} = 143.12\ \text{cm}^3$, $R_D = 55.00\ \text{cm}^3$

$\mu = 2.08 \pm 0.01$ D

60. 2,4,6-Tribromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
6.07	2.2806	1.1592
7.22	2.2842	1.1583
11.99	2.2971	1.1548
17.00	2.3129	1.1510
17.66	2.3153	1.1504
23.76	2.3336	1.1456

$\alpha = 2.97 \pm 0.03$, $\beta = {}^{-}0.759 \pm 0.005$

$P_{2\infty} = 248.56\ \text{cm}^3$, $R_D = 55.00\ \text{cm}^3$

$\mu = 3.08 \pm 0.02$ D

61. 2,3,4,5-Tetrabromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
4.06	2.2689	1.1603
4.10	2.2692	1.1600
5.06	2.2708	1.1594
6.24	2.2722	1.1584
8.22	2.2749	1.1568
9.01	2.2762	1.1561

$\alpha = 1.45 \pm 0.03$, $\beta = {}^{-}0.84 \pm 0.01$

$P_{2\infty} = 164.38\ \mathrm{cm}^3$, $R_D = 62.71\ \mathrm{cm}^3$

$\mu = 2.23 \pm 0.04$ D

62. 2,3,4,6-Tetrabromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
2.92	2.2726	1.1616
4.23	2.2775	1.1605
5.11	2.2797	1.1596
6.35	2.2828	1.1584
7.68	2.2864	1.1570

$\alpha = 3.19 \pm 0.10$, $\beta = {}^{-}0.87 \pm 0.04$

$P_{2\infty} = 307.22\ \mathrm{cm}^3$, $R_D = 62.71\ \mathrm{cm}^3$

$\mu = 3.46 \pm 0.08$ D

63. 2,3,5,6-Tetrabromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
5.93	2.2645	1.1633
9.56	2.2655	1.1629
11.15	2.2661	1.1628
15.06	2.2670	1.1624
17.72	2.2679	1.1622

$\alpha = 0.27 \pm 0.01$, $\beta = {}^{-}0.087 \pm 0.003$

$P_{2\infty} = 162.81\ \mathrm{cm}^3$, $R_D = 62.71\ \mathrm{cm}^3$

$\mu = 2.21 \pm 0.01$ D

64. Pentabromonitrobenzene

10^3W_2	ϵ_{12}	v_{12}
0	2.2630	1.1637
1.82	2.2656	1.1623
2.53	2.2669	1.1616
4.11	2.2693	1.1602
4.68	2.2708	1.1596
5.90	2.2729	1.1584

$\alpha = 1.69 \pm 0.06$, $\beta = {}^{-}0.90 \pm 0.02$

$P_{2\infty} = 208.64\ \mathrm{cm}^3$, $R_D = 70.43\ \mathrm{cm}^3$

$\mu = 2.60 \pm 0.06$ D

D.3 Results and Discussion of the Dipole Moment Investigation

1. Definition of the π -Inductive Effect and its Importance in Interpretation of the Dipole Moments of Organic Compounds

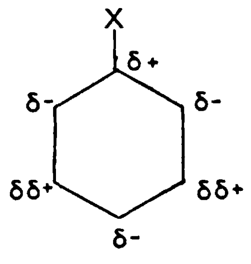
We mentioned earlier in the introduction page (12) the existence of an electronic effect called the π -inductive effect which arises from the polar nature of a substituent or substituent-carbon bond polarising the π -system without charge transfer. There has been much controversy over the past years to the existence of such a parameter. The assumption in the analysis of the ground-state properties is that the inductive effect is the same for saturated and unsaturated systems, but the spectroscopic evidence shows that even though substituents like halogens attract σ -electrons, they repel π -electrons. Therefore direct evidence for its existence in the ground state is not available.

From the physical and chemical properties(29) of the ground-states of halogenated molecules it has been deduced that the halogens are electron-attracting, (-I) effect, in the order F > Cl > Br > I and electron-donating (+M) effect, in the order F > Cl > Br > I.

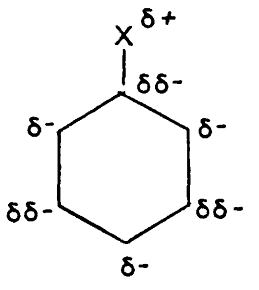
The spectroscopic data(30) which concerns only the electrons undergoing electronic transitions, namely π -electrons, defines the inductive effect as the changes occurring in the electrons of the hydrocarbon part due to the variation in the potential of the substituent, and the mesomeric effect is defined by the extent of interaction between the states of the type RX and the ionic states R^+X^- and R^-X^+. The halogens being predominantly electron-donors the order of mesomeric strengths I > Br > Cl > F is in accordance with the decrease in energy of the state R^-X^+ as determined by the ionization potential of the halogens, F > Cl > Br > I.

The evidence for the ground-state order has been explained by the fact that the p-halogenobenzoic acids are stronger acids than benzoic acid, as they should be from the influence of a -I effect, but the increase is smaller for fluorine than for chlorine(31), which may be due to the greater mesomeric effect of fluorine than chlorine. In the same way, the halogens deactivate the benzene ring to electrophilic substitution; yet are ortho/para-directing, and again the +M effect compensates for the -I effect.

In these halogenobenzenes, it has been suggested(36) that the $+I_\pi$ effect on π-electrons removes electrons from the position of substitution, builds up the electron density at the ortho- and the para-position, and reduces the electron density slightly at the meta-position. Valence-bond theory predicts an increase in density at the ortho- and the para-positions and no change at the meta-position or position of the substituent. Molecular-orbital theory would predict an increase in density at the ortho- and the para-positions, but a smaller increase at the meta- and the substituent position compared to the ortho- and para-positions. Therefore the $+I_\pi$ effect deactivates the meta-position while the +M effect activates it, and thus the sum of these two effects might explain the +M effect observed in the ground-state of the molecule, the total of ortho/para-directing effects.(36)



$+I_\pi$



+M

An alternative theoretical approach(32) has shown the possible existence of an I_π effect in addition to the I and M effects, suggesting that the calculations of the $+I_\pi$ effect produces a small contribution to the dipole moment in the sense $\overset{+}{X}\overset{-}{Ph}$. Its magnitude in the monosubstituted compounds is, in Debyes: -F, 0.3; -Cl, 0.19; -Br, 0.19. Various properties of the substituted benzenes have been calculated(33, 34) using the localized orbital model including an extended range of I_π effect. Also the localized orbital model(35) for the determination of substituent electronic effects on π-electron systems is successful in interpreting the electronic spectra of halogenobenzenes if the substituent inductive effect is separated into two terms, $-I_\sigma$ and $+I_\pi$ (36). Spiesecke and Schneider(37) have suggested that ^{13}C chemical shifts might be employed to obtain information about the π-electron density distributions in aromatic systems. In the case of mono-substituted benzene derivatives, the contribution to the substitutent constants from the anisotropy of the substituent at the <u>para</u>-position may be neglected as may the σ-inductive effect, so that the major contribution will arise from the change in π-electron density. The correction is surprisingly good and lends considerable support to the hypothesis that ground-state π-electron distributions are determined largely by the π-inductive effect of the substituent.

But it should be remembered also that Robertson and Matsen(38) have successfully described, in molecular orbital terms, the mean ultra-violet spectral properties of the halogenobenzenes, using a model containing only a single (-I) inductive effect in addition to a resonance (+M) effect. Sheppard and Sharts(39) have also argued that electron shifts in aromatic fluorine compounds may be explained in terms of I and M effects only, and that π-inductive effects are of secondary importance.

It is quite clear from the foregoing conclusions that more detailed calculations are needed to give an accurate picture of the electron densities induced in a hydrocarbon by a substituent and until these are determined a quantitative analysis of the ground-state properties in terms of inductive and mesomeric parameters will not be possible. Moreover, the evidence of the existence of I_π effect seems to depend on the particular method of application of molecular orbital theory. Direct evidence for it might be obtained together with some measure of its importance compared with the mesomeric effect from dipole moment studies. We have therefore determined the electric dipole moments of a range of polyhalogenobenzenes and nitrobenzenes which appear to suggest that the nitro-group may exert a considerable $-I_\pi$ effect. Similarly values for dipole moments of various halogen compounds suggest a marked $+I_\pi$ effect in fluorobenzene.

2. Electric Dipole Moments of Polyhalogenobenzenes

(a) The Dipole Moments of Polyfluoro-, Polychlorofluoro- and Polybromobenzenes and Discussion of the Results

The dipole moments of polyfluoro- and polybromo-benzenes measured in our laboratory together with their corresponding calculated and empirically calculated values are shown in Tables (1) and (2). The calculated moments are those obtained by the vector sum of their mono-substituted benzene derviative. The empirical moments are determined after empirical allowance for mutual induction between group moments. The values under the column μ_{obs} are the experimental dipole moments; column μ_{cal} are the calculated dipole moments from vectorial addition; and μ_{emp} are those obtained after allowance for mutual induction between groups.

Table (1)

Measured, calculated and empirically calculated dipole moments of some polyfluorobenzenes in cyclohexane at 298K

Compound	Observed Moment μ_{obs} (D)	Calculated Value μ_{cal} (D)	Empirically Calculated Value μ_{emp} (D)
Fluorobenzene	1.44	1.44	-
o-Difluorobenzene	2.47	2.49	2.46
m-Difluorobenzene	1.43	1.44	1.43
1,2,4-Trifluorobenzene	1.40	1.44	1.41
1,2,3,4-Tetrafluorobenzene	2.40	2.49	2.41
1,2,3,5-Tetrafluorobenzene	1.37	1.44	1.38
Pentafluorobenzene	1.40	1.44	1.36

Table (2)

Measured, calculated and empirically calculated dipole moments of polybromobenzenes in p-xylene at 298K.

Compound	μ_{obs} (D)	Calculated Value μ_{cal} (D)	Empirically Calculated Value μ_{emp} (D)
Bromobenzene	1.55	1.55	-
o-Dibromobenzene	2.08	2.68	2.08
m-Dibromobenzene	1.48	1.55	1.41
1,2,3-Tribromobenzene	2.08	3.10	2.08
1,2,4-Tribromobenzene	1.34	1.55	1.11
1,2,3,4-Tetrabromobenzene	1.47	2.68	1.56
1,2,3,5-Tetrabromobenzene	0.70	1.55	0.67
Pentabromobenzene	0.76	1.55	0.60

(i) Polyfluorobenzenes

In the absence of induction the moment of o-difluorobenzene is 0.02D higher than its observed value and so assignment of a moment of 1.42D to each carbon-fluorine bond moment by an angle of 60°, gives a value of 2.46D, in good agreement with the observed value 2.47D. In m-difluorobenzene a value of 1.43D can be assigned to each C-F bond moment, with an angle of 120° between them. This will result in a value of 1.43D, which is equal to the observed value (1.43D).

In the absence of inductive effects, the moments due to the 1,4-fluorines in 1,2,4-trifluorobenzene should cancel each other, leaving a moment equal to that of fluorobenzene 1.44D, but the moment of o-difluorobenzene is 2.47D, only 0.01D lower than the empirically calculated value. If the resultant of the 1,2-fluorine moments is taken as equal to that of o-difluorobenzene acting in the line bisecting an angle of 60° between the bonds of the 1,2-fluorine atoms and if the moment of 1.43D is assigned to the 4-fluorine, the resultant moment of the molecule is calculated to be 1.41D, in close agreement with the observed value of 1.40D. The moment of 1,2,3,4-tetrafluorobenzene can be treated as made up of two vectors with a 120° angle between them and a value equal to that of o-difluorobenzene, 2.47D, which is reduced by about 0.09D by the induction between the fluorine atoms. The 1- and 4-fluorine moments are reduced to 1.42D; the 3- and 4-fluorines each having two ortho-fluorine atoms are reduced to 1.39D. This gives a value of 2.41D, which is in close agreement with the observed moment of 2.40D. The moment of 1,2,3,5-tetrafluorobenzene should be equal to the difference between the value for 1,2,3-trifluorobenzene and that for fluorobenzene. Since we did not measure the moment of 1,2,3-trifluorobenzene, no comment can be given; however, the assignment of the appropriate empirical C-fluorine bond moments will give a value of 1.38D, which is in excellent agreement with the observed value for 1,2,3,5-tetrafluorobenzene, 1.37D. The moment of pentafluorobenzene should, in the absence of induction, be the same as that of fluorobenzene, the fluorines ortho to each other in the molecule lower the moments of one another, so that the total lowering by induction is 0.04D. The 1- and 5-fluorine atoms each having one ortho-fluorine will have moments equal to 1.42D, and the 2-,3- and 4-fluorines each having two ortho-fluorine atoms will be 1.39D. The overall moment of the molecule will be 1.36D, in reasonable agreement with the observed value 1.40D. Therefore examination of these polyfluorobenzene moments showed that they may be calculated with reasonable accuracy by assigning the following empirical values to the C-F moment in various environments: with one ortho-fluorine atom, 1.42D; with two ortho-fluorine atoms, 1.39D; and otherwise 1.43D. Bond angles of 60°, 120° and 180° are used as appropriate. The reduction is twice as great for an ortho- than for a meta-substituent. A second ortho-fluorine substituent causes almost double the reduction caused by the first. These reductions in bond moments are consistent with a model in which mutual induction is the only effective mechanism for the observed reduction in the dipole moment of the molecule.

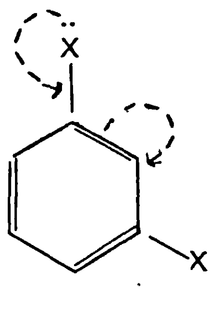
It is interesting that only these short-range forces are effective in changing the total moment of the molecule. Polysubstitution even by four or five fluorine atoms appears to have little effect on the electron density in the ring other than the purely additive effect expected from such substitution and no apparent saturation of effect is observed.

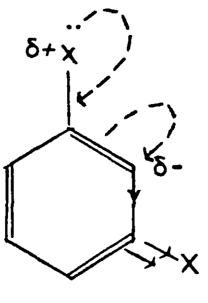
(ii) Polybromobenzenes

The best fitting empirical moment values in various environments for C-Br bond moments in polybromobenzenes are: with one ortho-bromine atom, 1.20D; with two ortho-bromine atoms, 0.90D; and otherwise, 1.41D. In the absence of induction, the moment of 1,2,3-tribromobenzene should be 3.10D, but a double ortho-effect lowers it by 1.02D. In the absence of inductive effects, the moments due to the 1,4-bromines in 1,2,4-tribromobenzene should cancel each other, leaving a moment equal to that of bromobenzene 1.55D, but the moment of o-dibromobenzene is 2.08D, about 22% lower than the calculated value. If the resultant of the 1,2-bromine moments is taken as equal to that of o-dibromobenzene and acting in the line bisecting a 60° angle between the bonds of the 1,2-bromine atom, and if the moment of 1.41D is assigned to the 4-bromine atom the resultant moment of the molecule is calculated to be 1.11D, compared with the observed value 1.34D. The moment of 1,2,3,4-tetrabromobenzene can be treated as the resultant of two vectors each equal to that of o-dibromobenzene, 2.08D, with an angle of 120° between them, which is reduced by 1.21D due to the induction between the bromine atoms. The resultant of the two vectors is, of course, 2.08D but their value will be reduced by the greater induction between the 2- and 3-bromines. A reduction of 1.55-0.90 = 0.65D gives close agreement with the observed moment (1.47D). The moment of 1,2,3,5-tetrabromobenzene should be equal to the difference between the value for 1,2,3-tribromobenzene and 1.41D, 2.08 - 1.41 = 0.67D. The difference between the observed and the calculated value is no more than the probable error. The moment of pentabromobenzene should, in the absence of induction, be the same as that of bromobenzene. The four ortho-effects present in the molecule lessen one another, so that the total lowering by induction is slightly less than that in 1,2,3-tribromobenzene and 1,2,3,5-tetrabromobenzene. The reduction is three times as great for an ortho- than for a meta-substituent. A second ortho-bromine substituent causes a further reduction almost equal to that calculated for the first.

The deviation between the vectorially calculated (without concern for induction) and the measured moments are not more than 5% in the case of polyfluorobenzenes. There is a much greater deviation up to 50% between the observed and calculated values in the moments of polybromobenzenes. The fact that the fluoro-group moment variation is almost negligible and that of bromo-group so great in polysubstitution over the ring is presumably due to the polarisability of these atoms. .This is due to the fact that, from optical data (such as electron refraction measurements), atomic valency shells having a higher principal quantum number are more polarisable than similar shells with a lower quantum number and that, in atoms of higher atomic number, the effect on polarisability of the greater distance of the valency electrons from the nucleus outweighs that of the greater imperfections of screening by the core electrons. Optical data also shows that bonds are more polarisable along their length than transversely. The small group refractivity of the C-F bond (1.44 cm^3) compared to that of the C-Br bond (9.39 cm^3) confirms this. Furthermore, the effect of substituents on inducing charge disturbance in π -system is related to the polarisability of the substituent and since the C-F bond is less polarisable than the other C-halogen groups its total inductive effect (-I and $+I_\pi$) is smaller than the others. This is in fact the reason for fluorobenzene having a smaller moment than the other halogeno-substituted benzenes. Also, more evidence can be obtained by comparing the dipole moments of halogen substituted pentafluorobenzenes. It has been suggested(22) that the increase in the moment from chloropentafluorobenzene, 0.63D, to bromopentafluorobenzene, 0.80D and iodopentafluorobenzene, 1.06D, is due to the polarisability of the halogens increasing in the order $I > Br > Cl > F$, therefore the effective moment of the carbon-halogen bond is increasingly reduced. Huang(22) interprets the change of dipole moments in terms of the sum of induction through the σ-bond (I_σ effect) and mesomerism (M effect) only.

The magnitude of these empirical moments, and their constancy, with increasing substitution of the ring are clearly consistent with a short-range inductive effect ($+I_\pi$), and not through the mesomeric (+M effect) of substituents. If the mesomeric effect is considered alone, our m-disubstituted benzenes would have moments higher than the corresponding mono-substituted ones. The reason for this is that the +M effect of each substituent would increase the charge density of the ring in the appropriate positions in such a way that there would be an enhancement of the $-I_\sigma$ effect of each halogen atom, thereby increasing the moment of the molecule. The diagram below illustrates the flow of charge from each substituent.





Littlejohn and Smith(20), as has already been mentioned, arrived at the conclusion that, although the total displacement of electrons brought about by induction is greater in meta-disubstituted benzenes than in the mono-substituted benzenes, the amount of induced moment in each substituent is less in the former than in the latter. Smyth and Lewis(19) also reached a similar conclusion, arguing that, since the effect of mutual induction is small any increase of moment caused by a decrease in +M character must be small. Littlejohn and Smith's(20) conclusion is in fact correct and confirms our suggestion, since it is quite clear that the total displacement of electrons due to induction which is the sum of (-I and $+I_\pi$) effect is greater in meta-substituted benzenes than in the mono-substituted benzenes. The fact that the resultant magnitude is less in the former than in the latter is due to the difference in the direction of action of -I and $+I_\pi$ effects which might compensate some part of each other's effect.

These measurements establish more evidence for the importance of the $+I_\pi$ effect, inductive π-repulsion, compared with the +M effect; the former, although similar to the +M effect, inducing a moment in the opposite direction to the primary group moment of the carbon-substituent bond, there will not be any charge transfer to the benzene ring to enhance the $-I_\sigma$ effect of each substituent as happens in the case of +M effect. Therefore, the classically defined mesomeric effect, which is described in the ground-state of the molecule, appears to be not very important. In fact as has been proposed by Clark et al(36), the sum of the $+I_\pi$ and the +M effect of the halogens described from spectroscopic properties of the molecules are the main factors and may indeed represent the mesomeric effect of a substituent in its ground-state.

Now in o-disubstituted benzenes we must consider the possibility that the $-I_\sigma$ effect of one halogen atom enhances the +M effect of a second, thereby reducing the overall moment of both halogen substituent atoms. This requires that the two electronic effects I_σ and +M be the only considered factors. However, examination of the dipole moments of

1,2-dichlorocyclohexanes(40) suggests that this is not a major contribution since similar reduction is seen in these saturated systems.

The out of plane deflection of about 18° for C-Br bonds observed from electron-diffraction measurements(16), where bromine atoms are ortho to each other, would give an apparent moment of only $1.55 \cos 18^\circ = 1.47D$ to each bromo-group which accounts for only 23% of the total reduction suggested from our empirical calculations.

Huang(22) has suggested that the magnitude of the atom polarisation in polysubstituted compounds should increase; being especially large for molecules with balanced dipoles, therefore the electric dipole moments of more highly substituted compounds should be anomalously large rather than small. Thus the assumption that atom polarisations are additive needs discussion. The atom polarisation or vibration polarisation is due to displacement of the atomic nuclei in the molecule, caused by the alternating field applied during the measurements of dielectric constant, the resulting periodic distortion may be described as composed of stretching and relative bending of the individual bonds. So the atom polarisation includes bond terms and interbond terms, whereas the former are probably additive, the latter may be less perfectly so, because the bending force constants may not be independent of the configuration. Further, Tiganik(41) and Smyth(19) have shown that the value of $(P_{2\infty} - R_D)$ approximates to zero in the cases of sym-trichloro-, sym-tribromobenzenes, trichloromesitylene and dichlorodurene. Also, our empirically calculated values of the C-halogen moments apply equally well to their corresponding di-, tri-, tetra- and penta-substituted benzenes as shown in Tables (1) and (2). Thus Huang's suggestion appears not to be applicable.

(iii) Polychlorofluorobenzenes

The dipole moments of polychlorofluorobenzenes measured in our laboratory, together with their corresponding calculated values as the vector sum of the fluorobenzene moment and the total moment of the chlorine substituents, which are equal in magnitude and direction to that of the corresponding polychlorobenzene compounds, are summarised in Table (3).

Table (3)

Measured and calculated dipole moments of some polychlorofluorobenzenes in cyclohexane at 298K

Compound	Measured Moment (D)	Calculated Value* (D)
Chlorobenzene	1.57	1.57
o-Chlorofluorobenzene	2.39	2.61
m-Chlorofluorobenzene	1.50	1.51
p-Chlorofluorobenzene	0.19	0.13
2,3-Dichlorofluorobenzene	2.45	2.67
2,4-Dichlorofluorobenzene	1.28	1.46
2,5-Dichlorofluorobenzene	1.42	1.44
2,6-Dichlorofluorobenzene	2.67	2.92
3,4-Dichlorofluorobenzene	1.23	1.23
3,5-Dichlorofluorobenzene	0.37	0.04
2,4,5-Trichlorofluorobenzene	0.11	0.19
3,4,5-Trichlorofluorobenzene	0.82	1.00
2,3,6-Trichlorofluorobenzene	2.00	2.33
2,3,4,6-Tetrachlorofluorobenzene	1.63	1.27
2,3,5,6-Tetrachlorofluorobenzene	1.19	1.44

*calculated assuming no change in C-Cl and C-F bond moments

Table (4)

Measured and empirically calculated dipole moments of polychlorobenzenes in benzene at 298K(25)

Compound	Observed Moment (D)	Empirically Calculated Value (D)
Chlorobenzene	1.58	-
o-Dichlorobenzene	2.25	2.27
m-Dichlorobenzene	1.48	1.48
1,2,3-Trichlorobenzene	2.44	2.44
1,2,4-Trichlorobenzene	1.25	1.24
1,2,3,4-Tetrachlorobenzene	1.87	1.95
1,2,3,5-Tetrachlorobenzene	0.97	0.96
Pentachlorobenzene	1.05	0.95

The dipole moments of polychlorobenzenes determined in dilute solution in benzene at 298K with the empirically calculated values, which are determined after allowance for mutual induction between group moments, are summarised in Table (4). These moments are quoted from the recent paper published by Sandall et al(25). This suggests (i) that the C-Cl bond (R_D=6.51 cm^3) has a polarisability greater than the C-F bond (R_D=1.44 cm^3) and therefore is affected more by further substitution in the benzene ring and (ii) that the reduction is due to the mutual induction between the chlorine atoms. The C-Cl moment is thus reduced to 1.31D, if there is a chlorine atom ortho to it, to 1.13D if two chlorine atoms are ortho to it, and to 1.48D otherwise. One ortho-chlorine atom reduces the moment of C-Cl by about 0.30D, and substitution of the second chlorine has an equal additional effect on it.

In polychlorofluorobenzenes we have tried to calculate a range of consistent empirical moments on the basis of mutual induction for fluorine and chlorine atoms in different positions over the benzene ring, the results of our calculations are summarised in Table (5). The good agreement between these empirically calculated moments and their corresponding observed values confirms our earlier suggestions of the dominance of mutual induction between substituent groups.

