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Aromatic properties of 8-hydroxyquinoline and its metal complexes

Invited Paper

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Abstract: Chelatoaromaticity (aromaticity of chelate complexes) has been recently recognized as an important property influencing the stability of chelate compounds. In this paper, aromaticity of various forms of 8-hydroxyquinoline (anion, neutral molecule, zwitterion and cation) as well as its chelate complexes with magnesium and aluminium ions are investigated. Aromatic properties of these compounds are analyzed using several aromaticity indices based on energetic, geometric, magnetic and electronic physical manifestations of this phenomenon. Results of performed calculations have shown different aromatic properties for the two rings (pyridine and benzene) occurring in the studied ligand. Aromaticity of these rings in metal complexes of 8-hydroxyquinoline is significantly higher than that in corresponding ligand anion. This means that during complexation the aromaticity of the ligand increases and the chelatoaromatic effect stabilizes the studied metal complexes. In contrast, metallocyclic rings of studied metal complexes have non-aromatic properties, and, consequently, the metallocyclic ring is not stabilized by chelatoaromaticity. We conclude that, in the complex, every 8-hydroxyquinoline unit and the metal ion are separated π-electronic systems.

Keywords: *8-hydroxyquinoline • Aromaticity • Chelatocomplexes • Chelatoaromaticity*

1. Introduction

8-Hydroxyquinoline is a ligand extensively used in coordination chemistry for the extraction and determination of metal ions [1,2]. The most relevant complex is that with the aluminium ion (studied in this paper) that is a common material in the organic light-emitting diodes [3]. Biological and medicinal properties of the studied ligand have also been investigated. It functions as an antiseptic, bacteriostat and fungistat agent [4], for which no evidence of its carcinogenicity has been found [5]. 8-hydroxyquinoline was the first compound used for cell labeling by indium ions [6,7]. Hovewer, this agent did not label cells satisfactory and it was toxic to the cells, particularly lymphocytes [8,9]. Moreover, it is used as a corrosion inhibitor that blocks active sites on the metal surfaces [10].

The present manuscript is a study of the aromatic properties of the 8-hydroxyquinoline system in its different forms. Potential chelatoaromatic properties of 8-hydroxyquinoline are the main topic of this study. The term chelatoaromaticity was introduced first in 1945 to explain the stability of Cu(II)-1,3-diketonate complexes by Calvin and Wilson [11]. In 1969, Kuhr and Muro were able to show by NMR that chelate rings of acetylacetonato metal complexes are non-aromatic [12]. Quite recently, a theoretical study using a magnetic criterion of aromaticity was performed for some metal