Table (5)

Measured and empirically calculated Dipole Moments of Polychlorofluorobenzenes

Fluorobenzene* Derivative	Measured Moment (D)	Empirically Calculated Moments (D)	Group Moments used in Calculation
2-Cl	2.39	2.39	1-1.42, 2-1.34
3-Cl	1.50	1.50	1-1.43, 3-1.56
4-Cl	0.19	-	- -
2,3-Cl_2	2.45	2.50	1-1.42, 2-1.13, 3-1.31
2,4-Cl_2	1.28	1.31	1-1.42, 2-1.34, 4-1.47
2,5-Cl_2	1.42	1.32	1-1.42, 2-1.34, 5-1.57
2,6-Cl_2	2.67	2.68	1-1.34, 2,6-1.34
3,4-Cl_2	1.23	1.23	1-1.44, 3,4-1.31
3,5-Cl_2	0.37	-	- -
2,4,5-Cl_3	0.11	0.13	1-1.42, 2-1.34, 4,5-1.31
3,4,5-Cl_3	0.82	1.00	1-1.44, 3,5-1.31, 4-1.13
2,3,6-Cl_3	2.00	2.13	1-1.34, 2-1.13, 3-1.31, 6-1.34
2,3,4,6-Cl_4	1.63	1.06	1-1.34,2,3-1.13, 4-1.31, 6-1.34
2,3,5,6-Cl_4	1.19	1.16	1-1.34, 2,6-1.13, 3,5-1.31

*The Fluorine atom is in position number 1.

In <u>ortho</u>-chlorofluorobenzene, the mutual induction between the chloro- and fluoro-groups causes a reduction of about 0.02D to the primary moment of the fluoro-group and of 0.23D on that of the chloro-group. The striking effect is that the reduction calculated for C-F bond moment is the same as if there was an ortho-fluorine substituent. Further, if the mesomeric interaction between each substituent were the major contribution to the lowering in their primary moments, one would expect a larger reduction than 0.02D in the fluoro-group moment, this group having stronger +M effect than the chlorine atom and therefore an enhancement in its +M effect, caused by the electro-negativity of the chlorine atom at the ortho- position.

In 2,6-dichlorofluorobenzene where there are two ortho-chlorine atoms the fluoro-group moment is apparently reduced to 1.34D, double the reduction caused where there were two ortho-fluorine atoms. The mutual induction between the two groups in meta-chlorofluorobenzene reduces the fluoro-group to 1.43D, and that of chloro-group to 1.56D, in both group moments the reduction is so small, 0.01D, that it can be neglected on the grounds of the experimental error. Therefore mutual induction for the two substituents at meta positions relative to each other is negligible, again giving stronger evidence for the dominance of $+I_{\pi}$ effect of each halogen substituent rather than combined inductive (-I) and mesomeric (+M) effects. It is difficult to give any comment on the p-chlorofluorobenzene moment, since the two halogen atoms occupy positions para- to one another, and the moment of this compound is small (0.19D) and therefore there is a large probable error in its determination. The situation is aggravated by the fact that an appreciable atom polarisation, 1.65 cm^3, arises from molecular vibrations and this becomes commensurate with the orientation polarisation (0.74 cm^3) which causes considerable error in moment determination. However, Janiak et al(42) have speculated over the direction of the resultant moment, suggesting, in the absence of direct experimental evidence, that although simple electro-negativity arguments indicate that -F is the negative end of the molecule, chlorine is in fact the negative end, since, on the basis of inductive π interactions, the stronger inductive effect of chlorine (the sum of its-I and $+I_{\pi}$) effects augment fluorine's interaction with the π-system.

In 3,5-dichlorofluorobenzene, in the absence of induction, the halogens are situated in such a way that the resultant of the two C-Cl moments meta- to each other will be directly opposed to the C-F moment and therefore the resulting moment is equal to that of p-chlorofluorobenzene. The observed value is very small (0.37D) and this invalidates any arguments about the exact magnitude of each C-halogen bond; however, the small moment should also be evidence for the near invariance of each C-halogen moment when they are in the meta-position to each other, a situation similar to a symmetrically trisubstituted benzene. Also, our empirically calculated values of the C-halogen moments apply equally well to their corresponding di, tri, tetra- and penta-chlorofluorobenzenes.

Both methods of calculating(18, 20) the induced moment were based on a consideration of the molecule as a system of several fragments polarised in the field created by the dipole of the polar group, an approach similar to the calculation ofpotential energy of interaction between two dipoles separated by a large distance, r, defined earlier in page (5). Therefore calculation of the induced moments depends rather critically upon the location assumed for the dipoles and the values of the permittivity, D, of the medium. Also, in such a calculation, only the effect of the electrostatic field created by the polarisable substituent is taken into consideration and the effect of successive polarisations of the σ-bonds, i.e. the σ-induction effect is ignored. It should be mentioned that, although there are methods in which the effect of the polarisation of each bond present in the molecule can be calculated(43, 44), each of these methods takes into consideration different components of the inductive effect (through space and through bond) leading to results agreeing fairly well with one another. In both methods the I_π effect is not considered and through space and through bond effects cannot be separated completely from one another.

3. Electric Dipole Moments of Polyhalogenonitrobenzenes

(a) The Dipole Moments of Polyfluoronitro- and Polybromonitro-benzenes and Discussion of the Results

The dipole moments of polyfluoro- and polybromo-nitrobenzenes together with the results of their corresponding calculated values are presented in Tables (6) and (7). The calculated values are on the basis that the total moment of the halogen substituent is equal in magnitude and direction to that of the corresponding polyhalogenobenzene compound. Their empirically calculated values include correction for inductive effects. The figures under μ_{exp} are the experimental dipole moments, μ_{cal} those obtained on the basis of vectorial additivity and μ_{emp} the empirically calculated moments.

Table (6)

Measured, Empirically calculated and calculated dipole moments of polyfluoronitrobenzenes in cyclohexane at 298K

Compound	Measured Moment μ_{exp}(D)	Empirically Calculated Moments μ_{emp}(D)	Calculated Moments μ_{cal} (D)
Nitrobenzene	4.06		
o-Fluoronitrobenzene	4.64	4.63	4.94
m-Fluoronitrobenzene	3.47	3.56	3.56
p-Fluoronitrobenzene	2.57	2.59	2.62
2,4-Difluoronitrobenzene	3.31	3.26	3.57
2,6-Difluoronitrobenzene	5.15	5.07	5.49
3,4-Difluoronitrobenzene	2.25	2.29	2.28
2,3,4-Trifluoronitrobenzene	2.90	3.35	2.98
2,4,5-Trifluoronitrobenzene	2.61	2.33	2.63
2,4,6-Trifluoronitrobenzene	3.49	3.59	4.06
2,3,4,5-Tetrafluoronitrobenzene	1.86	1.93	2.28
2,3,4,6-Tetrafluoronitrobenzene	3.03	3.01	3.57
*2,3,5,6-Tetrafluoronitrobenzene	3.28	3.34	4.06
Pentafluoronitrobenzene	1.98	1.98	2.66

*This moment is quoted from the reference, W.A. Sheppard 'The Chemistry of the Cyano Group', ed. Z. Rappoport, Interscience, New York, (1970), 215.

Table (7)

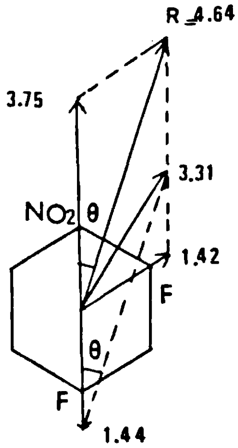
Measured, Empirically calculated and calculated dipole moments of polybromonitrobenzenes in p-xylene at 298 K

Compound	Measured Moment μ_{exp}(D)	Empirically Calculated Moments μ_{emp}(D)	Calculated Moments μ_{cal}(D)
o-Bromonitrobenzene	4.24	4.25	5.02
m-Bromonitrobenzene	3.42	3.55	3.55
p-Bromonitrobenzene	2.66	2.66	2.51
2,3-Dibromonitrobenzene	3.77	3.83	4.56
2,4-Dibromonitrobenzene	2.93	2.91	3.56
2,5-Dibromonitrobenzene	3.41	3.36	4.06
2,6-Dibromonitrobenzene	4.53	4.53	5.54
3,4-Dibromonitrobenzene	2.53	2.49	2.49
3,5-Dibromonitrobenzene	2.55	2.65	2.58
2,3,4-Tribromonitrobenzene	2.89	2.80	3.52
2,3,5-Tribromonitrobenzene	2.08	2.73	3.58
2,4,5-Tribromonitrobenzene	2.55	2.32	2.72
2,4,6-Tribromonitrobenzene	3.08	3.13	4.06
3,4,5-Tribromonitrobenzene	2.10	1.96	1.98
2,3,4,5-Tetrabromonitrobenzene	2.23	2.08	2.88
2,3,4,6-Tetrabromonitrobenzene	3.46	2.66 ±0.3	3.75
2,3,5,6-Tetrabromonitrobenzene	2.21	2.90 ±0.3	4.06
Pentabromonitrobenzene	2.60	2.30 ±0.3	3.30

The intention of the present study over this range of compounds is to reveal evidence from dipole moment measurements about the importance of the $-I_{\pi}$ effect of the nitro-group relative to its -M effect. We have centered our attention on the nitro-group which is sensitive to steric hindrance of conjugation and to which most of our arguments are applied. One possible approach to an investigation into the relative importance of the mesomeric and π-inductive effects of the nitro-group in conjugated systems is via the study of steric hindrance to mesomerism, for, if the mesomeric effect is eliminated, the remaining differences in moment between aromatic and aliphatic systems should be due to inductive effects only. In a theoretical approach we have tried to compute very approximately the apparent nitro-group moment after allowance for induction, and particularly in the sterically hindered derivatives. We have therefore used an empirical approach similar to that of our polyhalogenobenzenes to solve the present problem. Relevant dipole moments are listed in Tables (8) and (9).

(i) Polyfluoronitrobenzenes

The first attempt is to try to calculate the apparent substituent moments in ortho-fluoronitrobenzene. To do so we should first determine the approximate location of the relevant moment in the molecule and then use the value of its angle as an adjustable parameter to determine the apparent carbon-substituent moments of the molecule. The value of θ can be calculated from the moment of 2,4-difluoronitrobenzene by applying the vectorial additivity role to the following three vectors, that of the o-fluoronitrobenzene 4.64D, the apparent moment of the C-F bond in fluorobenzene 1.44D, and the angle θ, having as a resultant the moment of 2,4-difluoronitrobenzene (3.31D). The adjustment of this value in o-fluoronitrobenzene resulted in apparent moments of 3.75D for nitro-group and 1.42D for fluoro-group.



The striking effect is that the moment of the fluoro-group is the same as that in o-chlorofluorobenzene. Thus the chlorine atom and the nitro-group may cause similar induction in the fluoro-group moment; this is likely to be true since the carbon-fluorine bond is so little polarisable.

In meta-fluoronitrobenzene, it seems that both groups have an almost negligible inductive effect on each other since by using the observed moment of nitrobenzene 4.06D and that of fluorobenzene 1.44D with an angle of 120° between them it will give a moment of 3.56D which, within experimental error is in agreement with the observed value 3.47D. We are strengthened in the belief that this difference is due to experimental error since the corresponding values for the bromonitro compounds suggest a similar conclusion.

In p-fluoronitrobenzene the moment of 4.06D for the nitro-group and for the carbon-fluorine bond 1.47D gives a resultant moment equal to 2.59D which again is in good agreement with the observed value (2.57D).

The empirical calculation of these moments may be carried out for the other fluoronitrobenzenes. The results show consistent apparent moments for fluoro- and nitro-groups in various environments. A fluorine atom having: one ortho nitro-group, 1.42D; one meta nitro-group 1.44D; one para nitro group, 1.47D and where there is an ortho-fluorine atom and at the same time an ortho nitro-group, 1.39D. Similarly the results for the nitro-group having (a) one ortho fluorine atom 3.75D; (b) one meta fluorine 4.06D; (c) one para fluorine 4.06D and (d) two ortho fluorines 3.63D, are obtained. It will be noticed that the nitro-group moment is reduced even more by further substitution of fluorine atoms over the ring, i.e. to 3.63D in 2,3,4,5-tetrafluoronitrobenzene, 3.47D in 2,3,4,6-tetrafluoronitrobenzene and 3.37D in 2,3,5,6-tetrafluoro- and pentafluoro-nitrobenzene. Our results disagree with Huang's(22) suggestion about the importance of the mesomeric effect of the nitro-group. He was trying to suggest that the difference between the dipole moment of p-fluoronitrobenzene and that of pentafluoronitrobenzene was due to the steric inhibition of the mesomeric effect of the nitro-group in pentafluoronitrobenzene plus the importance of an electrostatic field effect between the ortho-fluorine and the nitro-group. The van der Waal's radii of the fluorine atom and the nitro-group indicates the absence of a steric inhibition between the two substituents. Therefore the nitro-group and the benzene ring are probably in the same plane. Due to the mesomeric effect of the nitro-group one would expect a larger value for the $C-NO_2$ bond moment in these compounds. In fact the reduction observed in the nitro-group moment on polysubstitution of the fluorine atoms is due to the negative inductive (-I) power of the fluorine atom, which outweighs its positive inductive π-repulsion ($+I_{\pi}$) effect, therefore reducing electron density in both the π- and σ-framework of the ring system so effectively that the $-I_{\pi}$ effect of the nitro-group is repressed.

Table (8)

Measured and Empirically calculated Dipole Moments of Polyfluoronitrobenzenes

Nitrobenzene* Derivative	Measured Moment (D)	Empirically Calculated Moment (D)	Group Moments used in Calculation
2-F	4.64	4.63	NO_2-3.75, 2-1.42
3-F	3.47	3.56	NO_2-4.06, 3-1.44
4-F	2.57	2.59	NO_2-4.06, 4-1.47
2,4-F_2	3.31	3.26	NO_2-3.75, 2-1.42, 4-1.44
2,6-F_2	5.15	5.07	NO_2-3.65, 2,6-1.42
3,4-F_2	2.25	2.29	NO_2-4.06, 3,4-1.42
2,3,4-F_3	2.90	3.35	NO_2-3.75, 2,3-1.39, 4-1.42
2,4,5-F_3	2.61	2.33	NO_2-3.75, 2,4,5-1.42
2,4,6-F_3	3.49	3.59	NO_2-3.61, 2,6-1.42, 4-1.44
2,3,4,5-F_4	1.86	1.93	NO_2-3.63, 2,3,4-1.39, 5-1.42
2,3,4,6-F_4	3.03	3.01	NO_2-3.47, 2,3-1.39, 4,6-1.42
2,3,5,6-F_4	3.28	3.34	NO_2-3.37, 2,6-1.39, 3,5-1.42
2,3,4,5,6-F_5	1.98	1.98	NO_2-3.37, 2,3,4,5,6-1.39

*The nitro-group is in position number 1.

(ii) Polybromonitrobenzenes

A similar method must be used to calculate the apparent substituent moments in ortho-bromonitrobenzene. The calculation leads to an estimated value of 17° for angle θ, leading to the C-Br bond moment to be 1.20D and the nitro-group moment 3.52D. The empirically calculated moment for ortho-bromonitrobenzene will then be 4.25D, (c.f. the experimental value

4.24D). The empirically calculated moment of m-bromonitrobenzene 3.55D is obtained by assigning the following empirical values: for C-Br bond 1.55D and C-NO_2 group 4.06D, which is the same as in nitrobenzene, the experimental value being 3.42D.

In p-bromonitrobenzene, taking the moment of the nitro-group to be 4.06D, and a C-Br bond moment of 1.40D results in a calculated moment of 2.66D. The empirical calculations carried out over the whole range of polybromonitrobenzenes suggest the following empirical bond moments for the bromo-group: with one ortho nitro-group, 1.20D; one meta nitro-group, 1.55; one para nitro-group 1.40D and where there is both an ortho bromine and an ortho nitro-group, 0.90D.

The nitro-group moment is reduced to 3.52D when there is an ortho bromo-group and remains at 4.06D when there is a meta bromo-group and again at 4.06D when there is a para bromine atom. With two ortho bromine atoms the moment of the nitro-group is reduced to 3.33D.

Probably because of difficulties in the purification of the compounds 2,3,4,6- and 2,3,5,6-tetrabromo- and pentabromo-nitrobenzenes, the assignment of empirical values of the nitro-group moments in these compounds is subject to uncertainty. However, considering the nitro-group moment to be 3.20 ± 0.3D, the moment of 2,3,4,6-tetrabromonitrobenzene will be 2.66 ± 0.3D which is 0.8D lower than its measured moment (3.46D). The moment of 2,3,5,6-tetrabromonitrobenzene will be 2.90 ± 0.3D, about 0.69D higher than its measured moment (2.21D). The moment of pentabromonitrobenzene will be 2.30 ± 0.3D, about 0.3D lower than its measured moment (2.60D).

Table (9)

Measured and Empirically Calculated Dipole Moments of Polybromonitrobenzenes

Nitrobenzene* Derivative	Measured Moment (D)	Empirically Calculated Moment (D)	Group Moments used in Calculation
2-Br	4.24	4.25	NO_2-3.52, 2-1.20
3-Br	3.42	3.55	NO_2-4.06, 3-1.55
4-Br	2.66	2.66	NO_2-4.06, 4-1.40
2,3-Br_2	3.77	3.83	NO_2-3.52, 2-0.90, 3-1.20
2,4-Br_2	2.93	2.91	NO_2-3.52, 2-1.20, 4-1.40
2,5-Br_2	3.41	3.36	NO_2-3.52, 2-1.20, 5-1.55
2,6-Br_2	4.53	4.53	NO_2-3.33, 2,6-1.20
3,4-Br_2	2.53	2.49	NO_2-4.06, 3,4-1.20
3,5-Br_2	2.55	2.65	NO_2-4.06, 3,5-1.41
2,3,4-Br_3	2.89	2.80	NO_2-3.52, 2,3-0.9, 4-1.20
2,3,5-Br_3	2.08	2.73	NO_2-3.52, 2-0.9, 3-1.20, 4-1.41
2,4,5-Br_3	2.55	2.32	NO_2-3.52, 2,4,5-1.20
2,4,6-Br_3	3.08	3.13	NO_2-3.33, 2,6-1.20, 4-1.40
3,4,5-Br_3	2.10	1.96	NO_2-4.06, 3,5-1.20, 4-0.9
2,3,4,5-Br_4	2.23	2.08	NO_2-3.52, 2,3,4-0.90, 5-1.20
2,3,4,6-Br_4	3.46	2.66 $\pm$0.3	NO_2-3.20 $\pm$0.3, 2,3-0.90, 4,6-1.20
2,3,5,6-Br_4	2.21	2.90 $\pm$0.3	NO_2-3.20 $\pm$0.3, 2,6-0.9, 3,5-1.20
Pentabromonitrobenzene	2.60	2.30 $\pm$0.3	NO_2-3.20 $\pm$0.3, 2,3,4,5,6-0.90

*The nitro-group is in position number 1.

Littlejohn and Smith's(20) suggestion is that the mesomeric power of the nitro-group will reduce the electron density of the ring and therefore increase the +M effect of the halogen substituent. This is inconsistent with our measured moments since an increase in the nitro-group moment followed by a decrease in the C-X bond moment with the appropriate angle of 120° would result in an imaginary value for the C_{ar}-X bond moment in the case of meta-halogenonitrobenzenes.

Moreover, although consideration of the the van der Waal's radii of the fluorine atom and the nitro-group predicts no steric obstruction to the coplanarity of the nitro-group with the ring in molecules such as 2,6-difluoro-, 2,4,6-trifluoro- and 2,3,4,6-tetrafluoro-nitrobenzenes, the apparent nitro-group moments obtained after allowance for induction are similar to those in polybromonitrobenzenes. However, in the latter compounds there is strong evidence for deflection of the nitro-group out of the plane of the benzene ring, therefore one would expect a greater reduction of the nitro-group moment due to obstruction of its -M effect in these compounds. Also, Trotter(45) pointed out that the C-N bond in nitrobenzene is not appreciably shortened when compared to nitromethane or to 2,4,6-trimethyl-nitrobenzene.(46) More confirmation has been given from recent results(47, 48,49) in aromatic sterically hindered and non-hindered derivatives. The lengths of the C-N bonds in these cases are 1.466 and 1.486 Å (compared with nitromethane 1.470 Å) and do not depend on the twisting angle of the nitro-group. Therefore, as has already been mentioned, Sutton's concept of the mesomeric dipole moment, based on comparison of similar conjugated and non-conjugated molecules is wrong and in fact the explanation of the enhancement of the moment of nitrobenzene compared with that of an aliphatic nitro-compound is due to $-I_\pi$ effect. The partial positive charge on the nitrogen atom will be unaffected by the angle of rotation of the nitro-group relative to the aromatic ring, and the effect, like the -M effect gives rise to the necessary alternation of charge around the ring. Comparison of the experimental and calculated figures shows clearly that the empirical correction for induction is sufficient to account for the observed values without any change in the mesomeric moment of the nitro-group.

In the case of fluorobenzene, where one expects a large $+I_\pi$ effect on theoretical grounds, such direct evidence for the effect cannot be obtained, since steric hindrance to mesomerism is not possible. However, examination of the data in Table (10) shows a powerful repulsive inductive effect by fluorine atoms, and to a lesser extent chlorine and bromine atoms in saturated systems.

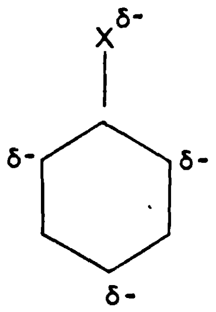
Table (10)

Dipole Moments of some Halogen Compounds (Gas Phase)*

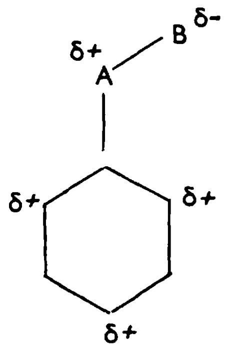
Compound	μ/D	Compound	μ/D	Compound	μ/D
Hydrogen fluoride	1.91	Methyl fluoride	1.81	Fluorobenzene	1.61
Hydrogen chloride	1.08	Methyl chloride	1.87	Chlorobenzene	1.70
Hydrogen bromide	0.79	Methyl bromide	1.79	Bromobenzene	1.70
Hydrogen Iodide	0.38	Methyl iodide	1.64	Iodobenzene	1.70

*A.L. McClellan, Tables of Experimental Dipole Moments, 1963, W.H. Freeman & Co.

Whereas the moment of methyl iodide is 1.26D higher than that of hydrogen iodide, the moment of methyl fluoride is lower than that of hydrogen fluoride by 0.1D, suggesting a moment change due to repulsion between the lone pairs of the fluorine atom and the bonding C-H electron pairs of at least 0.3D in the opposite direction to the -I effect. That a further reduction in moment should take place in fluorobenzene does not seem unlikely, since the aromatic system is more polarisable, and in any case, π-electron density is situated directly on the carbon atom to which the fluorine atom is attached. The $-I_\pi$ effect of the nitro-group and the $+I_\pi$ effect of the fluorine atom are illustrated in the figure below.



$+I_\pi$



$-I_\pi$

II. Nuclear Magnetic Resonance Studies

N.1 Introduction

1. Calculation of Shielding Constants and their Empirical Correlation with other Molecular Properties of the Molecules

Resonance absorption, corresponding to the reorientation of the nuclear magnetic moment with respect to the applied magnetic field direction, occurs at a frequency given by the Larmor equation, $\nu = g \beta H_0 / h$, g is the nuclear gyromagnetic ratio, β is the nuclear magneton and Ho is the magnetic field at the nucleus. However, the magnetic field at a nucleus differs to a small but measurable extent from the magnetic field in the macroscopic sample. The applied magnetic field interacts with the motion of the electrons in the system, which thereby contribute a component to the net magnetic field at the nucleus, the electronic component is proportional to the applied field and is usually in the opposite direction.

$$H_{\text{effective}} = H_0(1 - \sigma) \qquad (19)$$

Where σ is the shielding constant of the nucleus.

The effect may be considered as internal diamagnetism or magnetic shielding of the nucleus. The magnitude of the nuclear magnetic shielding depends upon the nucleus and the electronic structure of the sample in which it is observed.

The shielding calculation by quantum mechanics is only good for the hydrogen nucleus in a simple molecule and lack of knowledge of the exact ground and excited state wave functions in complex molecules makes such calculations difficult.

The understanding of chemical shift changes caused by introducing substituents into the molecule is however a different problem from the calculation of total shielding constants. In order to understand the latter, attempts have been made to express the shielding constant of the nucleus under consideration as a sum of contributions from different atoms or bonds in the molecule, and to correlate with other molecular properties such as dipole moment or electro-negativity of the substituent group. It is this semi-empirical approach to the understanding of changes in chemical shifts which will be reviewed in this introduction and the empirical correlations will be considered.

(a) General Theory of Chemical Shielding

Factors influencing Chemical Shifts

The chemical shielding observed by the conventional high resolution nmr technique for a species in solution is not that of an isolated molecule, but is modified by the surrounding medium.

$$\sigma_{(\text{observed})} = \sigma_{(\text{molecule})} + \sigma_{(\text{medium})} \qquad (20)$$

The term $\sigma_{(\text{medium})}$ is generally known as the solvent effect, and thus before attempting to analyse the factors affecting the shielding constant of a nucleus in an isolated molecule, $\sigma_{(\text{molecule})}$, initially it is necessary to calculate or eliminate the solvent effect. It has been suggested(50) that $\sigma_{(\text{medium})}$ may have contributions from five sources.

$$\sigma_{(\text{medium})} = \sigma_B + \sigma_A + \sigma_W + \sigma_E + \sigma_C \qquad (21)$$

A full discussion of these terms is given by Emsley and Phillips(50), an outline of each term, its relevance and indication of what precautions have been taken to allow for it in some parts of the present work are given here.

The term σ_B is due to the modification of the magnetic field experienced at the nucleus by the bulk magnetic susceptibility, $\mathcal{X}$, of the solvent. This can be calculated if $\mathcal{X}$ is known, but is best eliminated by measuring the chemical shift relative to an internal reference compound.

The term σ_A occurs whenever the solvent molecules have an anisotropic magnetic susceptibility and collisions between solute and solvent molecules are such as to lead to an averaged value of the magnetic susceptibility in the sphere immediately around the solute nucleus which is different from the bulk value, $\mathcal{X}$, thus the term will be of importance for disc-shaped molecules such as benzenes or rod-like solvents, e.g. carbon disulfide. . Although the effect is calculable, it is best eliminated by using a magnetically isotropic solvent (e.g. carbon tetrachloride) and an internal reference of similar nature to the solute.

The term σ_W is a contribution arising from the van der Waal's interaction between the solute and solvent molecules. This interaction originates from the electrostatic forces between the electrons immediately surrounding the observed nucleus and those in neighbouring molecules and decreases rapidly with the distance between the groups. An approximate expression for σ_W has been derived(51) in terms of the mean value of the square of the time-dependent electric field, $\langle F^2 \rangle$ and it has been suggested(52)

$$\sigma_W = -B \langle F^2 \rangle \qquad (22)$$

Where B is a constant, that $\langle F^2 \rangle$ will be proportional to r^{-6}. Considerable problems occur in the definition of B and $\langle F^2 \rangle$, since theoretical treatments of σ_W show both these parameters depend on the mutual orientation of the solute and solvent molecules and will thus only be a constant for molecules of similar size and shape, whilst B depends on the nature of the nucleus and its electronic environment. In order to eliminate σ_W as far as possible, Emsley and Phillips proposed(53) the use of an internal reference compound of similar chemical and physical shape to the molecule under investigation, and suggested that $CFCl_3$ should be used as the reference in ^{19}F nmr.

The term σ_E occurs only in the case of polar molecules, it arises from the reaction field set up by the polarisation of the surrounding medium by the electric dipole of the solute. This electric field modifies the shielding by:

$$\sigma_E = -A E_Z - B E^2 \qquad (23)$$

Where E is the field at the nucleus and E_Z is the component along the bond of the atom of interest. B is taken to be identical with that for the van der Waal's interaction. A is a measure of the polarisability of the electrons around the nucleus in the bond direction, and as with B, will vary according to the nuclear species and electronic environment. Consequently, accurate determination of σ_E is difficult, with A, B and E being ill-defined, and thus its elimination requires the use of an internal reference with dipole moment and values of A and B equal to those of the sample. This is not achievable practically if a series of compounds of varying polarity are to be examined, and thus to reduce this effect to a minimum it is best to use a non-polar reference and a non-polar solvent, in order that the reaction field of the reference is eliminated and that of the sample is minimised.

The last term is the Shielding expression, σ_C, which is included to take into account any specific "chemical" interactions which occur between solute and solvent, e.g. hydrogen bonding, complexation. The definition is not a precise one, since the presence of specific interactions are generally not predictable and hence not calculable. Thus it is usual to conclude that any variation in the observed shielding not attributable to any of the other effects is due to a specific interaction. However, this approach must be viewed with caution, since it is equivalent to defining σ_C as:

$$\sigma_C = \sigma_{(\text{medium})} - (\sigma_B + \sigma_A + \sigma_W + \sigma_E) \qquad (24)$$

and thus σ_C will contain all the accumulated errors in the other terms. If internal referencing is in use (for which it is assumed σ_A and σ_B are zero) then errors in σ_E and σ_W may be the cause of the discrepancy in equation (24). Possible sources of error are that the medium is not isotropic, and any anisotropy could be misinterpreted as an indication of directional forces between solute and solvent which are called "chemical" as opposed to physical interactions. If, however, the value of σ_C obtained from equation (24) is considerably larger than any of the other terms, then this interpretation is less ambiguous. Because of the ill defined nature of the "chemical" effects, no one approach can be used in their elimination, but it is reasonable to assume the possibility of such occurence is reduced if a non-polar solvent and reference are used.

An additional factor which should be taken into account, when attempting to measure the chemical shift of a nucleus in an isolated molecule $\sigma_{(molecule)}$, is the effect of the concentration of the solution. The chemical shift of any nucleus varies to a greater or a lesser degree as the concentration is changed, due to changes in the bulk properties of the mixture and variations in the associative interactions of the solute molecules. Unfortunately, these changes are neither linear, nor closely related for two different solutes, and thus shifts measured at a standard concentration need not necessarily reflect the shielding of the nucleus for an isolated molecule in the pure solvent. Such a value may only be obtained through recording the shift at a series of concentrations and extrapolating to infinite dilution.

It may be concluded from the foregoing comments that observation of the ^{19}F chemical shift in polychlorofluorobenzenes in the non-polar solvent (cyclohexane), relative to the non-polar aromatic reference, (1,3,5-trichloro-2,4,6-trifluorobenzene), should eliminate σ_A and σ_B for this range and minimise the contribution from the other terms by using fairly dilute samples, 0.5 molar of the solute in the solvent. For the measurement of ^{13}C chemical shifts, the different technique necessary for recording spectra and the use of concentrated solutions restricted the choice of possible experimental precautions. For these measurements, spectra of all the range of polybromo- and polybromo-nitro- benzenes are recorded in the same solvent and at the same concentration, and signals are referenced to the "internal" TMS peak. When these precautions are taken, the observed shifts are then a more accurate measure of changes of nuclear shielding produced by the molecule itself.

It is now possible to consider the factors affecting the shielding constant within the molecule. Generally this is considered to be separable(54,55) into two parts, called the diamagnetic and paramagnetic terms, but it has been pointed out(56) that localised intramolecular contributions should be taken into account,

$$\sigma_{\text{(molecule)}} = \sigma_d + \sigma_p + \sigma_I \qquad (25)$$

The diamagnetic term σ_d arises from the (diamagnetic) circulation of electrons (mainly s electrons) centred upon the nucleus in the applied magnetic field. The magnitude of the shielding is dependent upon the electron density at the nucleus and in the case of fluorine and ^{13}C chemical shifts, this term has been shown to account(56) for only 1% of the total shielding constant. The value of σ_d can be described using the Lamb formula ;

$$\sigma_d = \frac{e^2}{3mc^2} \sum_i \langle r_i^{-1} \rangle \qquad (26)$$

where $\langle r_i^{-1} \rangle$ is the mean inverse distance of electron i from the nucleus and the summation is over all electrons on the nucleus of interest.

The contribution of σ_I may be separated(57) into four terms.

$$\sigma_I = \sigma_a + \sigma_d + \sigma_e + \sigma_w \qquad (27)$$

The term σ_a arises from the diamagnetic circulation of electrons upon atoms or bonds remote from the nucleus under investigation. In solution this effect is averaged over all molecular orientations with respect to the direction of the applied magnetic field and hence the term will be zero except in the case of groups with a marked anisotropy in their diamagnetic susceptibility, e.g. the carbonyl group, C=O. For an axially symmetric group the effect is given(58) by:

$$\sigma_a = \frac{\Delta X}{3r^3 N_o}(1 - 3\cos^2\theta) \qquad (28)$$

Where r is the distance between the group concerned and the nucleus, ΔX is the difference in diamagnetic susceptibility of the group in the directions parallel and perpendicular to the group, N_o is Avogadro's number and θ is the angle between r and the group axis. Since the magnitude depends only on properties of the group and the molecular geometry, the effect is independent of the nucleus under study, and although the term is of importance in proton nmr, the much wider range of fluorine chemical shifts enables the effect to be safely ignored.

The term σ_d arises from the circulation of electrons in delocalised systems, and like the neighbouring atom anisotropy term, the contribution is independent of the nucleus under investigation, and therefore assumes a lesser importance in the case of fluorine chemical shifts.

The term σ_e is produced by the influence of electric fields on the shielding of the nucleus; the expression for σ_e is similar to that given for solvent reaction fields, except that the electric field E arises from permanent bond dipoles which are present with the molecule.

$$\sigma_e = -AE_z - BE^2 \qquad (29)$$

A and B are constants with similar significance to those defined for the solvent reaction fields.

The term σ_w expresses the effect of van der Waal's interactions, and arises because any group present in a molecule has associated with its electron distribution a fluctuating dipole moment, which produces a time-dependent electric field, F. The average square value $\langle F^2 \rangle$ is non-zero and again the expression for σ_w is similar to that used for solvent interactions. An approximate expression$^{(52)}$ for $\langle F^2 \rangle$ has been obtained as,

$$\langle F^2 \rangle = \sum_i 3 P_i I_i \Big/ r_i^6 \qquad (30)$$

and although this was originally derived for solute-solvent interactions, it has been shown$^{(59)}$ that this can be applied to intramolecular situations. P_i is the polarisability of the electron group, I_i is the first ionization potential and r_i the distance separating the fluorine atom from the C-X electron group.

The most important factor contributing to the observed molecular shielding is σ_p, the paramagnetic term, and is responsible for the large variation in ^{19}F and ^{13}C chemical shifts observed in practice. It arises from the restrictions imposed upon the circulation of the electrons by chemical bonding, i.e. the electron distribution is not spherically symmetric. It is not proposed to go into the theoretical aspects of this term, but to examine the structural features within the molecule which influence it in an empirical fashion. According to the expression for σ_p derived by Karplus and Pople$^{(60)}$, the major parameters are ΔE, the mean average excitation energy, the dimensions of the 2p orbital (in the $\langle r^{-3} \rangle_{2P}$ term), and a term including changes in bond orders to adjacent atoms. The apparent dependence on charge density is generally rationalised on the basis of the $\langle r \rangle_{2p}$ term.

$$\sigma_P = \frac{-e^2\hbar^2}{2\,m^2c^2\Delta E}\langle r^{-3}\rangle_{2p}\,\sum_B Q_{AB} \qquad (31)$$

2. Empirical Correlation in ^{19}F Shielding Parameters

Background

Each of the factors discussed in section (a) may have a varying importance in different types of compounds. Sometimes more than one of them may have a relevant contribution in any given situation. However, if the comparison of the shielding parameters is confined to a series of closely related compounds it is possible to limit the number of factors to be considered to one. For example, the ^{19}F magnetic shielding in some binary covalent fluorides was found$^{(61)}$ to decrease approximately linearly with increasing electro-negativity of the atom to which the fluorine is bonded. Therefore the more tightly electrons are held by the atom bonded to the fluorine, the less effective they are in shielding the fluorine.

Analogously, an examination of the chemical shifts in conjugated systems may reveal information about the π-electron distribution, and with known electron distribution, chemical shifts should be predictable. The approach to interpret substituent effects upon ^{19}F shielding in aromatic fluorine containing molecules by use of a variety of molecular orbital methods, ranging from the simple Huckel Molecular Orbital (HMO) theory to VESCF methods, have been of interest for many years. Generally it is assumed that in para-substituted fluorobenzenes the interacting groups are sufficiently separated for σ bond effects to be negligible and to relate the observed shielding changes to π-electronic density variation upon the carbon atom α to fluorine. But there is a great deal of research suggesting that even at such distances "electric field" or σ bond transmitted effects may be important(62,63).

Although direct relationships between the various structure-reactivity parameters such as those of Hammett or Taft and nmr substituent chemical shifts (S.C.S) are not obvious, many linear correlations have been observed between them. Gutowsky et al(64,65,66) studied ^{19}F shifts of a wide range of mono-substituted fluorobenzenes and some polysubstituted fluorobenzenes in order to determine the electron distribution by measuring the effect of the substituent group on the ^{19}F shielding. For poly-substituted fluorobenzenes they only investigated the extent to which the substituent effects are additive. Their chemical shift values were evaluated by comparing fluorobenzene with a substituted fluorobenzene, and any interaction between the substituent and the fluorine atom would not necessarily be the same as that between fluorine and the hydrogen atoms in the unsubstituted fluorobenzene. They suggested that chemical shift values for polysubstituted benzenes might be used to investigate the transmission mechanism of the substitutent effects. The inductive effect, particularly, could operate directly through space as well as via the benzene nucleus. If this is so, an ortho substituent could block at least partially the direct inductive effect of an adjacent meta substituent. An approximately linear correlation between the observed shift δ, and Hammett(67) substituent constant, σ, was reported and discussed in detail. The assumption being that these parameters in some way reflect

π -electron distribution. A better $\sigma-\delta$ correlation was found when the meta- and para-substituents were considered separately$^{(64)}$. Taft$^{(68)}$ re-examined Gutowsky's$^{(65)}$ ^{19}F shifts for the corresponding ring atoms in benzene derivatives and suggested a correlation between the shift, δ , for meta- and para-substituted compounds, and inductive and resonance parameters, σ_I and σ_R. The separation of Hammett σ_P values into two compounds is based on the equation

$$\sigma_P = \sigma_I + \sigma_R \qquad (32)$$

With σ_I as a measure of the effect of substituent group to attract or repel electrons through space or via bonds of the benzene system, while σ_R is a measure of the effect of substituent group to attract or repel electrons through resonance interaction (p- π overlap) with the π molecular orbitals of benzene. For the separation of Hammett σ_p into σ_I and σ_R, he made three primary assumptions.

1. Only resonance and inductive effects contribute to reactions in meta- and para-substituted benzene derivatives.

2. The inductive effect of a substituent is the same from either the meta- or the para- position, $I^m = I^p$.

3. The ratio of the resonance effect of a substituent in the meta position to that of the same substituent in the para position is a constant, independent of the substituent, $\frac{R^m}{R^p} = \alpha$

σ_I is obtained from the σ values of a series of aliphatic compounds which are free from resonance effect, and σ_R is obtained from $\sigma_R = P - \sigma - \sigma_I$.

The relationship between Δ_p (the chemical shift of fluorine in para-X-fluorobenzenes referred to the members of the series in which X=H) and σ_I and σ_R is:

$$\Delta_P = -5.83\,\sigma_I - 18.8\,\sigma_R + 0.8 \qquad (33)$$

While the corresponding meta-substituent chemical shift differences are given by the equation:

$$\Delta_m = -5.83\,\sigma_I + 0.2 \qquad (34)$$

Taft concluded that both resonance and inductive effects are important in the para position but only the inductive effect is important in the meta position.

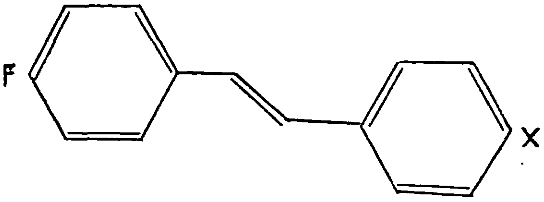
σ Values are normally not defined for ortho-substituted compounds, because of steric effects involved at this position. The primary justification for dividing the Hammett σ values into σ_I and σ_R is empirical, the theoretical significance of it is doubtful as, pointed out by Emsley and Phillips(69).

Ager, Phillips, et al(70) reviewed the question. The approach they adopted was to study first a related aromatic system in which the interacting groups were so far apart that σ-bond effects must be negligible. Using a semiempirical HMO method together with more sophisticated Linear Combination of Atomic Orbital Molecular Orbital (L.C.A.O-MO) theories for a series of 4-X-fluorobenzenes, they predicted that the π-electron densities upon the carbon atom bonded to fluorine (and upon the fluorine atom itself) in 4-X-4'-fluoro-trans stilbenes (IV) are linearly related to those in

4-X-fluorobenzenes by an equation:

$$\delta_{\pi(C-F)(\text{benzene})} = K\,\delta_{\pi(C-F)(\text{stilbenes})} \qquad (35)$$

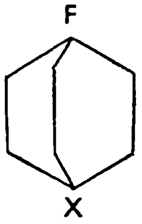
Assuming full conjugation for series of 4-X-4'-fluoro-trans stilbenes they



(IV)

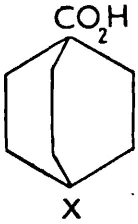
calculated the π-electron densities at the C-4' in the series and a plot of two sets of calculated values yield a value for k of 8.072 and concluded that if the substituent chemical shift in stilbene series were solely controlled by the π-electronic changes, then the effective π contributions to the substituent chemical shift, ($\Delta\,\pi_{cal}$) in the para-X-fluorobenzenes could easily be calculated, and should be 8.072 times larger than the corresponding S.C.S. in 4-X-4'-fluoro-trans stilbenes. Comparison of the calculated values of the effective π contribution of substituent X to chemical shifts ($\Delta\,\pi_{cal}$) with the corresponding experimental ones ($\Delta_{observed}$) in para-X-fluorobenzenes showed very poor agreement, therefore sigma effects do contribute to fluorine shielding in para-substituted fluorobenzenes and the latter must be expressed in dual-parameter terms allowing for both sigma and π effects.

In the series 1-fluoro-4-X-(2,2,2)bicyclooctanes (V), it was suggested that factors contributing to the shielding of the ^{19}F nuclei were mainly through σ-bond or through space interactions (the polar effects). Therefore they tried to correlate the ^{19}F substituent chemical shifts in the series of the compounds (V) below with the parameter ($\Delta_{observed}$)-($\Delta\pi_{cal}$) which was defined as the difference between the substituent chemical shift of a series of para-substituted fluorobenzenes and their corresponding calculated values obtained from the equation (35).



(V)

Since this parameter represents the magnitude of any through σ-bond or through space effect of the substituent on the ^{19}F shielding in the para-substituted fluorobenzenes, the agreement between the two parameters was good, since both groups caused an upfield shift of the fluorine compared with X=H, and further, a correlation with a high degree of precision was found between the ($\Delta_{observed}$)-($\Delta\ \pi_{cal}$) values and the σ_I parameter as a measure of the inductive power of the substituent group, defined from the ionization constant of the analogous series of (2,2,2)bicyclooctane carboxylic acids (VI).



(VI)

According to the above observation therefore they established a two-parameter equation expressing the ^{19}F para-S.C.S. in fluorobenzene.

$$\Delta_p = -21.06\,\sigma_p + 15.75\,\sigma_I \qquad (36)$$

The difference between the above equation and that of Taft is in the fact that the parameters used in equation (36) are experimentally derived (σ_p from ionization constants of p-substituted benzoic acids and σ_I from ionization constants of compounds of type (VI), whereas the σ_R parameters used in Taft's equation are ill-defined and are not obtainable by any independent measurement.

Similar treatments made to correlate Δ_m S.C.S. in meta-substituted fluorobenzenes (using the observed S.C.S. in 4-substituted-3'-fluoro-trans stilbenes), leads to the conclusion that π interactions alone may account for the shielding changes, which is in complete disagreement with the previous conclusions such as those of Taft et al(71), which assume that the meta-S.C.S. are almost wholly dependent upon the inductive effect of the group X and that the π-electronic effects are negligible.

Ager and Phillips(70), tried to correlate Taft's σ_R parameter with the ^{19}F S.C.S. values in 4-fluoro-4'-X-, 4-fluoro-3'-X-, and 3-fluoro-4'-X-trans stilbenes. It was pointed out by them that in this series, the conjugation between the substituent and π-electrons of the ring was the major factor in S.C.S. changes. But the correlation was non-existent, which indicated that the observed S.C.S. values were not directly related to such resonance effects. However, a very precise linear correlation was found between this data and the appropriate Hammett σ parameters. The high precision of these correlations indicated that σ_p might be a much better measure of the net π interaction between the group X and the aromatic ring than is σ_R. They obtained an explicit relationship with a high degree of precision between Δ_p and Hammett σ_m and σ_p parameters in para-X-fluorobenzenes.

$$\Delta_p = -21{\cdot}0567\,\sigma_p + 15{\cdot}7480\,\sigma_m \qquad (37)$$

Similar treatments correlating Δ_m S.C.S. in meta-substituted fluorobenzenes with σ_p were made and the appropriate equation was found to be:

$$\Delta_m = -8{\cdot}85\,\sigma_p \qquad (38)$$

Their final conclusion was that it is unnecessary to separate the σ_p of Hammett into σ_R and σ_I in order to interpret shielding data, since σ_R is ill-defined and is not obtainable by any independent measurements, whereas σ_p and σ_m both can be(72). The results were interesting, for Taft's equation has been interpreted as showing that σ-bond inductive effects are only important in determining meta-S.C.S., while equation (38) indicates that resonance interactions are of major importance compared to induction. Taft's(71) results and those of Ager, Phillips et al(70) are probably equally valid as judged by their success in calculating S.C.S, but each leads to directly opposing interpretation in terms of modes of electronic interactions.

Swain and Lupton(73), separated the reactivity parameter of various types of electronic effects into a general two-parameter equation involving a field inductive part, F, and a resonance (or π interaction) part, R.

$$\sigma = fF + rR \qquad (39)$$

The values of F are in fact refined σ_I values, based upon observation of the dissociation constants of 4-substituted-bicyclo(2,2,2)octane carboxylic acids. The values of R are based upon the assumption that in the case of 4-trimethyl ammonio benzoic cation, $\underline{p}$-$Me_3N^+ . C_6H_4 . CO_2H$, the dissociation constant of the carboxylic acid is solely determined by the F interaction of the Me_3N^+ group and its resonance contribution, R, is zero. Phillips et al(70) analysed all substituent parameters in terms of the F and σ_p values of Taft.

$$\sigma = fF + r\sigma_p \qquad (40)$$

This is because there was some doubt about the choice of origin of the R values, for the substituent effects of the group Me_3N^+ upon ^{19}F shielding in 4-fluoro-4'-trimethyl ammonio-trans-stilbene is large, (-1.49 ppm), and probably arises from an interaction with the π system (i.e. an R type interaction).

They reached the conclusion that groups such as $-NR_2$, -OR or -SR will be -electron donating (or repelling) compared with hydrogen, and that the halogens will be π-electron accepting (or attracting) with fluorine the least effective. This is exactly the order given by Godfrey(74) but not by Swain and Lupton(73) who preserved the more traditional idea that all groups such as $-NR_2$, -OR, -SR and halogens which possess a lone pair of π- symmetry are π-electron donors, while few groups (e.g. $-NO_2$) are π-electron acceptors.

More recently Sutcliffe and co-workers(75) suggested a van der Waal's effect which could be approximated by the mean square electric field of the substituent as given by the expression $\frac{3PI}{r^6}$, where P is the polarisability of the group, I is the ionization potential and r is the distance between the fluorine and C-X group. Subsequently, Hruska, Hutton and Schaefer(76) reported a linear correlation of the chemical shift of ^{19}F atoms ortho to a substituent in benzene derivatives with an empirical quantity Q,

$$Q = \frac{P}{I r^3} \qquad (41)$$

where P is the polarisability of the C-X bond (X=H, F, Cl, Br, I), r is the C-X bond length and I is the first ionization potential of the substituent X. The rationalisation of the use of Q is based on the assumption that the paramagnetic contribution should be inversely proportional to a mean excitation potential and is used as an approximation. It was found that Q correlated both ortho fluorine and proton chemical shifts in the benzenes and cis and trans vinyl compounds. The very fact that the range of trans vinyl proton chemical shifts is larger than the cis suggested that the 'ortho effect' was not a van der Waal's effect but rather was transmitted through the π-electron system. The term P/r^3 is dimensionless, and it was later shown that correlations with I alone were not as satisfactory as those with Q(77).

The calculation of Q values are limited to single atom substituents, such as halogen because of the lack of appropriate data for P and I for a multi-atom substituent group. By making use of the good linear plot(78) of the ortho proton shifts in o-dihalobenzenes vs the Q values, Smith and Roark(79) have obtained experimental values of Q for CH_3O, CN, NO_2 and CH_3 groups; they fitted the averaged observed shifts of proton-3 in 1-halo-2-OCH_3-(CN, NO_2)-benzenes into the plot and read off the values of Q.

Recently, Smith and Proulx(80) used the F and R values of Swain and Lupton(73) and the Q values determined by Schaefer et al(77) and made a multiple regression analysis in order to see what range of applicability such a correlation might have. The nuclei involved are proton, carbon, fluorine and selenium (one case). The compounds vary from the simple vinyl compounds, substituted benzenes and naphthalenes to both 5-and 6-membered heterocycles and ortho-X-toluenes.

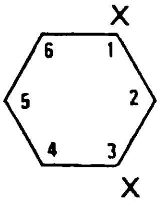
3. Empirical Correlations in ^{1}H Shielding Parameters

Background

Corio and Dailey(81) have examined an extensive series of mono-substituted benzenes in an attempt to evaluate the relative electron densities at the ortho-, meta- and para-positions for the various substituents, but no care was taken to eliminate intermolecular interactions and it is difficult to assess the theoretical significance of their measurements. Diehl(82) showed that the ^{1}H chemical shifts of the ring hydrogen nuclei in meta- and para-disubstituted benzenes can be calculated empirically by assuming the substituent effects on the chemical shifts to be additive. Good correlation between the calculated and observed chemical shift values have been observed. His measurements were taken in fairly dilute solutions with hexane (5 mole %). He suggested that in para-disubstituted benzenes involving the substituents X and Y the chemical shift contribution from the substituents will be:

$$\delta^{XY}_{O:X} = S_{O:X} + S_{m:Y} \quad , \quad \delta^{XY}_{O:Y} = S_{O:Y} + S_{m:X}$$

Where $\delta^{XY}_{O:X}$ and $\delta^{XY}_{O:Y}$ are the chemical shifts of protons ortho to substituents X and Y respectively and $S_{o:x}$, $S_{o:y}$, $S_{m:x}$ and $S_{m:y}$ are the substituent effects for protons ortho- and meta- to the substituents X and Y respectively in corresponding mono-substituted benzenes. However, it should be mentioned that this method of calculation does not give any absolute value for the substituent effects. To do this, we need to consider the chemical shifts in meta-disubstituted benzenes in terms of substituent effects $S_{o:x}$, $S_{m:y}$ etc. If the meta-disubstituted molecule m-$C_6H_4X_2$ is designated,



then the chemical shift contributions due to the substituent effects can be written:

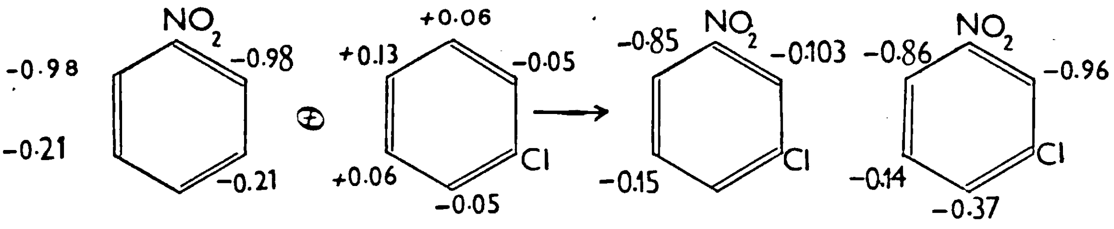
$$\delta_2 = 2S_{o:x} \quad , \quad \delta_4 = S_{o:x} + S_{p:x} \quad , \quad \delta_5 = 2S_{m:x}$$

Hence in a symmetrical para-disubstituted benzene the chemical shifts of protons $\delta_2 = \delta_3 = \delta_5 = \delta_6 = S_{o:x} + S_{m:x} = \delta_H$

Therefore these relationships provide a simple check on the additivity concept since the chemical shift of the hydrogen nuclei in p-$C_6H_4X_2$ should be equal to the mean of the chemical shifts δ_2 and δ_5 in the m-$C_6H_4X_2$. Therefore to calculate absolute values of the substituent chemical shift contributions, it is necessary to examine meta-disubstituted molecules of the type m-$C_6H_4X_2$ and m-$C_6H_4Y_2$; $S_{o:x}$ and $S_{m:x}$ can be obtained directly from the chemical shifts δ_2 and δ_5. Knowing a value of $S_{m:x}$, the chemical shift contribution $S_{p:x}$ can be derived from δ_4. Diehl(82) calculated the absolute chemical shift contributions $S_{o:Br}$, $S_{m:Br}$ and $S_{p:Br}$ for bromine substituent from the measured chemical shifts in meta-dibromobenzene.

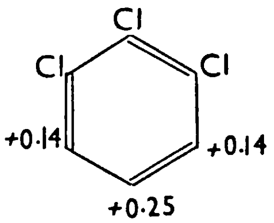
Observed Chemical Shifts (ppm)	Calculated Substituent Effects (ppm)
$\delta_2 = -0.44$	$S_{o:Br} = -0.22$
$\delta_4 = \delta_6 = -0.16$	$S_{p:Br} = +0.06$
$\delta_5 = +0.21$	$S_{m:Br} = +0.11$

In the same way he predicted the absolute values for the chemical shift contributions for many substituents. A good correlation has been observed between the calculated and observed chemical shift values for meta-disubstituted benzenes. For example, in meta-chloronitrobenzene, these values are:

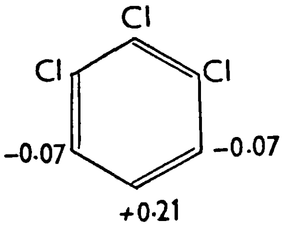


Calculated Observed

But he noticed that for ortho-disubstituted benzenes as well as all substituted benzenes with appreciable permanent dipole moments, the agreement is much poorer. For example, in the compound 1,2,3-trichlorobenzene ($\mu = 0.8D$) the calculated chemical shifts are quite different from the measured values.

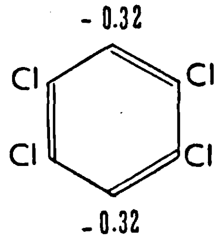


Calculated

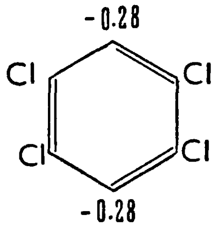


Observed

Conversely, in the symmetrical molecule 1,2,4,5-tetrachlorobenzene (which has no dipole moment) there is reasonable agreement between observed and calculated chemical shift values.



Calculated



Observed

Diehl(82) made no-attempt to interpret the benzene substituent effects in terms of the electric field produced by the permanent dipole of the aromatic molecule since the approach is known to give poor results for some substituted benzenes (e.g. halobenzenes) and furthermore does not reflect resonance effects in the benzene rings. Diehl(82) preferred to discuss his measured substituent effects in terms of Hammett σ parameters. Since the electronic distribution at the ortho-position is very similar to that at the para-position to the substituent, he tried to correlate the substituent effect at the ortho-position, S_o, with σ_p which is the Hammett constant for the para-position. Most of the substituents have contributions which lie on a straight line except halogens and the cyano group, although the halogens show a linear correlation among themselves. Diehl(82) suggested that the anomalous behaviour of the halogens is mainly due to the strong neighbouring diamagnetic anisotropic effects at the ortho-position. However, to date no consistent set of magnetic anisotropies has been produced for the halogens which lead to meaningful results in aromatic systems.

Brey and Lawson(83) have made a similar attempt and reached the same conclusion. They found that the chemical shifts of penta-substituted benzenes and 2,6-disubstituted phenols cannot be predicted by an additivity method.

Martin and Dailey(84) have accurately measured the ^{1}H chemical shifts of a large series of <u>para</u>-disubstituted benzenes and have found that the measured shifts obey the relation:

$$\delta = d_o(R_1) + \nu(R_1)\, d_m(R_4) \qquad (42)$$

where δ is the chemical shift of the hydrogen nucleus ortho to substituent R_1 and meta to substituent R_4, d_o and d_m are characteristic ortho and meta shielding parameters and ν's are empirical constants and are measures of the susceptibility of the proton ortho to R_1 to a perturbation of the substituent para to R_1, ν decreases as d_o increases. This is a refinement on the work of Diehl(82) and others in that ν is not always unity. These substituent constants work well to predict the values of the proton chemical shifts in para-disubstituted benzenes, meta-disubstituted benzenes and for the remote protons of ortho-disubstituted benzenes. Martin and Dailey(84) found that protons adjacent to the substituents in a series of symmetrical ortho-disubstituted benzenes gave chemical shifts consistently downfield by substantial amounts from the predicted values, (deviations as large as 0.5 ppm were found).

Smith and Cole(78) noted that the chemical shifts of protons adjacent to a given halogen, when compared with their symmetrically substituted analogues, were independent of the nature of the non-adjacent halogen in unsymmetrical ortho-dihalobenzenes.

The chemical shifts of aromatic protons ortho to a varying group of substituents, have been found to correlate well with the parameter Q, (76,77,78,79) the definition of which has been given in page (94) equation (41). Since the Q effect seems to operate through the π

system, it is not clear why the effect at H_6 is blocked from variation at C_2 by a substituent at C_1 in ortho-C_6H_4XY. Specific van der Waal's interactions of the type discussed by Richardson and Schaefer(85) are not incorporated in Q, though there is a trend for Q values to increase with the size of the substituent.

The problem of discrimination between different effects introduced by substituents in chemical shift measurements is even more difficult and complex in polysubstituted benzenes since substituent interactions will introduce further variables. In more highly substituted benzenes there must be at least one pair of substituents situated ortho to one another (except of course for 1,3,5-trisubstituted benzenes). Therefore large deviations of observed shifts from those calculated by existing additivity schemes are to be expected. There is only one published paper(85) which proposes a somewhat different additivity scheme applicable to proton shifts in a variety of polyhalosubstituted benzenes. Richardson and Schaefer(85) suggested that such large deviations are probably due to steric interaction between the ortho substituents. The interaction can be accommodated in an empirical scheme by assigning a parameter $D(X_o-X_m) \equiv D(X,Y)$ to a pair of substituents placed ortho (X) and meta (Y) to the proton whose chemical shift is required, and it is assumed that the shift of any proton can be found as the sum of the parameter D and a parameter d_p. This assumption is consistent with the fact that in a 1,2-disubstituted benzene the ortho interaction is not such as to interfere with the additive effect of protons 4 and 5(78). It is also consistent with the evidence(79) that, in a 1-X-2-Y-benzene the shift of proton-4 is linearly related to the shift of proton-3 in the 1-Y-benzene. Their above formula is only applicable to compounds in which only one pair of substituents are placed ortho to each other. Thus, 1,2,3-, 1,2,3,4- or 1,2,3,4,5-substituted benzenes would fall outside the present scheme; the deviations get larger in magnitude as the degree of substitution and the size of the substituents increase. The existence of an 'ortho' interaction between X and Y substituents and its 'steric' nature was confirmed by a plot of D(X,Y)-D(H,Y); keeping X constant, (Y=H,F,Cl,Br,I); (which is therefore a measure of the effect of the interaction between X and Y in the proton shift ortho to X) against the van der Wall's radius of Y. It was indicated that there is an algebraic decrease of D(X,Y)-D(H,Y) as the size of Y increases. Increased perturbation due to crowding of the ortho C-H bond is expected to lead to an increased downfield shift, as observed. They noticed that the D(Br,Y) values do not vary regularly with the van der Waal's radius of Y, because the meta shift due to Y increases algebraically in going from fluorine to iodine and partly cancels the algebraic decrease in D(Br,Y), naively expected on steric grounds.

4. Carbon-13 Nuclear Magnetic Resonance

The advent of proton noise decoupling and Fourier transform (FT) technology has enabled carbon-13 nmr to become a relatively accessible spectroscopic technique with currently available instrumentation.

Observation of ^{13}C provides a useful probe with which to examine the chemical environment of all carbons at the various sites within a molecule, whether or not they bear more readily detectable nuclei such as proton or fluorine. The carbon-13 isotope has a spin of $+\frac{1}{2}$, and hence yields sharp absorption signals, and the low natural abundance (1.1%) implies that the probability of spin-spin interaction with second carbon nucleus is very low (10^{-4}): consequently the only coupling observed will be with other nuclei of high natural abundance (e.g. ^{1}H, ^{19}F, ^{31}P).

Although the factors influencing ^{13}C Shielding have not been investigated as fully as for fluorine or proton nuclei, the general outline presented in chapter (a) will be applicable. Since the carbon nucleus has a p electron valency shell, it is considered(86) that the paramagnetic term will provide the dominant contribution to the magnetic shielding. If an electro-negative atom is substituted on carbon, an inductive withdrawal of electrons causes a "shrinking" of the 2p orbital, and the resultant increase in magnitude of σ_p, decreases the shielding of the carbon.

5. Mechanisms of Spin Coupling

The simplest way to enter a discussion of the mechanisms of spin-spin coupling is to consider the general expression of Ramsey(87) used to describe the interaction J_{AB} between nuclei of spin $\frac{1}{2}$.

$$J_{AB} = J_{1AB} + J_{2AB} + J_{3AB} + J_{4AB} \tag{43}$$

J_{1AB} arises from the direct interaction of one nuclear dipole with the other, and is very large (typically 30k Hz). However, in the fluid state, rapid tumbling of molecules averages this to zero, and so it does not enter into normal consideration. The remaining mechanisms all involve the molecular electrons and may thus be described as electron coupled interactions.

The second contribution, J_{2AB}, arises through the nuclear magnetic moment of A interacting with the orbital electron currents, which in turn interact with the moment of B, and vice versa. This term is usually referred to as the orbital-orbital coupling, or spin-orbital coupling.

J_{3AB} is produced by a dipole interaction between the nuclear magnetic moment of A and the associated electron spin magnetic moments; the electron dipoles interact with the magnetic dipole of nucleus B and thus "pass on" the "spin information" necessary for coupling. This term is known as the dipole-dipole coupling, or spin-dipole coupling.

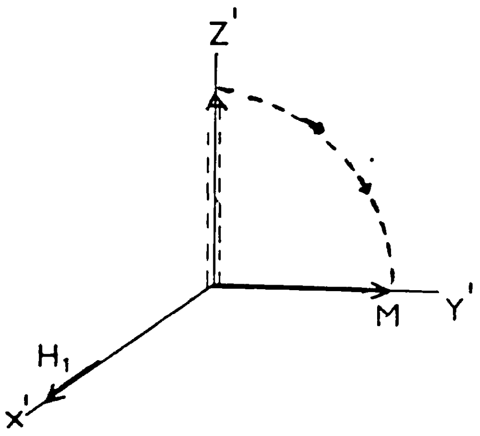
The fourth term J_{4AB} is an interaction between the nuclear magnetic moment and electron spin in s orbitals, which have non-zero value at the nucleus. Expressed alternatively, it arises from the fact that an electron associated primarily with one nucleus has a finite probability of being at the other nucleus, and hence transmitting spin information directly. Due to the nature of the term, this is known as the Fermi contact interaction.

In the case of interproton coupling, this term accounts for ca. 98% of the observed coupling, with the other two terms only making minor contributions. However, fluorine couplings are very much larger than those involving protons alone and it has been suggested(88) that the spin-orbital and spin-dipole couplings (J_{2AB} and J_{3AB}) become more effective when the atoms concerned possess p or d atomic orbitals. A theoretical treatment by Pople(88) has shown that, notwithstanding the large contribution to geminal H-F coupling by the spin-orbit mechanisms (estimated value 13.3Hz) the predominant term is the Fermi contact for the observed range of couplings (44 to 81 Hz).

N.2 Experimental

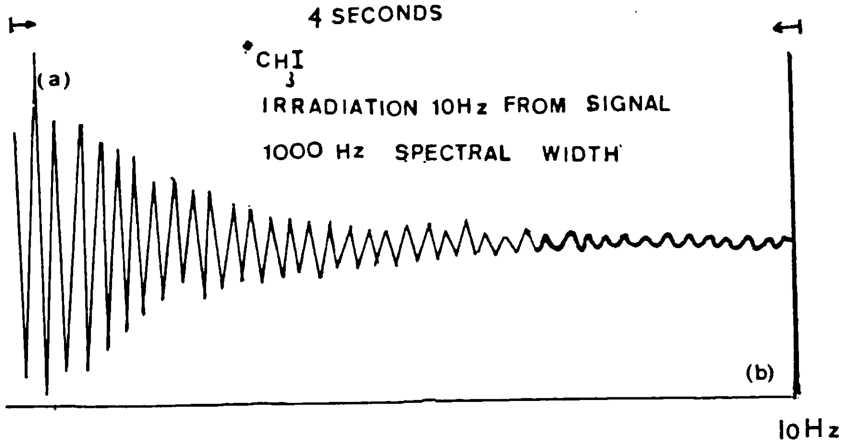
1. Experimental Technique of Pulse Fourier Transform NMR

Basically this technique uses a short, intense pulse of radio frequency energy to excite simultaneously all the resonances of a given type of nucleus and observe the total response of the sample. During a pulse experiment, the magnitude of H_1 (the radio-frequency field, applied along the x' axis) remains constant and the angle Φ , through which M (magnetisation vector) processes around H_1 is controlled by varying the time the pulse is applied.



A 90° pulse along x' rotates M from the equilibrium position to the Y axis.

The pulse is short (~ 5 to 50 μ sec) and the bandwidth of excitation must be sufficient to simultaneously excite all the nuclei of one type in the sample. For this requirement, the magnitude of the irradiation field H_1, must be sufficient to cause the magnetisation of all the nuclei of the same species to process the same angle about H_1, and the time t_p for which the pulse is applied should be short compared to the relaxation times T_1 and T_2 of the nuclei. The rate at which the pulses may be repeated depends on the relaxation times of the nuclei in the sample. If $T_1 \approx T_2^*$, where T_2^* is the apparent spin-spin relaxation time that includes both relaxation due to T_2 processes and relaxation due to magnetic field inhomogeneity, the pulse can be repeated after approximately $3T_2^*$ with no loss in signal intensity. After the pulse is turned off a signal is induced in the receiver coil which is in the form of oscillating currents, proportional to the resonance frequencies and inetnsities of all the resonating nuclei. The plot of the signal versus time as the nuclei return to equilibrium after the pulse is called the free induction decay FID. The F I D corresponding to absorption of one frequency is an exponentially decaying sine wave. The frequency of the sine wave is the difference between the centre (carrier) frequency of the radio-frequency excitation pulse and the radio-frequency for that particular absorption (the Larmor frequency for that nucleus). This is shown in the figure below,



(a) Time domain - F I D; (b) frequency domain - Spectrum (CH_3I, ^1H decoupled).

where the Larmor frequency is 10Hz from the centre frequency of the radio-frequency carrier. The F I D shown in the above figure was recorded for

4 sec; the sine wave contains 40 cycles, and thus the procession frequency is $^{40}/_{4}$ = 10Hz. The FT spectrum of the F I D is shown in part (b) of the above figure. The radio-frequency carrier was located at the far right during irradiation. The single peak is found 10Hz from the right limit (the full spectral width is 1 KHz). The FT abstracts all the frequency components out of the complex wave form present in the F I D.

A digital computer is used for sampling the F I D and storage for sensitivity enhancement. In practice the sampling rate is usually set to be greater than 2 Δ (Δ is the entire range of chemical shifts, measured with respect to the radio-frequency, Hz). For proton spectra at 100 MHz (1000 Hz spectral width), sampling rates of at least 2000 points sec^{-1} are required. Similarly, carbon-13 spectra at 25 MHz (5000 Hz spectral width) require sampling rates of at least 10,000 points sec^{-1}. The sampling time also determines the resolution of the transformed frequency domain spectrum; e.g. in order to achieve a resolution of R Hz, the F I D must be sampled for at least $^{1}/_{R}$ sec. If the sampling time is too long, the $^{S}/_{N}$ decreases due to the fact that the noise content of the F I D increases towards the tail-end of the F I D. The resolution will ultimately be determined by the available data storage capacity (memory) of the digital computer. For a proton spectrum at 100 MHz with a resolution of 0.5 Hz, at least 4000 (4K) data points are used to avoid folding back the high-frequency noise. For a resolution of 1 Hz for carbon-13 spectra at 25 MHz, a memory of 16K is required, taking into account the larger sampling rates for the noise. These requirements can be met using "minicomputers" with about 8-12K of memory (actually 8192-12,288 words), and a portion of the memory usually must be used to store the computer program.

2. Chemical Shift and Spin-Spin Coupling Measurements

(i) Polyfluoro- and Polyfluoronitrobenzenes

The chemical shift of all the fluorine nuclei present in the polyfluoro- and polyfluoronitro-benzenes were recorded as pure compounds, with $CFCl_3$ as an external reference, at 56.4 MHz on a Perkin Elmer R-12B nuclear magnetic resonance spectrometer in order to check the purity and the identification of these compounds.

(ii) Polychlorofluorobenzenes

The chemical shifts of the polychlorofluorobenzenes on solutions containing 0.5 mole/lit of the sample and 0.2 mole/lit of the reference (1,3,5-trichloro-2,4,6-trifluorobenzene) in distilled cyclohexane were recorded at 56.4 MHz on a Perkin Elmer R-12B nuclear magnetic resonance spectrometer. The reference 1,3,5-trichloro-2,4,6-trifluorobenzene, and the non-polar solvent cyclohexane were used in order to minimise differences in terms $\Delta \sigma_E$, and $\Delta \sigma_W$, already described in the introduction.

(iii) Polybromo- and Polybromonitro-benzenes

The proton and carbon-13 chemical shifts and coupling constants of all the polybromo-and polybromonitro-benzenes were recorded to low field of internal TMS on JEOL-FX90Q spectrometer with 8 K data points. The carbon-13 spectra were run at a spectral width of 5000 Hz operating at 22.50 KHz in the FT mode, and locked to the deuterium resonance of the solvent. Samples were prepared in 10-mm tubes, usually at a concentration of 0.6 molar in deuterated-chloroform.

N.3 Results and Discussion

1. Spectral Analysis

(i) Polyfluoro- and polyfluoronitro-benzenes

Table (21), page 144, contains the chemical shifts of all the fluorine nuclei present in polyfluoro- and polyfluoronitro-benzenes which are quoted relative to external $CFCl_3$.

(ii) Polychlorofluorobenzenes

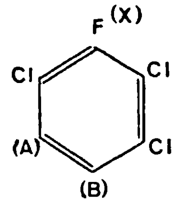
The "three- and two-spin" systems were analysed and their J_{FH} values are reported in Table (11). The spectral analysis of 2,3,6-trichlorofluorobenzene as an example of our three-spin systems is given in page 109. Table (22), page 146, gives the ^{19}F chemical shift differences from sym-$C_6F_3Cl_3$ in ppm.

(iii) Polybromo- and polybromonitro-benzenes

The proton chemical shifts of these compounds are summarised in Tables (12) and (13) in ppm to low field of internal TMS. Their H-H coupling constants are reported in Table (14). In the dibromobenzene series, the "four-spin" systems, their proton spectrum are analysed and the couplings are observed directly from the spectra. Although no H-H coupling has been observed in our *p*-dibromobenzene spectrum, a paper published by Read, Cresely, Butler and Leomker(89) reports values for *ortho*-, *meta*- and *para*- H-H coupling constants. The "three-spin" systems such as tribromobenzenes and dibromonitrobenzenes were easy to analyse, their coupling parameters were directly obtained from their spectrum. *Meta*- and *para*-bromonitro-benzenes as "four-spin" and "two-spin" systems respectively, due to the reduction in complexity of parameters, were directly analysed and their H-H couplings were observed directly from the spectrum.

The ^{13}C chemical shifts were measured from proton noise decoupled -^{13}C spectrum, and the spectral analysis was facilitated by using selective ^{13}C-(^{1}H) experiments, assignments were based on spin coupling measurements and relative intensities. These ^{13}C shieldings are given in Tables (15) and (16) together with some literature values. The long-range ^{13}CH coupling constants and all the directly bonded ^{13}CH coupling constants are reported in Table (17), where the spectra were first-order coupling constants were obtained directly from the spectrum.

The nmr spectra of 2,3,6-trichlorofluorobenzene



The proton nmr spectrum of the compound is known as an ABX system, the two protons making up the AB part of the spectrum and fluorine atom the X part. Eleven lines are observed. This situation usually arises as J_{AB} approaches $\nu_A - \nu_B$ or $(\nu_A + \nu_B)/2$ approaches $\frac{1}{2}(J_{AX} - J_{BX})$. In the AB part of the spectrum, in order to decide on the correct location of the transition lines it is necessary to calculate $\frac{1}{2}|J_{AB} + J_{BX}|$ from the centres of the two AB subspectra and compare these values with the value obtained from $|J_{AX} + J_{BX}|$ from the X part of the spectrum. Lines 9 and 12 yield a value of 5.12 Hz for $|J_{AX} + J_{BX}|$, the overlapping of the lines 1,3,5 and 7 in the AB part will give a value of 2.7 Hz for $\frac{1}{2}|J_{AX} + J_{BX}|$. The frequency separation between lines 10 and 11 yields $2|D_+ - D_-| = 2.82$ Hz and separations between lines 14 and 15 yields $2|D_+ + D_-| = 20.39$ Hz which with the other quantities D_+ and D_- (90) helps in the calculation of the J_{AX}, J_{BX} and J_{AB} parameters. Therefore from:

$$\begin{array}{lll} 2\left|D_+ - D_-\right| = 2.82\ \text{Hz} & & D_- = 4.393\ \text{Hz} \\ & \longrightarrow & \\ 2\left|D_+ - D_-\right| = 20.39\ \text{Hz} & & D_+ = 5.803\ \text{Hz} \end{array}$$

giving a value of 7.528 Hz to J_{AX} and -1.25 Hz to J_{BX} and J_{AB} = 8.78 Hz seen from the AB part of the spectrum as repeating spacings of

$$J_{AB} = (\nu_1 - \nu_2) = (\nu_3 - \nu_2) = (\nu_5 - \nu_2) = (\nu_7 - \nu_2)$$

from the equations,

$$D_+ = \tfrac{1}{2}\left[\left[\nu_A - \nu_B + \tfrac{1}{2}(J_{AX} - J_{BX})\right]^2 + J^2_{AB}\right]^{\frac{1}{2}}$$

$$D_- = \tfrac{1}{2}\left[\left[\nu_A - \nu_B - \tfrac{1}{2}(J_{AX} - J_{BX})\right]^2 + J^2_{AB}\right]^{\frac{1}{2}}$$

The value of $\nu_A - \nu_B$ = 3.2 Hz is the best chemical shift difference, correlating well with the spectrum.

A schematic drawing of an ABX spectrum with the repeated spacings:

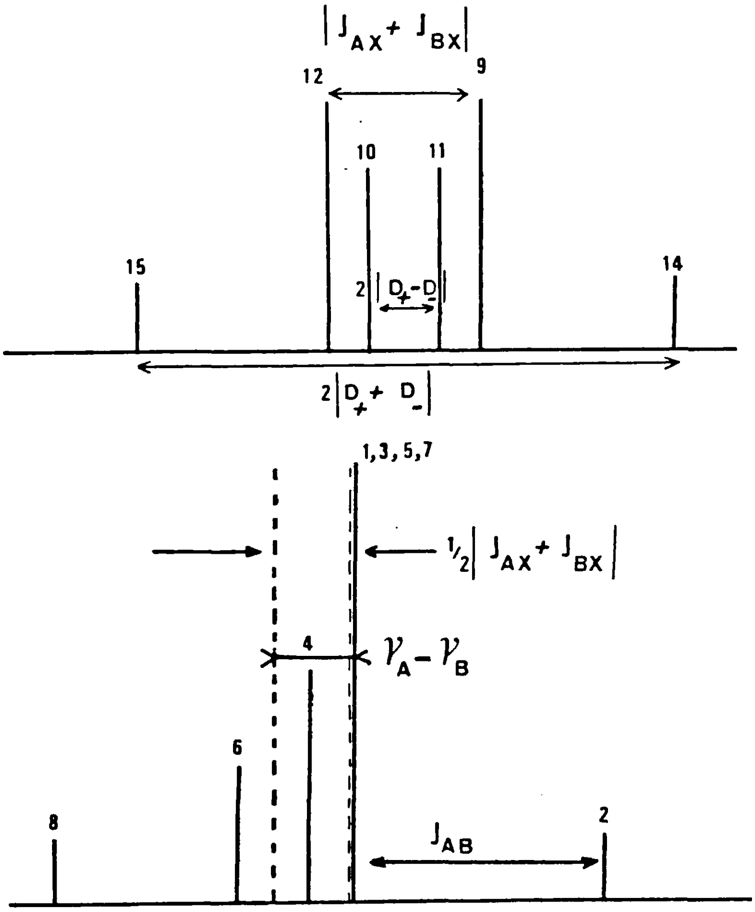


Table (11)

The observed and calculated ortho-, meta- and para- F-H coupling constants in polychlorofluorobenzenes

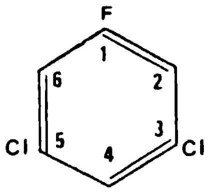
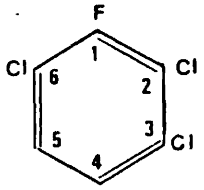
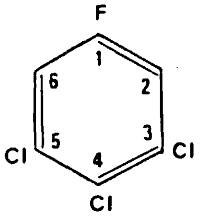
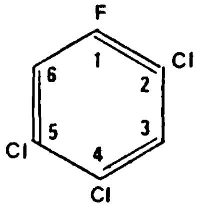
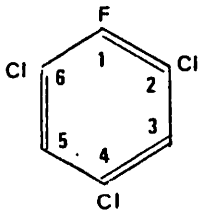
Compound	Coupling in Hz
	$J_{12} = J_{16} = 7.53$ $J_{14} = 0.42$
	$J_{15} = 7.53$ $J_{14} = 1.25$
	$J_{12} = J_{16} = 7.78$
	$J_{16} = 8.64$ $J_{13} = 7.50$
	$J_{13} = J_{15} = 5.78$

Table (11) continued

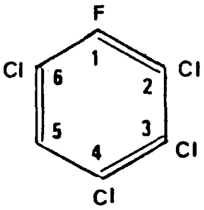
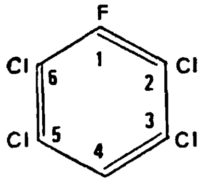
Compound	Coupling in Hz
	$J_{15} = 6.59$
	$J_{14} = 2.30$

Table (12)

Observed ^1H Chemical Shifts of Polybromobenzenes, 0.6 molar in chloroform-d, downfield from internal TMS in ppm

Compound	Chemical Shift relative to TMS in ppm (lit. value in parenthesis)
Bromobenzene[a]	$\delta_2 = \delta_6 = 7.24$
	$\delta_3 = \delta_5 = 7.503$
	$\delta_4 = 7.28$
o-Dibromobenzene[b]	$\delta_3 = \delta_6 = 7.585$
	$\delta_4 = \delta_5 = 7.122$
m-Dibromobenzene	$\delta_2 = 7.653$
	$\delta_4 = \delta_6 = 7.404$
	$\delta_5 = 7.061$
p-Dibromobenzene	$\delta_2 = \delta_3 = \delta_5 = \delta_6 = 7.321$
1,2,3-Tribromobenzene	$\delta_4 = \delta_6 = 7.537$
	$\delta_5 = 6.986$
1,2,4-Tribromobenzene	$\delta_3 = 7.735$
	$\delta_5 = 7.242$
	$\delta_6 = 7.442$
1,3,5-Tribromobenzene	$\delta_2 = \delta_4 = \delta_6 = 7.590$
1,2,4,5-Tetrabromobenzene	$\delta_3 = \delta_6 = 7.852$ (7.852)
1,2,3,4-Tetrabromobenzene	$\delta_5 = \delta_6 = 7.413$
1,2,3,5-Tetrabromobenzene	$\delta_4 = \delta_6 = 7.697$
Pentabromobenzene	$\delta_6 = 7.917$

(a) These proton shifts are reported from the work of L. Ernst and V. Wray, J. Mag. Resonance; (1977), 25, 123-139.

(b) Reported from the work of S. Castellano and R. Kostelnik, Tetrahedron Letters; (1967), 51, 5211.

Table (13)

Observed ^{1}H Chemical Shifts of Polybromonitrobenzenes, 0.6 molar in Chloroform-d, downfield from internal TMS in ppm

Compound	Chemical Shift relative to TMS in ppm
o-Bromonitrobenzene$^{(a)}$	$\delta_3 = 7.71$
	$\delta_4 = 7.40$
	$\delta_5 = 7.44$
	$\delta_6 = 7.78$
m-Bromonitrobenzene	$\delta_2 = 8.356$
	$\delta_4 = 7.843$
	$\delta_5 = 7.454$
	$\delta_6 = 8.18$
p-Bromonitrobenzene	$\delta_2 = \delta_6 = 8.107$
	$\delta_3 = \delta_5 = 7.687$
2,3-Dibromonitrobenzene	$\delta_4 = 7.646$
	$\delta_5 = 7.342$
	$\delta_6 = 7.849$
2,4-Dibromonitrobenzene	$\delta_3 = 7.91$
	$\delta_5 = 7.596$
	$\delta_6 = 7.79$
2,5-Dibromonitrobenzene	$\delta_3 = 7.974$
	$\delta_4 = 7.965$
	$\delta_6 = 7.584$
2,6-Dibromonitrobenzene	$\delta_3 = \delta_5 = 7.697$
	$\delta_4 = 7.311$

Table (13) continued

Compound	Chemical Shift relative to TMS in ppm
3,4-Dibromonitrobenzene	$\delta_2 = 8.452$ $\delta_5 = 7.811$ $\delta_6 = 8.043$
3,5-Dibromonitrobenzene	$\delta_2 = \delta_6 = 8.296$ $\delta_4 = 7.983$
2,3,4-Tribromonitrobenzene	$\delta_5 = 7.516$ $\delta_6 = 7.779$
2,4,5-Tribromonitrobenzene	$\delta_3 = 8.016$ $\delta_6 = 8.122$
2,3,5-Tribromonitrobenzene	$\delta_4 = \delta_6 = 8.411$
3,4,5-Tribromonitrobenzene	$\delta_2 = \delta_6 = 8.405$
2,4,6-Tribromonitrobenzene	$\delta_3 = \delta_5 = 7.798$
2,3,4,5-Tetrabromonitrobenzene	$\delta_6 = 7.936$
2,3,4,6-Tetrabromonitrobenzene	$\delta_5 = 7.954$
2,3,5,6-Tetrabromonitrobenzene	$\delta_4 = 8.031$

(a) These proton shifts are reported from the analysis published by William B. Smith and James L. Roark, J. Am. Chem. Soc., (1967), 89, 5018.

Table (14)

The observed values for ortho-, meta- and para- H-H coupling constants in polybromo- and polybromonitro-benzenes

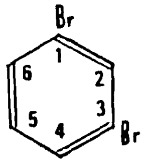
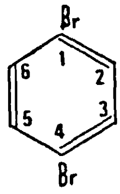
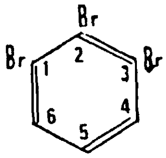
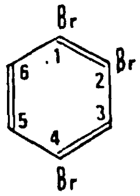
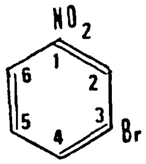
Compound	ortho H-H coupling in Hz	meta H-H coupling in Hz	para H-H coupling in Hz
	$J_{56}=J_{54}=9.03$	$J_{26}=J_{24}=1.95$	-
	$J_{23}^{*}=(8.41)$	$J_{26}^{*}=(2.38)$	$J_{25}^{*}=(0.46)$
	$J_{54}=J_{56}=8.1$	-	-
	$J_{56}=8.55$	$J_{35}=1.96$	-
	$J_{65}=8.06$ $J_{45}=8.55$	$J_{62}=1.96$ $J_{42}=1.96$	-

Table (14) continued

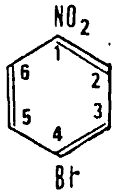
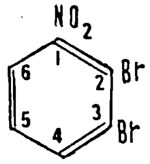
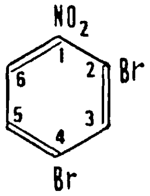
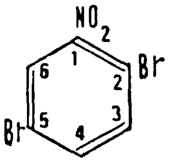
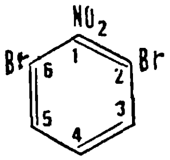
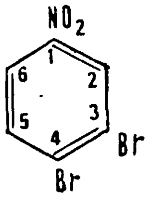
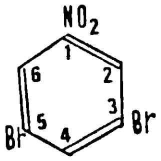
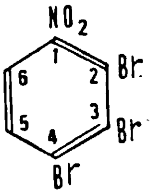
compound	ortho H-H coupling in Hz	meta H-H coupling in Hz	para H-H coupling in Hz
	$J_{56}=9.01$	-	-
	$J_{65}=7.82$ $J_{45}=8.06$	$J_{64} = 1.71$	-
	$J_{65}=8.54$	$J_{35}=1.71$	-
	-	$J_{46}=1.71$	-
	$J_{43}=J_{45}=8.14$	$J_{53}=1.29$	-
	$J_{65}=8.79$	$J_{26}=2.44$	-

Table (14) continued

Compound	ortho H H coupling in Hz	meta H-H coupling in Hz	para H-H coupling in Hz
	-	$J_{42}=J_{46}=1.43$	-
	$J_{56}=8.6$	-	-

*Although in our spectrum a singlet is observed, in reference (89), these couplings have been reported.

Table (15)

Observed ^{13}C Chemical Shifts of Polybromobenzenes, 0.6 molar in Chloroform-d, downfield from internal TMS in ppm

Compound	Chemical Shifts in ppm
Bromobenzene	$\delta_{C1} = 122.599$
	$\delta_{C2} = \delta_{C6} = 131.589$
	$\delta_{C3} = \delta_{C5} = 130.018$
	$\delta_{C4} = 126.876$
o-Dibromobenzene	$\delta_{C3} = \delta_{C6} = 133.702$
	$\delta_{C4} = \delta_{C5} = 128.447$
	$\delta_{C1} = \delta_{C2} = 124.818$
m-Dibromobenzene	$\delta_{C1} = \delta_{C3} = 123.192$
	$\delta_{C4} = \delta_{C6} = 130.289$
	$\delta_{C5} = 131.048$
	$\delta_{C2} = 134.406$
p-Dibromobenzene	$\delta_{C1} = \delta_{C4} = 121.134$
	$\delta_{C2} = \delta_{C5} = \delta_{C6} = \delta_{C3} = 133.215$
1,2,3-Tribromobenzene	$\delta_{C1} = \delta_{C3} = 126.06$
	$\delta_{C2} = 127.53$
	$\delta_{C5} = 129.04$
	$\delta_{C4} = \delta_{C6} = 132.348$

Table (15) continued

Compound	Chemical Shift in ppm
1,2,4-Tribromobenzene	$\delta_{C4} = 121.459$
	$\delta_{C1} = 123.896$
	$\delta_{C2} = 125.955$
	$\delta_{C5} = 131.698$
	$\delta_{C6} = 134.677$
	$\delta_{C3} = 136.194$
1,3,5-Tribromobenzene	$\delta_{C3} = \delta_{C1} = \delta_{C5} = 123.5$
	$\delta_{C2} = \delta_{C4} = \delta_{C6} = 133.2$
1,2,3,5-Tetrabromobenzene	$\delta_{C1} = \delta_{C3} = 126.55$
	$\delta_{C2} = 121.35$
	$\delta_{C5} = 126.714$
	$\delta_{C4} = \delta_{C6} = 134.786$
1,2,3,4-Tetrabromobenzene	$\delta_{C6} = \delta_{C5} = 132.619$
	$\delta_{C1} = \delta_{C4} = 128.989$
	$\delta_{C2} = \delta_{C3} = 124.709$
Pentabromobenzene	$\delta_{C1} = \delta_{C5} = 124.763$
	$\delta_{C4} = \delta_{C2} = 127.96$
	$\delta_{C6} = 135.598$

Table (16)

Observed ^{13}C Chemical Shifts of Polybromonitrobenzenes, 0.6 molar in chloroform-d, downfield from internal TMS in ppm

Compound	Chemical Shifts in ppm
o-Bromonitrobenzene	$\delta_{C2} = 111.567$
	$\delta_{C3} = 122.8$
	$\delta_{C5} = 125.598$
	$\delta_{C4} = 130.582$
	$\delta_{C6} = 132.316$
	$\delta_{C1} = 147.35$
m-Bromonitrobenzene	$\delta_{C1} = 148.708$
	$\delta_{C2} = 137.603$
	$\delta_{C5} = 130.668$
	$\delta_{C4} = 126.659$
	$\delta_{C3} = 122.813$
	$\delta_{C6} = 122.109$
p-Bromonitrobenzene	$\delta_{C2} = \delta_{C6} = 124.98$
	$\delta_{C4} = 129.964$
	$\delta_{C3} = \delta_{C5} = 132.62$
	$\delta_{C1} = 146.975$

Table (16) continued

Compound	Chemical Shifts in ppm
2,3-Dibromonitrobenzene	$\delta_{C2} = 117.125$
	$\delta_{C6} = 123.409$
	$\delta_{C5} = 128.881$
	$\delta_{C3} = 127.851$
	$\delta_{C4} = 136.465$
	$\delta_{C1} = 152.067$
2,4-Dibromonitrobenzene	$\delta_{C2} = 115.608$
	$\delta_{C6} = 126.714$
	$\delta_{C4} = 127.310$
	$\delta_{C3} = 131.481$
	$\delta_{C5} = 137.440$
	$\delta_{C1} = 148.492$
2,5-Dibromonitrobenzene	$\delta_{C2} = 113.224$
	$\delta_{C5} = 121.405$
	$\delta_{C6} = 128.447$
	$\delta_{C3} = 136.140$
	$\delta_{C4} = 136.248$
	$\delta_{C1} = 150.171$
2,6-Dibromonitrobenzene	$\delta_{C2} = \delta_{C6} = 113.441$
	$\delta_{C4} = 128.122$
	$\delta_{C3} = \delta_{C5} = 132.7$
	$\delta_{C1} = 151.201$

Table (16) continued

Compound	Chemical Shifts in ppm
2,3,5-Tribromonitrobenzene	$\delta_{C4} = \delta_{C6} = \delta_{C3} = \delta_{C5} = 126.84$
	$\delta_{C2} = 135.508$
	$\delta_{C1} = 146.614$
3,4,5-Tribromonitrobenzene	$\delta_{C3} = \delta_{C5} = 126.714$
	$\delta_{C2} = \delta_{C6} = 126.876$
	$\delta_{C4} = 128.014$
	$\delta_{C1} = 135.598$
2,4,6-Tribromonitrobenzene	$\delta_{C2} = \delta_{C6} = 114.524$
	$\delta_{C4} = 124.655$
	$\delta_{C3} = \delta_{C5} = 135.165$
2,3,4,5-Tetrabromonitrobenzene	$\delta_{C2} = 117.016$
	$\delta_{C3} = 125.088$
	$\delta_{C6} = 127.093$
	$\delta_{C5} = 132.239$
	$\delta_{C4} = 133.377$
2,3,4,6-Tetrabromonitrobenzene	$\delta_{C2} = 112.303$
	$\delta_{C6} = 118.262$
	$\delta_{C4} = 128.014$
	$\delta_{C3} = 129.097$
	$\delta_{C5} = 136.086$

Table (16) continued

Compound	Chemical Shifts in ppm
2,3,5,6-Tetrabromonitrobenzene	$\delta_{C2} = \delta_{C6} = 116.258$ $\delta_{C3} = \delta_{C5} = 126.172$ $\delta_{C4} = 137.603$
Pentabromonitrobenzene	$\delta_{C2} = \delta_{C6} = 116.312$ $\delta_{C3} = \delta_{C5} = 129.91$ $\delta_{C4} = 131.698$

Table (17)

Observed ^{13}C-hydrogen coupling constants, when carbon atom is one bond, two bond, three bond and four bond from hydrogen atom in polybromo- and polybromonitro-benzenes in Hz

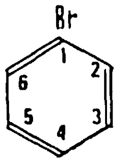
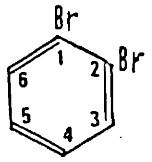
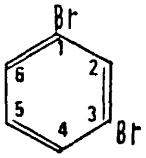
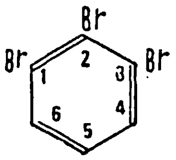
Compound	$^1J_{cn-Hn}$ in Hz	$^3J_{cn-Hi}$ in Hz	$^4J_{cn-Hi}$ in Hz
	$^1J_{22}=^1J_{66}=166.4$ $^1J_{33}=^1J_{55}=165.7$ $^1J_{44}=162.8$	$^3J_{24}=7.14$ $^3J_{26}=5.00$ $^3J_{42}=7.14$ $^3J_{46}=7.14$	
	$^1J_{33}=^1J_{66}=166.5$ $^1J_{44}=^1J_{55}=165.0$	$^3J_{46}=^3J_{53}=8.55$	
	$^1J_{22}=175.0$ $^1J_{55}=166.0$ $^1J_{44}=^1J_{66}=170.0$	$^3J_{24}=6.0$ $^3J_{26}=5.0$ $^3J_{46}=8.0$ $^3J_{42}=6.0$ $^3J_{35}=^3J_{15}=11.0$	
	$^1J_{44}=^1J_{66}=178.22$ $^1J_{55}=166.33$	$^3J_{46}=^3J_{64}=8.54$ $^3J_{24}=^3J_{26}=8.55$ $^3J_{15}=^3J_{35}=10.98$	$^4J_{36}=^4J_{14}=2.45$

Table (17) continued

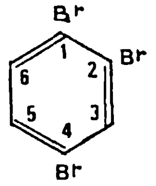
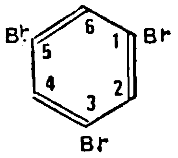
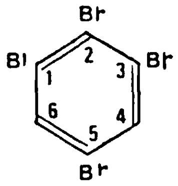
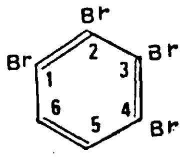
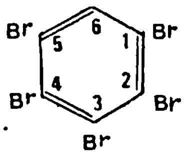
Compound	$^1J_{cn\text{-}Hn}$ in Hz	$^3J_{cn\text{-}Hi}$ in Hz	$^4J_{cn\text{-}Hi}$ in Hz
	$^1J_{33}$=173.34 $^1J_{66}$=170.9 $^1J_{55}$=169.68	$^3J_{35}$=6.1 $^3J_{53}$=6.1	
	$^1J_{66}$=$^1J_{22}$=$^1J_{44}$= 174.56 (174.3)	$^3J_{62}$=6.1	
	$^1J_{44}$=$^1J_{66}$=175.17	$^3J_{64}$=$^3J_{46}$=6.11 $^3J_{24}$=$^3J_{26}$=3.66	$^4J_{36}$=$^4J_{14}$=2.44
	$^1J_{66}$=$^1J_{55}$=170.9		
	$^1J_{66}$=175.79	$^3J_{46}$=$^3J_{26}$=8.55	

Table (17) continued

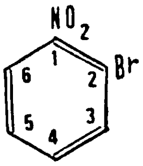
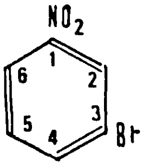
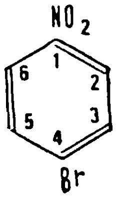
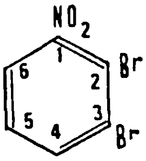
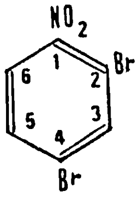
Compound	$^1J_{cn-Hn}$ in Hz	$^3J_{cn-Hi}$ in Hz	$^4J_{cn-Hi}$ in Hz
	$^1J_{66}=167.23$ $^1J_{44}=164.80$ $^1J_{55}=167.85$ $^1J_{33}=170.89$	$^3J_{53}=8.54$	
	$^1J_{22}=168.46$ $^1J_{55}=168.46$ $^1J_{44}=174.57$ $^1J_{66}=170.89$		
	$^1J_{33}={}^1J_{55}=172.12$ $^1J_{22}={}^1J_{66}=170.9$		$^4J_{36}={}^4J_{52}=4.89$ $^4J_{25}={}^4J_{63}=4.89$
	$^1J_{44}=171.505$ $^1J_{55}=169.68$ $^1J_{66}=170.09$	$^3J_{46}=8.55$ $^3J_{64}=8.55$	
	$^1J_{33}=173.34$ $^1J_{55}=175.17$ $^1J_{66}=172.12$	$^3J_{53}=6.1$ $^3J_{35}=6.1$	

Table (17) continued

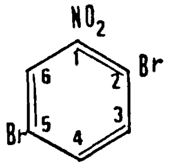
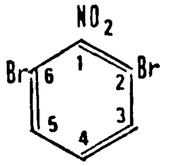
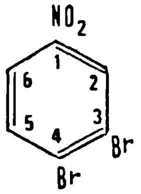
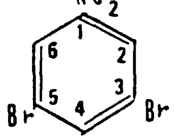
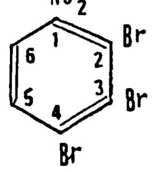
Compound	$^{1}J_{cn-Hn}$ in Hz	$^{3}J_{cn-Hi}$ in Hz	$^{4}J_{cn-Hi}$ in Hz
	$^{1}J_{44}=170.9$ $^{1}J_{66}=177.61$ $^{1}J_{33}=170.9$	$^{3}J_{46}=6.1$ $^{3}J_{64}=6.1$	
	$^{1}J_{55}={}^{1}J_{33}=172.115$ $^{1}J_{44}=168.45$	$^{3}J_{35}=7.33$ $^{3}J_{24}={}^{3}J_{64}=10.98$	
	$^{1}J_{55}=173.34$ $^{1}J_{66}=177.61$ $^{1}J_{22}=172.73$		
	$^{1}J_{44}=174.56$ $^{1}J_{66}={}^{1}J_{22}=178.78$	$^{3}J_{42}={}^{3}J_{46}=6.1$ $^{3}J_{24}={}^{3}J_{64}=6.1$	
	$^{1}J_{66}=174.56$ $^{1}J_{55}=172.12$	$^{3}J_{26}=8.54$ $^{3}J_{35}=10.99$ $^{3}J_{46}=8.54$	$^{4}J_{36}=2.44$

Table (17) continued

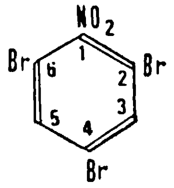
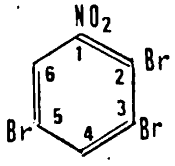
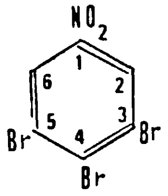
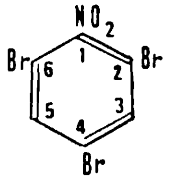
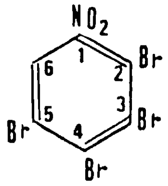
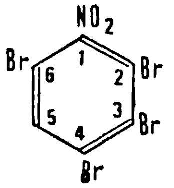
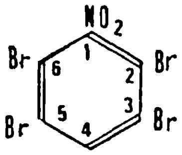
Compound	${}^1J_{cn-Hn}$ in Hz	${}^3J_{cn-Hi}$ in Hz	${}^4J_{cn-Hi}$ in Hz
	${}^1J_{33}=175.78$ ${}^1J_{66}=174.56$		
	${}^1J_{44}={}^1J_{66}=177.0$	${}^3J_{24}={}^3J_{26}=8.55$ ${}^3J_{46}={}^3J_{64}=4.88$	
	${}^1J_{66}={}^1J_{22}=177.0$	${}^3J_{26}={}^3J_{62}=4.88$ ${}^3J_{42}={}^3J_{46}=8.55$	
	${}^1J_{33}={}^1J_{55}=177.0$	${}^3J_{35}={}^3J_{53}=6.11$	
	${}^1J_{66}=175.79$	${}^3J_{46}=8.55$ ${}^3J_{26}=8.55$	${}^4J_{36}=4.88$

Table (17) continued

Compound	$^1J_{cn-Hn}$ in Hz	$^3J_{cn-Hi}$ in Hz	$^4J_{cn-Hi}$ in Hz
	$^1J_{55}$=178.22	$^3J_{35}$=8.54	$^4J_{25}$=4.88
	$^1J_{44}$=175.78	$^3J_{24}$=$^3J_{64}$=8.55	

2. Chemical Shifts of ^{19}F and ^{1}H Nuclei in Polyhalogeno- and Polyhalogenonitro-benzenes and Critical Observations in the Additivity of the Substituent Constants

In order to explain the deviation from additivity of chemical shifts observed in this work it is better to understand, at least in a qualitative fashion, the behaviour of the chemical shifts of monosubstituted benzenes. The substituent effect on the chemical shifts of the meta and para ^{1}H, ^{19}F or ^{13}C nuclei in a substituted benzene is nearly an order of magnitude larger than that found at the corresponding gamma and delta position in an aliphatic compound(91,92). This enhanced transmission of perturbation is a property of the delocalised π-electron system peculiar to the benzene ring. In other words, as has already been mentioned in our introduction, it is due to the σ_d term, the ring current effect, which gives a dominant contribution to the total screening constant of the nucleus. Other terms such as diamagnetic shielding and paramagnetic shielding which are proportional to the amount of electric charge located at the nucleus are also important. Another dominant factor is the σ_e term, the electric field due to the presence of localised electric charge or dipole at some point in the molecule. The outstanding features of these terms for each position on the ring and their relative importance for each particular nucleus under nmr observation will be discussed below.

It appears to be uniformly agreed that proton chemical shifts at the position para to a varying set of substituents are controlled by variations in electron density and numerous calculations support this contention. Among the latest of these are a series of ab initio calculations of π and σ-electron densities carried out by Taft and co-workers(93). Fukunaga and Taft(94) suggested that for ^{19}F chemical shifts, the major importance of field transmissions of substituent polar effects on these shifts in para-substituted fluorobenzenes is placed in strong doubt.

Shielding of a meta proton varies over a relatively small range and has been proved(84) to correlate poorly with reactivities and ^{13}C shifts. This agrees well with the predictions of both molecular orbital and valence bond theory that substituent perturbation of the π-system should be smallest at the meta-position. The perturbation of the π-system is in fact as has been defined earlier, due to the π-inductive effect which is the sum of π_F and π_σ effect of the substituent. In fact the electrostatic field mechanism, the I_F effect, is not contributing significantly to the shifts at the meta-position, since if this was true the shift variations at the meta-position would have been slightly larger than those at the para position.(84) The failure of this correlation suggests that the dipole field of the substituent does not contribute significantly to the meta or para proton chemical shifts in substituted benzenes. As the field effect of a point charge should vary approximately as $^1/_{r^2}$ (ignoring the cos term for the angular dependence of the C-H bond(95)), similar r values for 3- and 4 substituent derivatives are not unreasonable.

The ortho proton shieldings are usually the largest in any molecule. The shielding of protons ortho to a halogen tend strongly to low field in the order $F < Cl < Br < I$. The ortho carbon shifts also deviate strongly from the para shifts, in particular there is a large negative shift ortho to the heavier halogens and a large positive shift ortho to the nitro-group. The electric dipole field should have a sizeable effect at the ortho position, but would be similar in sign to the electron density effect. Therefore the conclusion is that π-electron charge density is a dominant factor in determining the ortho- and para- proton shifts and perhaps the meta shifts also, although the detailed mechanism determining these relatively small shifts is obscure.

It is generally accepted that, in a polysubstituted benzene derivative, in which the substituents are ortho to each other, steric interactions are sometimes significant. In general, the difference between the observed shielding and that predicted by additivity (i.e. using data of monosubstituted benzenes) is quite large. The ^{1}H shifts of polybromo- and polybromonitrobenzenes are presented in Tables (18) and (19) respectively.

Table (18)

Observed$^{(a)}$ and Calculated ^{1}H Chemical Shifts of Polybromobenzenes relative to Benzenes in ppm

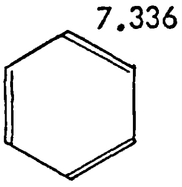
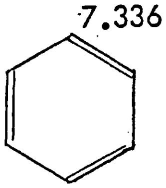
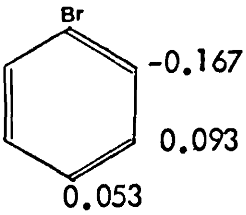
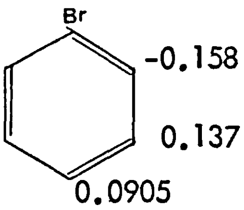
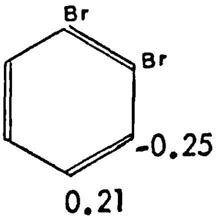
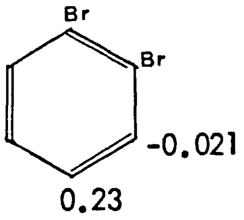
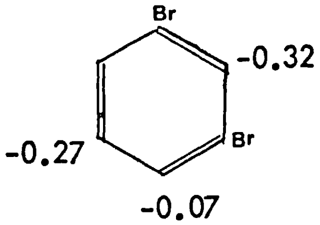
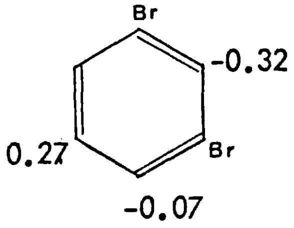
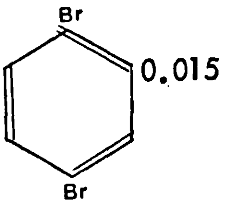
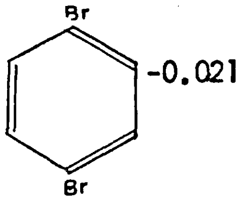
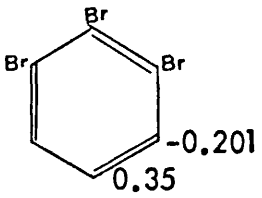
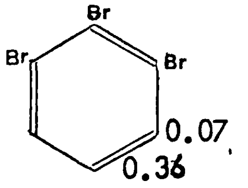
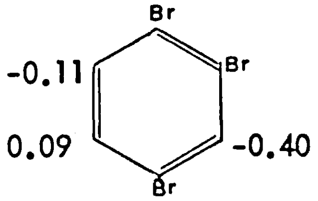
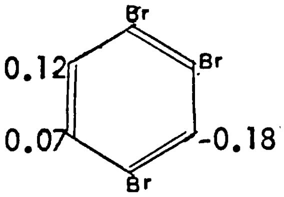
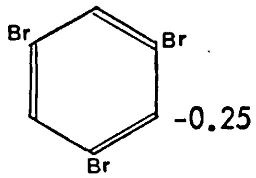
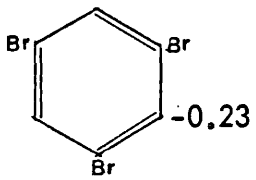
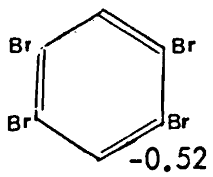
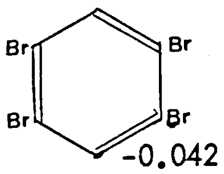
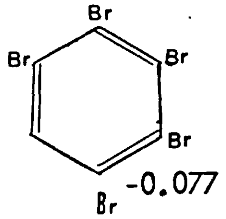
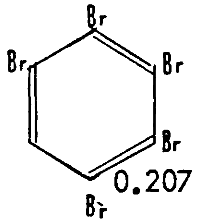
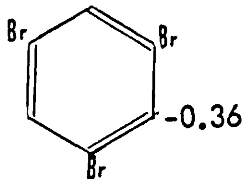
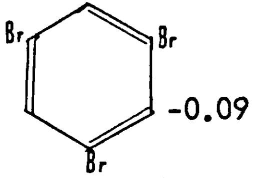
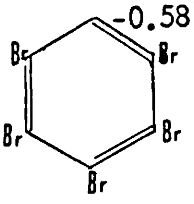
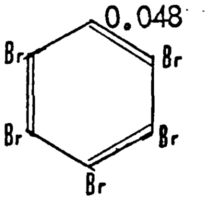
Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
	
	
	
	
	

Table (18) continued

Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
	
	
	
	
	
	
	

*Benzene ^1H chemical shift is quoted from the reference, P.N. Preston, L.N. Sutcliffe and B. Taylor, Spectrochim Acta, (1972), 28(A), 197.

(a) The observed values are the differences between $(\delta_{benzene} - \delta_{ArBr})$

Table (19)

Observed and Calculated ^{1}H Chemical Shifts of Polybromonitrobenzenes Relative to Benzene* in ppm

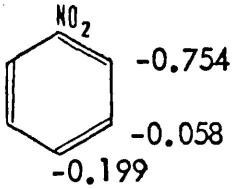
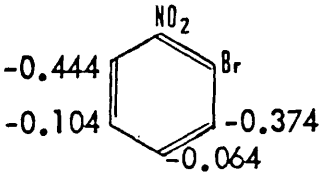
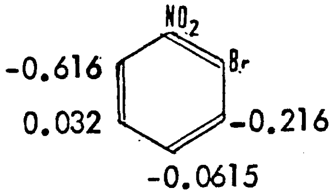
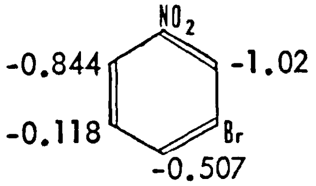
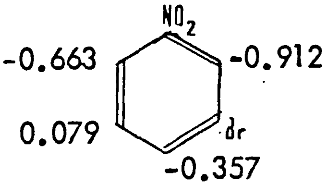
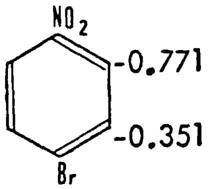
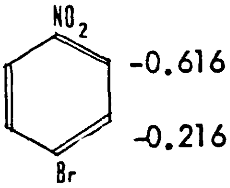
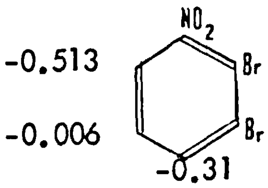
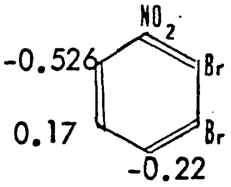
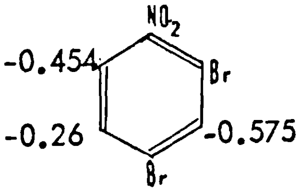
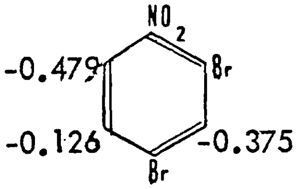
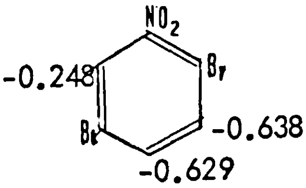
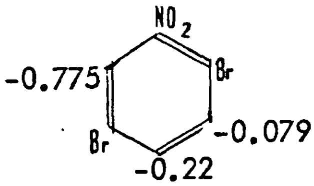
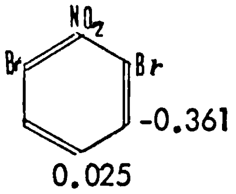
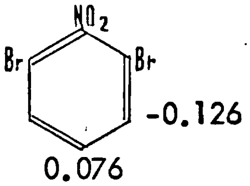
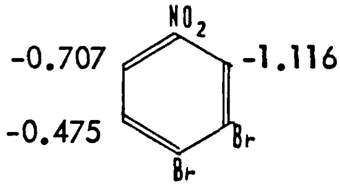
Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
(a)  	
 	
 	
 	
 	
 	
 	

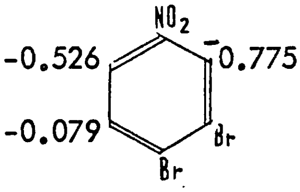
Table (19) continued

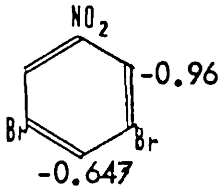
Observed Chemical Shifts Relative to Benzene* in ppm | Calculated Chemical Shifts Relative to Benzene* in ppm

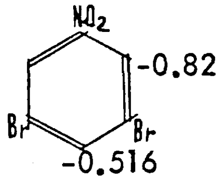


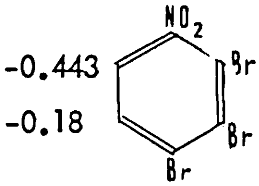


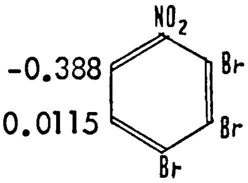


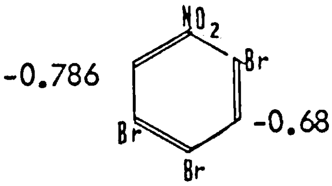


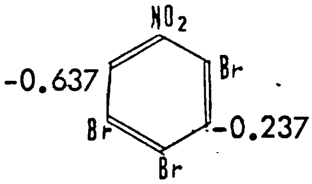


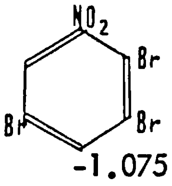


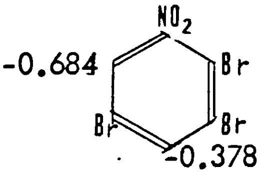


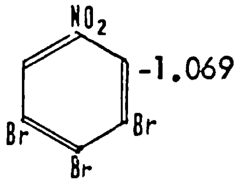


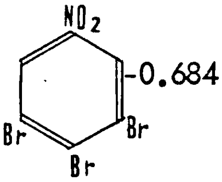


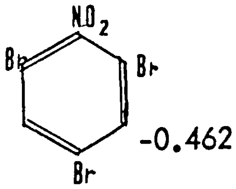












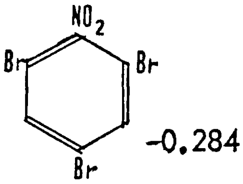
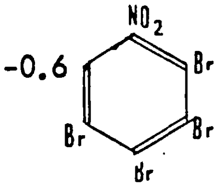
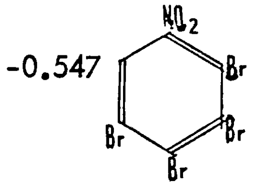
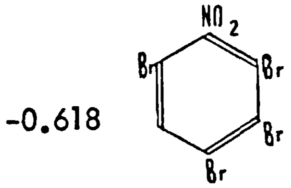
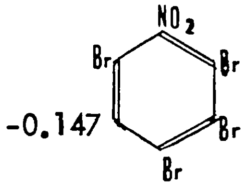
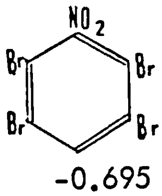
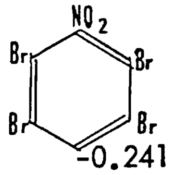


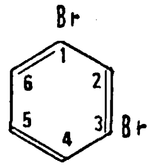
Table (19) continued

Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
 -0.6	 -0.547
 -0.618	 -0.147
 -0.695	 -0.241

*Benzene ^{1}H chemical shift is quoted from the reference, P.N. Preston, L.N. Sutcliffe and B. Taylor, Spectrochim Acta; (1972), 28(A), 197.

(a) Nitrobenzene ^{1}H Chemical shifts is quoted from reference, R.W. Crecely, J.H. Read, Jr. R.S. Butler and J.H. Goldstein, Spectrochim Acta; (1968), 24(A), 685.

The calculated chemical shifts were determined by considering the additivity scheme suggested by Diehl(82). The proton substituent constants for positions ortho-, meta- and para- to the bromine atom are determined from the observed proton chemical shifts in m-dibromobenzene and are summarised below.



$\delta_2 = 2S_{o:Br}$ $\delta_5 = 2S_{m:Br}$ $\delta_4 = \delta_6 = S_{o:Br} + S_{p:Br}$

Observed ^{1}H Chemical Shifts of m-dibromobenzene relative to Benzene in ppm

$\delta_2 = {}^{-}0.317$

$\delta_4 = \delta_6 = {}^{-}0.068$

$\delta_5 = {}^{+}0.275$

Calculated Substituent Effects in ppm

$S_{o:Br} = {}^{-}0.1585$

$S_{m:Br} = {}^{+}0.1375$

$S_{p:Br} = {}^{+}0.0905$

In polybromonitrobenzenes the calculated proton chemical shifts for different positions were obtained by the additivity scheme of substituent constants which are obtained from proton shifts of m-dibromobenzene and that of nitrobenzene.

In order to observe the extent to which additivity of proton shifts prevail in polyfluorobenzenes, we have tried to calculate these chemical shifts and compare them with their corresponding experimental values determined by Victor et al(96). It is obvious from the data presented in Table (20) that here also, there is a large deviation between the observed and calculated chemical shifts.

Table (20)

Observed[(a)] and Calculated ^{1}H Chemical Shifts of Polyfluorobenzenes Relative to Benzene* in ppm

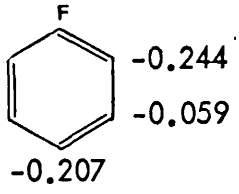
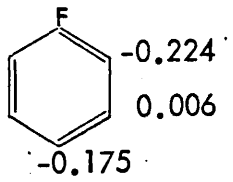
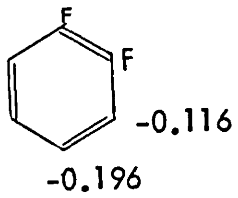
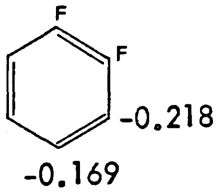
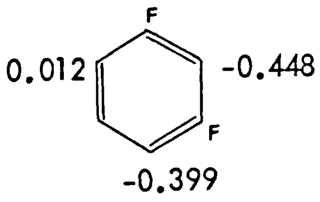
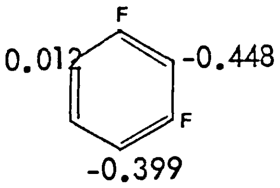
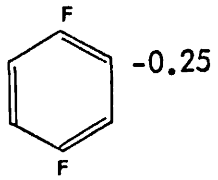
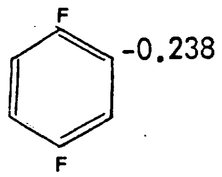
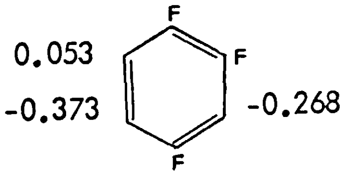
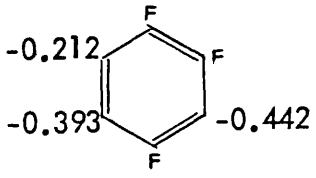
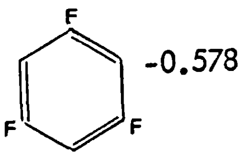
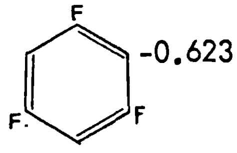
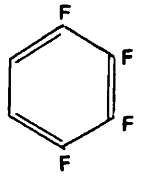
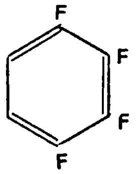
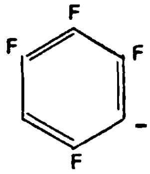
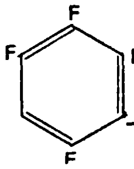
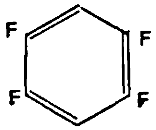
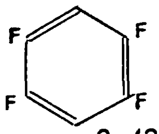
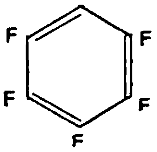
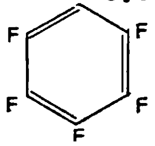
Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
	
	
	
	
	
	

Table (20) continued

Observed Chemical Shifts Relative to Benzene* in ppm	Calculated Chemical Shifts Relative to Benzene* in ppm
-0.155 	-0.387 
 -0.358	 -0.617
 -0.034	 -0.436
-0.053 	-0.611 

(a) Quoted from reference Victor Wray, Ludger Ernst and Ernst Lustig, J. Mag. Resonance., (1977), 27, 1-21.

* Benzene ^{1}H Chemical shift is quoted from the reference, P.N. Preston, L.N. Sutcliffe and B. Taylor, Spectrochim. Acta., (1972), 28(A), 197.

The observed shifts are the differences between ($\delta_{\text{benzene}} - \delta_{\text{ArF}}$).

In general, it can be seen from these results that large deviations are observed for compounds having several ortho- interactions. The deviations are even larger in polybromonitrobenzenes, which is due to an increase in the degree of non-symmetric distribution of the substituents over the ring, which will therefore give a higher polar character to the molecule and also a greater ortho-interaction. In compounds with zero dipole moments and no ortho-interaction, the deviation between the observed and calculated proton chemical shifts are quite small. For example in our Tables we have,

Compound	deviation in ppm $\Delta = (\delta_{obs} - \delta_{cal})$
p-dibromobenzene	0.04
1,3,5-tribromobenzene	-0.02
1,3,5-trifluorobenzene	0.04
p-difluorobenzene	-0.01

The deviations between the observed and calculated proton shifts in 3,5-dibromonitrobenzene are small, being of the order of -0.14 ppm. This is a polar molecule with an observed moment equal to 2.55D, but there are no substituents ortho to one another. In molecules such as 1,2,4,5-tetrafluoro- and 1,2,4,5-tetrabromo-benzenes the deviations between the chemical shifts are 0.402 ppm and -0.478 ppm respectively. Although they are non-polar, there are substituents ortho to one another. Therefore, it must be concluded that ortho-interaction is the most important factor. The fact that only nearest protons are affected by the interaction indicates that this effect is not transmitted via the bonding orbitals of the molecule. The rapid fall-off with distance suggests a short-range, high-order electrostatic field effect arising in the highly asymmetric charge distribution in the perturbed substituents. This can be confirmed from the results in Tables (18), (19) and (20), e.g. the chemical shifts of the protons 4 and 5 in *o*-dibromo- and *o*-difluoro-benzenes correlate well with their calculated values, the deviations being about $^{-}$0.02 ppm in both cases. Also, in 1,2,3-tribromobenzene the shift of proton 5 is only 0.01 ppm to high field from its calculated shift, or in *o*-bromonitrobenzene the proton 4- chemical shift is in good agreement with its calculated value, being only - 0.002 ppm downfield from it. However, proton 3 in *o*-dibromobenzene is observed to resonate at $^{-}$0.25 ppm whereas the predicted value is -0.021 ppm.

It appears therefore that the deviation of observed and calculated chemical shifts for *ortho* protons most probably arises from the change in the electric dipole moment of the halogen substituent when a second substituent is placed *ortho* to the first. This effect is very much less in protons more distant from the substituent and we may conclude that a large fraction of the chemical shifts of a proton attached to a substituent arises from a short-range interaction with the substituent. It appears that the chemical shifts of the more distant proton is much more dependent on a factor which is not modified by the second substituent *ortho* to the first. This effect is not purely a steric effect since it is very probable that a distortion of, for example, the bromine atom out of the plane of the benzene ring would alter the substituent effect at all the positions around the ring.

The ^{19}F shifts of polyfluoro- and polyfluoronitro-benzenes were in the first place compared with their corresponding calculated values, which are determined on the basis of the additivity of substituent constants. These substituent constants in fact present the effect of fluorine atoms being in *ortho*- *meta*- and *para*-positions to each other. They were determined from the differences observed between fluorine chemical shifts of the *ortho*-, *meta*- and *para*-difluorobenzenes with that of fluorobenzene and those of fluorine *ortho*-, *meta*- and *para*- to the nitro-group from the corresponding monofluoronitrobenzenes. They are summarised in Table (21) part (a).

Table(21)

Observed and calculated ^{19}F Chemical Shifts of Polyfluoro- and Polyfluoronitro-benzenes referenced to External Trichlorofluoromethane in ppm

Compound	Observed ^{19}F Shifts Relative to $CFCl_3$ in (ppm)	Calculated ^{19}F Shifts Relative to $CFCl_3$ in (ppm) (a)	Calculated ^{19}F Shifts Relative to $CFCl_3$ in (ppm)(b)
Fluorobenzene	δ_1=117.4	-	-
o-Difluorobenzene	$\delta_1 = \delta_2$=143.7	143.7	135.8
m-Difluorobenzene	$\delta_1 = \delta_3$=110.7	110.7	115.1
p-Difluorobenzene	$\delta_1 = \delta_4$=120.4	120.4	123.9
1,2,3-Trifluorobenzene	$\delta_1 = \delta_3$=136.0	137.4	133.3
	δ_2=162.5	170.0	154.4
1,2,4-Trifluorobenzene	δ_1=143.4	146.7	142.4
	δ_2=133.3	137.0	133.3
	δ_4=115.6	113.7	121.3
1,2,3,4-Tetrafluorobenzene	$\delta_1 = \delta_4$=141.5	140.0	139.8
	$\delta_2 = \delta_3$=158.4	163.3	151.79
1,2,3,5-Tetrafluorobenzene	$\delta_1 = \delta_3$=133.7	130.3	131.74
	δ_5=115.4	107.0	118.76
	δ_2=168.0	173.0	160.86
Pentafluorobenzene	δ_3=160.8	156.6	149.22
	$\delta_1 = \delta_5$=145.2	133.3	137.2
	$\delta_2 = \delta_4$=169.0	166.3	158.29

Table (21) continued

Compound	Observed ^{19}F Shifts Relative to $CFCl_3$ in (ppm)	Calculated ^{19}F Shifts Relative to $CFCl_3$ in (ppm) (a)	Calculated ^{19}F Shifts Relative to $CFCl_3$ in (ppm) (b)
o-Fluoronitrobenzene	δ_2=119.6	119.6	126.75
m-Fluoronitrobenzene	δ_3=110.5	110.5	113.29
p-Fluoronitrobenzene	δ_4=103.1	103.1	108.02
2,4-Difluoronitrobenzene	δ_2=113.2	112.9	124.18
	δ_4=99.3	96.4	105.45
2,6-Difluoronitrobenzene	δ_2= δ_6=113.65	112.9	124.18
3,4-Difluoronitrobenzene	δ_3=134.1	136.8	131.77
	δ_4=127.8	129.4	126.50
2,4,6-Trifluoronitrobenzene	δ_4=100.3	89.7	102.88
	δ_2= δ_6=117.1	106.2	121.6
2,4,5-Trifluoronitrobenzene	δ_5=140.1	139.8	138.27
	δ_2=118.8	115.9	130.68
	δ_4=123.8	122.7	123.93
2,3,4,5-Tetrafluoronitrobenzene	δ_2=147.4	142.2	149.16
	δ_4=154.0	133.1	142.41
	δ_3=144.5	156.4	147.68
	δ_5=138.5	133.1	135.7
2,3,4,6-Tetrafluoronitrobenzene	δ_3=161.0	166.0	156.75
	δ_4=124.0	116.0	121.36
	δ_2=136.0	132.5	140.09
	δ_6=124.0	109.2	128.11
Pentafluoronitrobenzene	δ_2= δ_6=153	135.5	146.8
	δ_3= δ_5=165.5	121.6	154.2
	δ_4=153.2	142.3	139.8

(a) Calculated values based on additivity of substituent chemical shifts.

(b) Calculated values based on the three parameter equation.

The ^{19}F chemical shifts of polychlorofluorobenzenes summarised in Table (22) are also compared with their calculated values determined from the additivity of the fluorine substituent constants, defined as the difference in ppm between the fluorine shifts at ortho-, meta- and para-positions to the chlorine atom in monochlorofluorobenzenes and that of fluorobenzene. The fact that there are smaller deviations between the observed and calculated shifts in ^{19}F shieldings than in proton shieldings is because in atoms containing p-electrons such as ^{13}C and ^{19}F with nuclear spins greater than zero, the paramagnetic effect is dominant, and complex long-range shielding influences of other electronic centres on chemical shifts for these nuclei are usually unimportant. Therefore, ^{19}F chemical shifts are influenced but little by the variety of shielding mechanisms which affect ^{1}H chemical shifts.

Table (22)

Observed and calculated[(a)], ^{19}F Chemical Shifts of Polychlorofluorobenzenes (quoted as the difference between the ^{19}F nmr shift of 1,3,5-Trichloro-2,4,6-trifluorobenzene 0.2M and Polychlorofluorobenzene 0.5M in cyclohexane)

Compound	Observed Chemical Shift in ppm	Calculated Shift in ppm	$\Delta = (\delta_{obs} - \delta_{cal})$ in ppm
Fluorobenzene	0.000	-	-
o-Chlorofluorobenzene	+2.00	-	-
m-Chlorofluorobenzene	-1.88	-	-
p-Chlorofluorobenzene	3.27	-	-
2,3-Dichlorofluorobenzene	-3.14	0.12	+3.26
2,4-Dichlorofluorobenzene	4.91	5.27	-0.36

Table (22) continued

Compound	Observed Chemical Shift in ppm	Calculated Shift in ppm	Δ = (δ_{obs} - δ_{cal}) in ppm
2,5-Dichlorofluorobenzene	-0.779	0.12	-0.90
2,6-Dichlorofluorobenzene	2.17	4	-1.83
3,4-Dichlorofluorobenzene	0.905	1.39	-0.38
3,5-Dichlorofluorobenzene	-3.26	-3.76	+0.50
2,3,6-Trichlorofluorobenzene	-4.00	2.12	-6.12
3,4,5-Trichlorofluorobenzene	0.185	-0.49	+0.69
2,4,5-Trichlorofluorobenzene	2.18	2.39	-0.21
2,4,6-Trichlorofluorobenzene	4.82	7.27	-2.95
2,3,4,6-Tetrachlorofluorobenzene	-2.589	5.39	-7.90
2,3,5,6-Tetrachlorofluorobenzene	-8.89	0.24	-9.10

(a) Calculated values are defined in the discussion.

Negative values for chemical shifts upfield from 1,3,5-trichloro-2,4,6-trifluorobenzene, and positive values are for downfield shifts.

Also, another series of calculated ^{19}F chemical shifts of polyfluoro- and polyfluoronitro-benzenes are given in Table (21) part (b) and of polychlorofluorobenzenes in Table (23), which are calculated from a series of three parameter equations determined from linear multiple regression analysis using Swain and Lupton(73) field and resonance parameters F and R, and a semi empirical parameter Q. The Q parameters and F and R values used for shift calculations are represented below:

Values of Q

Substituent	Q (^{13}C and ^{19}F)
H	2.28
F	1.04
Cl	2.55
Br	3.16
I	3.98
NO_2	1.80

all obtained from the original definition in Ref. (76)

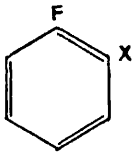
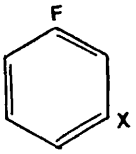
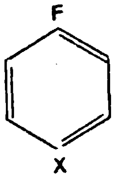
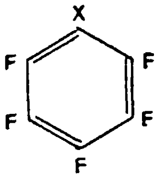
Resonance and Field Constants

Substituent	F	R
Br	0.727	-0.176
Cl	0.690	-0.161
F	0.708	-0.336
NO_2	1.109	0.155
H	0.000	0.000

Table (24) lists the regression coefficients of F, R and Q and the coefficient of correlation (r), derived for the substituents used in our work and are quoted from the recent paper of Smith and Proulx.(80).

Table (24)

Coefficients of aF + bR + cQ + d, for Chemical Shifts in a Variety of Systems

System		a	b	c	d	r
	F	6.00	5.23	11.8	24.76	0.967
	F	3.57	0.44	-0.43	0.55	0.962
	F	-5.19	-27.20	-0.59	1.65	0.984
	F-2	7.00	1.30	10.75	-0.55	-0.967
	F-3	-3.01	-3.17	-0.46	1.06	0.964
	F-4	-4.49	-22.74	-1.36	-5.15	0.990

For polychlorofluorobenzenes, a comparison of the correlation factors, calculated to be 0.388 for additivity and 0.837 for the three parameter equation of Smith and Proulx(80) suggest that the three parameter equation gives a better correlation between the observed and calculated ^{19}F shieldings. But it is worth noting that the ^{19}F shifts of 3,5-dichlorofluorobenzene and 3,4,5-trichlorofluorobenzene give perfect correlation when the additivity of substituent effects is considered.

Table (23)

Observed and Calculated ^{19}F Chemical Shifts of Polychlorofluorobenzenes (quoted as the difference between the ^{19}F nmr shift of 1,3,5-trichloro-2,4,6-trifluorobenzene 0.2M and the polychlorofluorobenzenes 0.5M in cyclohexane.

Compound	Observed Chemical Shifts in ppm	Calculated Chemical Shifts in ppm	Δ in ppm
Fluorobenzene	0.000	-	-
o-Chlorofluorobenzene	+2.00	-0.373	+2.373
m-Chlorofluorobenzene	-1.88	-3.081	+1.201
p-Chlorofluorobenzene	+3.27	+0.944	+2.326
2,3-Dichlorofluorobenzene	-3.14	-3.454	+0.314
2,4-Dichlorofluorobenzene	+4.91	+0.571	+4.339
2,5-Dichlorofluorobenzene	-0.779	-3.454	+2.675
2,6-Dichlorofluorobenzene	+2.17	-0.746	+2.87
3,4-Dichlorofluorobenzene	+0.905	-2.137	+3.042
3,5-Dichlorofluorobenzene	-3.26	-6.162	+2.902
2,3,6-Trichlorofluorobenzene	-4.00	-3.827	-0.173
3,4,5-Trichlorofluorobenzene	+0.185	-5.218	+5.403
2,4,5-Trichlorofluorobenzene	+2.18	-2.51	+4.69
2,4,6-Trichlorofluorobenzene	+4.82	+0.198	+4.62
2,3,4,6-Tetrachlorofluorobenzene	-2.589	-2.88	+0.291
2,3,5,6-Tetrachlorofluorobenzene	-8.89	-6.908	-1.982

(a) Calculated values are defined in the discussion.

Negative values are for chemical shifts upfield from 1,3,5-trichloro-2,4,6-trifluorobenzene, and positive values are for downfield shifts.

Perfect additivity may be considered to occur only when the difference between observed and predicted shifts are within experimental error. Our deviations are clearly outside experimental error and what has already been accepted therefore as a moderate variation may in fact reflect small but definite effects arising from mutual interactions of the two or more substituents present. The rationalisation of non-additivity in terms of properties associated with an even alternant hydrocarbon implies that the modification of observed substituent effects depends upon whether the π-electron environment is sensitive to the nature of more than one substituent. If this is true it means that non-additivity can be accounted for in terms of redistribution of π-electron density. It could also be accounted for by consideration of local ΔE changes, but the Q parameter of Hruska et al(76) also does not give any good correlation with the observed ^{19}F chemical shifts of the range of polyfluoro- and polyfluoronitrobenzenes as well as in polychlorofluorobenzenes. However varying extents of non-additivity imply that the ΔE changes are dependent upon the mutual interaction of the two <u>ortho</u> substituents. No attempt will be made to distinguish between these as possible origins to non-additivity. Moreover, a single influence has often been cited to explain a particular observation within a limited series of compounds. But more extensive studies over a wide range of types of compounds have shown that several of the effects often operate simultaneously and that no single effect can account for the observed chemical shifts.

III. Reduction of Polybromobenzenes with Sodium Borohydride in Dimethyl Sulfoxide

R.1 Introduction

One still finds in current textbooks statements that unactivated aryl halides are unreactive with nucleophiles under conditions that give facile nucleophilic displacements with alkyl halides. The reaction of aryl halides with strong basic or nucleophilic reagents are relatively few and relatively straightforward. An aryl halide molecule presents several sites for possible attack by a nucleophilic reagent, depending on reaction conditions involved. A nucleophile may attack a halogenobenzene (1) at carbon bearing the halogen atom (2) on halogen to displace an aryl anion (3) at ortho-hydrogen to remove it and form an aryl anion which may then (4) expel a halide ion to form an aryne or (5) by putting an electron into an antibonding π-orbital to form a radical anion which then disintegrates to an aryl radical and halide ion.

Dehalogenation of aryl halides by nucleophilic substitution at the halogen centre has not been investigated widely and there appears to be no quantitative data in the literature. Moyer(97) discovered that 1,2,4-tribromobenzene when reacted with potassium t-butoxide in 50% t-butyl alcohol-50% dimethyl sulfoxide at 53°, loses the 2-bromine as bromide ion producing p-dibromobenzene as the main product. Bunnett and Victor(98) followed Moyer's work over a number of chloro, bromo, and iodo derivatives of benzene. They observed that halogen atoms located ortho to another halogen atom were preferentially removed and halogens flanked by other halogens in both positions were especially reactive. Other things being equal, deiodination occurred more readily than debromination, while dechlorination has not been observed and electron attracting substituents facilitate the reaction. They have also tried dehalogenation by t-BuOK in 50:50 mixtures of t-BuOH and certain other "aprotic" solvents. Observing that the dehalogenation fails to occur in t-BuOH alone, they concluded that reactivity depends on the cosolvent employed. They suggested that reactive cosolvents are "semiprotic" in the sense that they all have a methylene group α to a carbonyl, sulfonyl, or sulfinyl group which can yield protons to strong bases to form carbanions, but that truly aprotic solvents such as diphenyl sulfoxide, dimethyl formamide, and hexamethyl phosphoramide are ineffective. It has been found that dimethyl sulfoxide is the most effective cosolvent. Earlier(99) hexabromobenzene was reported to give pentabromo- and a mixture of tetra-bromo-benzenes together with sodium bromide, but no methoxy derivatives when treated with sodium methoxide in boiling ethyl methyl ketone. Later Collins and Suschitzky(100) investigated extensively the protodebromination of hexabromobenzene. When it is treated with sodium methoxide in methanol and ethyl methyl ketone, a mixture of tetrabromobenzenes was obtained and with hydrazine only 1,2,3,4-tetrabromobenzene was obtained. When the reaction was carried out with t-BuOK in a mixture of t-BuOH and dimethyl sulfoxide, symmetrical tribromobenzene was also produced. This suggested that appearance of the 1,3,5-tribromobenzene is probably due to the great reactivity of the dimethyl anion $\mathrm{MeSO.C\bar{H}_2}$: which caused the reaction to proceed much faster. According to reaction conditions, they have suggested that the debromination is caused by a nucleophilic attack on halogen, which is similar to the mechanism first put forward by Bunnett and his co-workers(98) to explain the dehalogenation and isomerisation in some oligohalogenobenzenes. The following sequence for the reaction seems likely:

$$\mathrm{MeO^- + MeCH_2.CO\,Me \rightleftharpoons MeOH + MeCH^-.COMe}$$

$$\mathrm{MeCH.^-COMe + C_6Br_6 \longrightarrow \left[C_6Br_5\right]^- + MeCHBr.COMe}$$

$$\mathrm{\left[C_6Br_5\right]^- + MeOH \longrightarrow C_6HBr_5 + MeO^-}$$

The methoxide ion first abstracts a proton from EMK, forming the anion $\mathrm{MeCH.^-COMe}$, which then attacks the most positive halogen moiety of the ring, capturing a $\mathrm{Br^+}$ ion and displacing a pentabromophenyl anion. The latter is protonated to form pentabromobenzene. They have suggested that a radical mechanism for the reaction is unlikely, since no biphenyls were detected when benzene was added to any of the reaction mixtures which produced debromination.

The use of various metal hydrides and selective reducing agents has attracted a considerable amount of interest in recent years. It occurred to us that one unexplored possibility in this area might be to employ the relatively mild reducing agent, sodium borohydride, in a polar aprotic solvent, dimethyl sulfoxide, to selectively displace halogens with the hydrogen. Few examples are to be found in the literature of the reduction of polyhalogenobenzenes by the complex sodium borohydride, only two compounds having been investigated(101). Reduction of 0.1M o-fluoroiodobenzene with 0.2M sodium borohydride in anhydrous DMSO at 50-55° produced 34% fluorobenzene and 58% unreacted o-fluoroiodobenzene after 75 minutes. In 80% aqueous DMSO, the same conditions produced 80% fluorobenzene and 9% o-fluoroiodobenzene. The reactivity of o-nitroiodobenzene was more pronounced, after only 15 minutes at room temperature 0.1M halide reacted with 0.2M borohydride in 80% aqueous DMSO to produce a 95% yield of nitrobenzene. Substituting deuterium oxide for water results in o-deuterionitrobenzene of 88% purity. Bell et al(101) suggested that greater reactivity of iodine compared to fluorine and the deuterium incorporation in the case of o-nitroiodobenzene is consistent with nucleophilic attack on halogen rather than with direct substitution on carbon.

R.2 General Outline of the Experiments

All the experiments were conducted as follows:

A weighed amount of the aromatic compound in dimethyl sulfoxide was prepared in a two-necked flask (equipped with condenser) maintained at the desired temperature in a water bath. The reagent sodium borohydride was then added directly to the solution. The amount of reagents and solvent were chosen so that the final solution was equimolar in sodium borohydride and aromatic compound. After the appropriate reaction times, listed in Table (25), the mixtures were worked up by diluting with water and extracting into chloroform, the extracts were dried ($MgSO_4$), the solvent was evaporated off and the products were analysed by gas-liquid chromatography (PYE Unican 104 chromatograph with flame ionisation-detector, using a 3 ft glass column packed with Apiezon L (15%) on chromasorb A.45-60 mesh). The identification of eluates was based on the comparison of retention times with those of authentic samples, except for the case of aryl methyl sulfide derivatives, since their authentic samples were not available. Their formation was confirmed by the combined g.l.c.-mass spectroscopic analysis of the reaction products of reduction of 1,2,3- and 1,2,4-tribromobenzene. After identification of the different components of the reaction products, quantitative analysis by g.l.c. was achieved by the method of "internal standardisation". The standard used was pentachlorobenzene.

Table (25)

Reduction of Polybromobenzenes with Sodium Borohydride in Dimethyl Sulfoxide

Entry	Compound	Polybromobenzene conc. molar	$NaBH_4$ conc. molar	Temp. ° C.	Time, hr.	Starting Material (% yield)	Others as Reaction Products (% yield)
1	Hexabromobenzene$^{(A)}$	0.041	0.049	100	0.25	not detected	95^{a}, 4^{b}, 1^{c} #
2	Pentabromobenzene$^{(A)}$	0.040	0.060	100	0.25	25.9	55.5^{c}, 7.6^{d}, 9^{f}, $2^{g,h,I,e}$
3	1,2,3,5-Tetrabromobenzene	0.040	0.040	100	0.33	34	6.8^{e}, 6^{I}, 22.6^{g}, 26.2^{h}, 4^{f}
4	1,2,3,4-Tetrabromobenzene	0.040	0.040	96	0.39	20	20.6^{I}, 3.31^{h}, 3.4^{g}, 54^{f}
5	1,2,4-Tribromobenzene	0.070	0.090	100	1	6	$5.2^{g,h}$, 88.0^{f}
6	1,2,3-Tribromobenzene	0.130	0.130	75	1	16	2.14^{h}, 1.57^{g}, 81.0^{f}

(A) Percentage yields of the compounds of the entries 1 and 2 were obtained from their nmr spectrum and not their glc analysis.

a - pentabromobenzene, b - pentabromo phenyl methyl sulfide, c - 1,2,4,5-tetrabromobenzene, d - 1,2,3,5-tetrabromobenzene, e - 1,3,5-tribromobenzene, f - phenyl methyl sulfide derivatives, g - para- and meta-dibromobenzene, h - o-dibromobenzene, I - 1,2,4-tribromobenzene

Product ratio only

* para- and meta-dibromobenzene could not be distinguished by glc under our conditions.

Further evidence was provided by the proton nmr spectrum of the reaction mixtures. The reaction mixture of hexabromobenzene showed a singlet at 7.92 ppm in chloroform-d which correlates with the literature chemical shift of pentabromobenzene in $CDCl_3$, and a singlet at 7.87 ppm which is the same as that of 1,2,4,5-tetrabromobenzene, the relative amounts of each being respectively 95% and 1%. Pentabromobenzene reduction product showed a singlet at 7.92 ppm due to the unreacted starting material, 25.9%, one at 7.87 ppm correlating with the chemical shift of 1,2,4,5-tetrabromobenzene (55.5%). In the proton nmr spectrum of both mentioned reaction mixtures, there are singlets in the aliphatic region (from about 1 to 2 ppm downfield of TMS). These singlets are due to the proton resonances of the methyl group in the aryl methyl sulfide derivatives.

Below is given the results of mass spectroscopic analysis of 1,4-dibromo phenyl methyl sulfide which is produced during the reduction of 1,2,4-tribromobenzene.

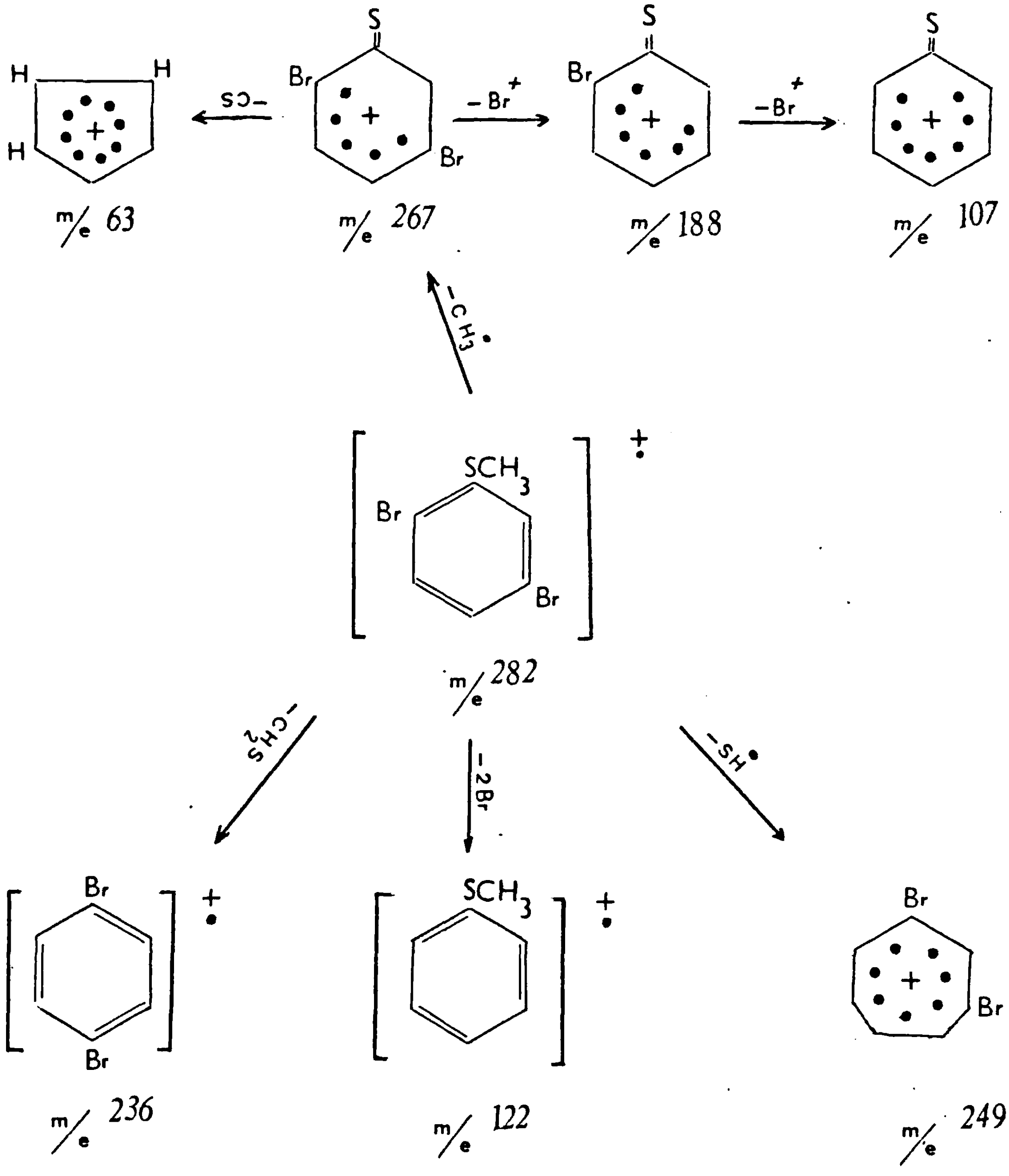
Table (26)

Partial Mass Spectrum of 1,4-Dibromo Phenyl Methyl Sulfide

m/e value	63	106	107	121	122	186	188	234	236
Relative abundance	28	5	16	15	30	30	31	2	6

m/e	238	247	249	251	265	267	269	280	282	284
R.A.	2	6	13	6	6	13	6	65	100	68

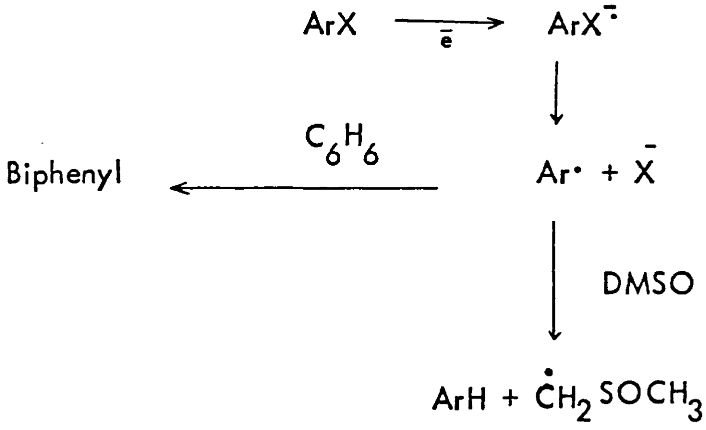
The mass spectroscopic analysis of thioanisole is reported by Bowie et al(103) and the following rearrangements have been observed during electron impact degradation. Loss of a methyl radical (m/e 267) followed by expulsion of carbon monosulfide (m/e 63), the elimination of thioformaldehyde to the benzene ion radical (m/e 236) and loss of a sulfhydryl radical (m/e 249). The fragmentations due to the loss of bromine atoms observed in our spectrum are also indicated in the diagram below:



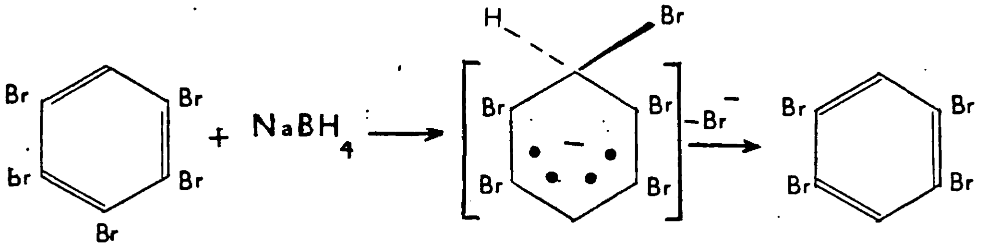
R.3 Results and Discussion

In Table (25) are summarised the reaction products together with conditions and yields for a variety of reactions of polybromobenzenes with sodium borohydride in dimethyl sulfoxide.

Three types of mechanism were envisioned as potentially responsible for the occurrence of dehalogenation. The reaction could conceivably involve the formation of a substituted aryl radical anion, which disintegrates to aryl radical and halide ion and then the aryl radical could abstract a hydrogen atom from perhaps DMSO to give the reduction products.



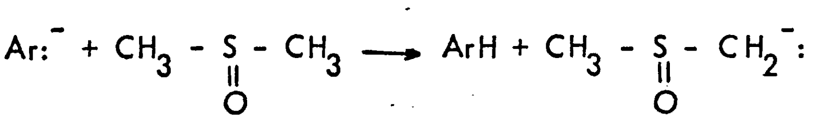
But this mechanism is unlikely to occur since Collins and Suchitzky(100) have reported that no biphenyl derivatives were detected when benzene was added to their mixtures of debromination. The second possible mechanism involves the addition-elimination pathway for aromatic nucleophilic substitution, as illustrated for pentabromobenzene, below:



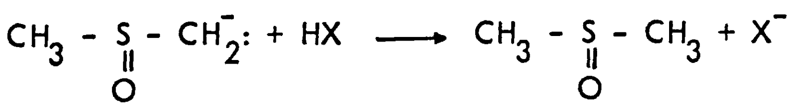
However, since Bell et al(101) observed that the halogens are reactive in the order iodine being more reactive than fluorine, which is in the reverse of the order for the addition-elimination mechanism, they therefore concluded that nucleophilic attack does not occur at the carbon bearing the halogen atom.

The third and most attractive possibility involves a nucleophilic attack of the borohydride ion on a halogen atom of the ring with accompanying displacement of a substituted phenyl carbanion as:

$$BH_4^- + Ar - X \longrightarrow BH_3 + Ar^-: + HX$$



$$Ar:^- + CH_3 - \underset{\underset{O}{\|}}{S} - CH_3 \longrightarrow ArH + CH_3 - \underset{\underset{O}{\|}}{S} - CH_2^-:$$

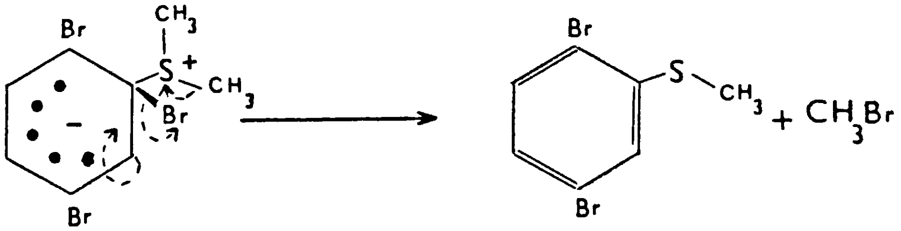


$$CH_3 - \underset{\underset{O}{\|}}{S} - CH_2^-: + HX \longrightarrow CH_3 - \underset{\underset{O}{\|}}{S} - CH_3 + X^-$$

The above mechanism was first suggested by Bell et al(101). Bunnett et al(98) also proposed this reaction pathway for aryl halide reductions by potassium t-butoxide in t-butyl alcohol-DMSO mixtures.

From our data in Table (25) it can be seen that reactions were fast (usual reaction time: 15 to 20 minutes) in DMSO at 100°C, but the reactions were never complete; some starting material always remained even after one hour of reduction. The choice of dimethyl sulfoxide as the solvent was due to its greater solvation of large polarisable anionic transition states over protic solvents. This is due to the steric resistance to solvation of bulky anions in protic solvents. But experiments with DMSO resulted in formation of sulfur-containing by products, which on the basis of g.l.c. and mass spectroscopic analysis were identified as substituted aryl methyl sulfides.

The formation of the corresponding aryl methyl sulfides can occur either through the attack of the aryl anion by $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > \overset{+}{S} - \overset{-}{O}$, followed by the cleavage of the CH_3O^- anion, or through the reduction of dimethyl sulfoxide to dimethyl sulfide because of the reducing power of BH_4^-. Dimethyl sulfide will then attack the bromobenzene forming an intermediate complex, as shown below, for the case of formation of 2,5-dibromophenyl methyl sulfide.



The reduction of DMSO to dimethyl sulfide is likely to be the case since we have repeated the reaction under the same conditions using this time sodium methoxide as the nucleophilic base. No aryl methyl sulfide derivative was identified. Therefore sodium borohydride acts not only as a nucleophilic base, but also as a reducing agent to provide dimethyl sulfide. Moreover, Brown and Rao(102) have already reported the reduction of DMSO to dimethyl sulfide in the mixture of $NaBH_4$ and diborane.

Hexabromobenzene is reduced initially to afford pentabromobenzene which then undergoes further debromination to afford 1,2,4,5-tetrabromobenzene. The relative amounts of each of the above, which were determined by running the proton nmr of the reaction mixture are, 95% pentabromobenzene, 1% of the tetrabromobenzene and 4% of aryl methyl sulfide derivatives. The high yield of pentabromobenzene makes this procedure particularly attractive for synthetic applications. Pentabromobenzene is initially reduced to sym-tetrabromobenzene which is then reduced to the corresponding tri- and di-bromobenzenes. 1,2,3,5-Tetrabromobenzene is reduced to symmetrical tribromobenzene, some 1,2,4 tribromobenzene together with _para_- and _meta_-dibromobenzene are produced also.

The above observations are confirmations of the earlier suggestion made by Bell et al(101) and Collins and Suschitzky(100) about the borohydride attack on halogen atom. If it is considered that the intermediate complex in the transition state resembles the molecule in its ground state, then it is reasonable that the 2-(4)- and the 3 bromine atoms in pentabromobenzene are the most likely to be removed first, since as we have earlier determined, in an empirical way, the C-Br bond with two _ortho_-bromine substituents has a moment which is 0.30D lower than when there is only one _ortho_-bromine substituent. Therefore these three bromine atoms are relatively less electronegative than the 1- and 5-bromine atoms of the ring. Alternatively the higher percentage of 1,2,4,5-tetrabromobenzene relative to that of the 1,2,3,5-derivative may be due to the greater inductive stabilisation of the intermediate anion, 1,2,4,5-$C_6HBr_4^-$, compared with the 1,2,3,5-$C_6HBr_4^-$ one. In the former the electron-withdrawing power of the four bromine substituents are more effective, being at the ortho- and meta-positions relative to the site of attack than on the latter which has two ortho-, one meta- and one para-bromine atoms relative to the site of attack. Reduction of 1,2,3,4-tetrabromobenzene affords as the main product 1,2,4-tribromobenzene, which then is reduced to para-dibromobenzene. Due to the lower polarity of the 2-(3)-carbon-bromine bonds (0.90D) over that of the 1-(4)-C-Br bonds (1.20D), the attack takes place mainly at the former position producing 1,2,4-tribromobenzene as the main product. Reduction of 1,2,4-tribromobenzene, according to Bunnett and Victor(98) affords p-dibromobenzene as the major reaction product. But with our g.l.c. analysis we were not able to separate p-dibromo- and meta-dibromo-benzene. Here the 2-bromine atom is the more likely to be attacked by borohydride ion since although the 1-(2) bromine atoms are found to have C-Br bond moments equal to 1.20D, compared to the 4-bromine atom at bond moment 1.41D, the 2-bromine atom is more readily displaced than the (1)-, since its intermediate anion is more stable, having one ortho-bromine and one meta-bromine atom, than one ortho- and one para-bromine atom. The fact that reduction of 1,2,3-tribromobenzene produces meta-dibromobenzene as the major product, again can confirm more strongly our defined mechanism, since the 2-bromine atom having two ortho-bromine substituents have a moment of 0.90D, which is smaller than the 1-(3) bromo-group moments, being 1.20D and the intermediate anion is also more stable having two *ortho*-bromine atoms, than the one with one *ortho* and one *meta*-bromine atoms.

IV. Preparation and Purification of Materials

P.1 Solvents

a) Commercial "AnalaR" grade cyclohexane was dried with sodium wire and then fractionally distilled under anhydrous conditions, the fraction boiling at 81°C at atmospheric pressure being collected.

b) Commercial grade p-xylene was dried with sodium wire, distilled in vacuo, the middle boiling fraction being collected and then fractionally frozen (m.p. 13.30°C), b.p. 137-138°C at atmospheric pressure (lit. m.p. 13.26°C, b.p. 137-138°C).

P.2 The Solutes

A. The following materials were commercially available.

a) The following compounds were fractionally distilled under anhydrous conditions, the middle boiling fraction being collected. The nmr analysis revealed no impurities. The literature values are those quoted in the Dictionary of Organic Compounds(104) unless otherwise stated. Boiling points are corrected to 760 mm Hg.

Fluorobenzene	b.p. 85°C	(lit. b.p. 85.1°C)
o-Difluorobenzene	b.p. 91-2°C	(lit. b.p. 91-2°C)
m-Difluorobenzene	b.p. 81°C	(lit. b.p. 82°C)
p-Difluorobenzene	b.p. 88°C	(lit. b.p. 89°C)
1,2,4-Trifluorobenzene	b.p. 86°C	(lit. b.p. 88°C)
1,2,3,4-Tetrafluorobenzene	b.p. 94°C	(lit. b.p. 93.5°C)
1,2,3,5-Tetrafluorobenzene	b.p. 84°C	(lit. b.p. 83°C)
Pentafluorobenzene	b.p. 80°C	(lit. b.p. 82°C)
Chlorobenzene	b.p. 131.5-132°C	(lit. b.p. 132°C)

b) The following compounds were distilled in vacuo, the middle boiling fraction being collected. The nmr analysis revealed no impurities, and for the polybromobenzene compounds their gas chromatographic analysis have also been checked.

Nitrobenzene	b.p. 110°C, 19 mm Hg
o-Fluoronitrobenzene	b.p. 86°C, 19 mm Hg
2,4-Difluoronitrobenzene	b.p. 80°C, 9 mm Hg
2,4,6-Trifluoronitrobenzene	b.p. 81°C, 20 mm Hg
2,3,4,5-Tetrafluoronitrobenzene	b.p. 80°C, 23.7 mm Hg
Pentafluoronitrobenzene	b.p. 64°C, 27 mm Hg
o-Chlorofluorobenzene	b.p. 50°C, 14 mm Hg
m-Chlorofluorobenzene	b.p. 56°C, 11 mm Hg
p-Chlorofluorobenzene	b.p. 54°C, 13 mm Hg
3,4-Dichlorofluorobenzene	b.p. 74°C, 11 mm Hg
Bromobenzene	b.p. 52°C, 13 mm Hg
o-Dibromobenzene	b.p. 64°C, 13 mm Hg
m-Dibromobenzene	b.p. 78°C, 18 mm Hg

c) The following compounds were recrystallised, their purity was checked by m.p. and nmr analysis, and gas chromatographic analysis of polybromobenzenes revealed no impurities.

p-Dichlorobenzene, recrystallised from acetic acid, m.p. 52°C
(lit. m.p. 53.1°C)

p-Dibromobenzene, recrystallised from alcohol, m.p. 88°C
(lit. m.p. 89°C)

o-Bromobenzene, recrystallised from alcohol, m.p. 43°C
(lit. m.p. 43°C)

m-Bromonitrobenzene, recrystallised from alcohol, m.p. 56°C,

(lit. m.p. 55.5°C)

2,5-Dibromonitrobenzene, recrystallised from alcohol, m.p. 85-6°C

(lit. m.p. 85-6°C)

B. The following compounds were kindly donated by Dr. R. Bolton. Their purities were checked by nmr analysis as well as by m.p. or b.p.

p-Fluoronitrobenzene, distilled in vacuo, b.p. 87°C, m.p. 26°C

(lit. m.p. 27°C)

3,4-Difluoronitrobenzene, distilled in vacuo, b.p. 168°C, 760 mm Hg

2,3,4-Trifluoronitrobenzene, distilled in vacuo, b.p. 92°C, 20 mm Hg

(lit. b.p. 92°C, 22 mm Hg)

2,4,5-Trifluoronitrobenzene, distilled in vacuo, b.p. 80°C, 17 mm Hg

2,3-Dichlorofluorobenzene, distilled in vacuo, b.p. 78-9°C, 12 mm Hg

2,4-Dichlorofluorobenzene, distilled in vacuo, b.p. 167-8°C, 760 mm Hg

2,5-Dichlorofluorobenzene, distilled in vacuo, b.p. 155°C, 760 mm Hg

3,4,5-Trichlorofluorobenzene, recrystallised from ethanol, m.p. 50°C

(lit. m.p. 52°C)

2,3,5,6-Tetrachlorofluorobenzene, recrystallised from ethanol, m.p. 70°C,

(lit. m.p. 72°C)

3,5-Dibromonitrobenzene, recrystallised from alcohol, m.p. 104°C

(lit. m.p. 106°C)

1,2,3,4-Tetrabromobenzene, recrystallised from light petroleum (b.p. 60-80°C) m.p. 60-63°C (lit. m.p. 62-63°C)

C. Preparation of Intermediate Compounds

2,6-Dichloro-3-nitrofluorobenzene

was prepared by nitration of 2,6-dichlorofluorobenzene according to the method of Klaassens and Schoot(105). 15g of 2,6-dichlorofluorobenzene, was added very gradually to 65 ml nitric acid (density 1.52), keeping the temperature between 50-60°C. The reaction mixture was heated up to 50-60°C and poured onto cracked ice. 2,6-Dichloro-3-nitrofluorobenzene was obtained by steam distillation as 19g of a yellow oil.

2,4-Dichloro-3-fluoroaniline(105)

0.081 mol of the liquid compound 2,6-dichloro-3-nitrofluorobenzene (17g) was suspended in an equal volume of ethanol, a solution of stannous chloride dihydride (54.27g) in concentrated hydrochloric acid (56.7 ml) was added cautiously to the boiling ethanol solution. The amino product was isolated by adding 30% sodium hydroxide solution and steam-distilling; the product was recrystallised from equal amounts of alcohol and water, yield 11.6g (80%), m.p. 87°C.

3,4,5-Tribromoaniline was prepared in an analogous manner from 3,4,5-tribromonitrobenzene and recrystallised from alcohol, m.p. 123°C.

2,4-Dibromoaniline(106)

67.5g of acetanilide and 82g anhydrous sodium acetate were mixed to a thick paste with glacial acetic acid, a solution of 51 ml of bromine in 500 ml glacial acetic acid was added and the mixture was heated on the steam bath. After 5-6 hours almost all the colour of bromine had gone, the mixture was poured into water (~ 1 litre) and the precipitate was washed with water and recrystallised from ethanol to give 2,4-dibromoacetanilide m.p. 146°C.

This dried material was dissolved in boiling alcohol and one tenth of this volume of concentrated hydrochloric acid was added slowly down the condenser, the mixture was then boiled for 8 hours, the alcohol distilled off using a rotary evaporator and the residue treated with aqueous sodium hydroxide. 2,4-Dibromoaniline was recrystallised from aqueous alcohol, m.p. 79-80°C.

2-Bromo-6-nitroaniline(107),(108)

This was prepared from nitration of o-bromoacetanilide with 14.6 ml of 70% nitric acid. The o-bromoacetanilide was prepared by adding drop by drop 20g of o-bromoaniline in 75.58 ml of acetic anhydride. 4- and 6-Nitroacetobromides precipitated as a green coloured solid, the crude product was dissolved in Witt-Uterman solution (8.7g of potassium hydroxide, 55.2 ml of water, 11.6 ml of ethyl alcohol). 2-Bromo-4-nitroaniline precipitated after 24 hours, and treatment of the filtrate remaining after separation of 2-bromo-4-nitroaniline, with glacial acetic acid gave a precipitate of 2-bromo-6-nitroaniline, m.p. 74-76°C after recrystallisation from ligroin (b.p. 40-60°C).

2,4,6-Trichloro-3-fluoronitrobenzene(109)

2,4,6-Trichlorofluorobenzene mixed with nitric acid (density 1.52) at 20°C and kept for 3 hrs at 60°C gave the nitro compound, yield 77% b.p. 216-20°C, 760 mm Hg.

D. The following compounds were prepared and their purity checked with nmr and, for some polybromobenzenes, gas chromatographic analysis showed no impurities either.

o-Fluoronitrobenzene

This was prepared(110) by decomposition of the corresponding diazonium fluoborate salt, made by diazotisation of o-nitroaniline (0.25 mol) with solution of sodium nitrite (0.25 mol) in a mixture of concentrated hydrochloric acid (0.75 mol) and 26 ml of water at -5°C. To the solution was added (0.34 mol) of sodium fluoborate in 120 ml of water. The crude product was distilled under vacuo, b.p. 86-87°C, 11 mm Hg (lit. b.p. 214-6°C, 760 mm Hg), yield 19g (54%).

2,6-Difluoronitrobenzene

This was prepared(111) by oxidation of 2,6-difluoroaniline (0.054 mol) in a 1N solution of peroxybenzoic acid in chloroform, prepared as described by Ogata and Sowaki(112). The corresponding nitroso compound obtained was then oxidised further with a solution of trifluoroacetic acid (2 ml per gram of ArNO) and 90% hydrogen peroxide (0.5 ml per gram), the product recrystallised from alcohol, m.p. 38°C (lit. m.p. 40°C), yield (55%).

i) The following compounds were prepared in an analogous way:

2,4,6-Tribromonitrobenzene, recrystallised from alcohol, m.p. 123°C, (lit. m.p. 125°C).

2,6-Dibromonitrobenzene, recrystallised from alcohol, m.p. 81°C (lit. m.p. 84°C)

2,3,4,6-Tetrafluoronitrobenzene

1,2,3,5-Tetrafluorobenzene was nitrated with a mixture of concentrated sulfuric acid and concentrated nitric acid at 0-10°C, following the method of preparation described by Finger et al(113). Vacuum distillation gave pure product b.p. 78°C, 20 mm Hg (lit. b.p. 78°C, 20 mm Hg.

(ii) The following compounds were prepared by the Balz-Schiemann reaction described by Pavlath and Olah(114):

2,6-Dichlorofluorobenzene, recrystallised from methanol, m.p. 33° C, (lit. m.p. 35°C), yield 73%.

3,5-Dichlorofluorobenzene, fractionally distilled, b.p. 157°C, 760 mm Hg (lit. b.p. 160°C, 760 mm Hg), yield 65%.

2,4,5-Trichlorofluorobenzene, recrystallised from alcohol, m.p. 63°C (lit. m.p. 64°C), yield 57%.

2,4,6-Trichlorofluorobenzene, distilled in vacuo, b.p. 205 °C, 760 mm Hg (lit. b.p. 208°C, 760 mm Hg), m.p. 11°C.

Method of Preparation

The corresponding amino compound (0.1 mol) was heated with 40 ml of concentrated hydrochloric acid and 40 ml of water, cooled to 5°C, and 7g sodium nitrite in 20 ml water added dropwise. The filtrate was then treated with 30g of 40% fluoboric acid, the precipitate filtered off and washed with ice and water, 30 ml methanol and 30 ml ether, giving the corresponding diazonium fluoborate salt. The decomposition of the salt was carried out in a flask protected by a condenser.

2,3,6-Trichlorofluorobenzene

From 2,4-dichloro-3-fluoroaniline

This was prepared by the Sandmayer reaction described by Klaassens and Schoot(105).

The amino compound (7g) dissolved in concentrated hydrochloric acid (9.7 ml) and water (9.7 ml) was diazotised with a solution of sodium nitrite (2.7g) in 5.8 ml water at 5°C, then to the well stirred solution of diazonium salt was added a suspension of cuprous chloride (3.9g) in concentrated hydrochloric acid (7.8 ml). The decomposition of the salt takes place with evolution of nitrogen.

2,3,6-Trichlorofluorobenzene was passed through a column of alumina in petroleum ether and distilled in vacuo, b.p. 110°C, 45 mm Hg and F.p. 10°C.

2,3,4,6-Tetrachlorofluorobenzene(109)

This was prepared by direct chlorination of 2,4,6-trichloro-3-fluoro-nitrobenzene with chlorine gas at 200-20°C, the product was recrystallised from alcohol, m.p. 24 °C (lit. m.p. 25-6°C), yield 73%.

1,2,4-Tribromobenzene(106)

2,4-Dibromoaniline (0.1 mol) was mixed with glacial acetic acid (25 ml) and 48% constant boiling point hydrobromic acid (75 ml). The mixture was treated at 0-5°C with a solution of sodium nitrite (7g) in water (15 ml), added dropwise. When most of the amine had dissolved to give the diazonium ion, the mixture was added to a suspension of cuprous bromide (30g) in 48% hydrobromic acid (100 ml) with shaking. On warming the mixture nitrogen was lost and 1,2,4-tribromobenzene was formed as an oil. Extraction of the product with chloroform, and washing with 2 x 100 ml water, 1 x 100 ml 0.5N sodium hydroxide and 1 x 100 ml water, drying over magnesium sulfate, and evaporation under reduced pressure gave the product. This was then purified by passing through a column of alumina in petroleum ether b.p. 40-60°C. The product recrystallised from alcohol, m.p. 42°C (lit. m.p. 44°C).

1,2,3-Tribromobenzene was prepared by the same procedure from 2,6-dibromoaniline and recrystallised from petroleum ether, m.p. 86°C (lit. m.p. 87-8°C).

1,2,3,5-Tetrabromobenzene(115),(116)

3,4,5-Tribromoaniline (0.03 mol) was diazotised in sulfuric acid (22 ml) by adding it to a solution of powdered sodium nitrite (4g) in sulfuric acid (22 ml) at 5°C, and pouring it onto ice (2 kg). A solution of cuprous bromide (10 gr) in 48% hydrobromic acid (50 ml) was added. The mixture was warmed to complete the elimination of nitrogen, and the tetrabromobenzene was filtered off and removed from the cooled solution by extraction with ether.

1,2,3,5-Tetrabromobenzene recrystallised from aqueous alcohol, m.p. 96°C, (lit. m.p. 98°C).

The following two compounds were prepared similarly:

3,4,5-Tribromonitrobenzene from 2,6-dibromo-4-nitroaniline, recrystallised from alcohol, m.p. 110°C (lit. m.p. 112°C).

2,3,5-Tribromonitrobenzene from 4,6-dibromo-2-nitroaniline, recrystallised from alcohol, m.p. 117°C (lit. m.p. 119°C).

2,3-Dibromonitrobenzene(107),(108)

10.8g of 2-Bromo-6-nitroaniline dissolved in 150 ml glacial acetic acid was added to 20 ml of 80% hydrobromic acid, at 0°C, followed by a solution of sodium nitrite (7g) in water. The resulting solution of diazonium salt was then added to a boiling solution of 80g cuprous bromide in a mixture of 20 ml 80% hydrobromic acid and 25 ml of water and 3 ml concentrated sulfuric acid. The product recrystallised from alcohol, m.p. 83°C (lit. m.p. 85°C).

1,2,4,5-Tetrabromobenzene(117)

p-Dibromobenzene (0.1 mol) was brominated at 150°C by addition of bromine (0.3 mol) in the presence of aluminium powder as catalyst. The product recrystallised from alcohol, m.p. 180°C (lit. m.p. 182°C).

Pentabromobenzene

This compound was prepared by reduction of hexabromobenzene (10g) with sodium borohydride (0.76g) in dimethyl sulfoxide as cosolvent (100 ml) at 100°C. The product recrystallised from acetic acid, m.p. 160°C (lit. m.p. 160-1°C).

p-Bromonitrobenzene(118)

This was prepared by nitration of bromobenzene (16g) in a mixture of 20 mls of concentrated nitric acid and 20 mls of concentrated sulfuric acid at 50-60°C and recrystallised from alcohol, m.p. 125°C (lit. m.p. 126-7°C).

iii) The following compounds were prepared by nitration of the corresponding bromo derivatives with fuming nitric acid (5 ml of nitric acid for each gram of aromatic halogen compound):

2,4-Dibromonitrobenzene(119)

From m-dibromobenzene at 0°C, recrystallised from alcohol, m.p. 60°C, (lit. m.p. 62°C).

3,4-Dibromonitrobenzene(120)

From o-dibromobenzene at 0°C, recrystallised from alcohol, m.p. 58°C (lit. m.p. 58-9°C).

2,3,4-Tribromonitrobenzene(121)

From 1,2,3-tribromobenzene at room temperature, recrystallised from alcohol, m.p. 83 °C (lit. m.p. 85.4°C).

2,4,5-Tribromonitrobenzene(121)

From 1,2,4-tribromobenzene at room temperature, recrystallised from alcohol, m.p. 92°C (lit. m.p. 93.5°C).

2,3,4,5-Tetrabromonitrobenzene(100)

From 1,2,3,4-tetrabromobenzene at 50-60°C for 2 hrs. recrystallised from light petroleum ether (b.p. 60-80°C), m.p. 107°C (lit. m.p. 106°C).

2,3,5,6-Tetrabromonitrobenzene(122)

From 1,2,4,5-tetrabromobenzene at 100°C for 12 hrs, recrystallised from alcohol, m.p. 161°C (lit. m.p. 168°C).

Pentabromonitrobenzene(122)

From pentabromobenzene at 80-90°C for 9 hrs, recrystallised from alcohol, m.p. 234°C (lit. m.p. 236°C).

2,3,4,6-Tetrabromonitrobenzene(122)

From 1,2,3,5-tetrabromobenzene with nitric acid of density (1.50) with moderate heating. Recrystallised from absolute alcohol, m.p. 92°C, (lit. m.p. 96°C).

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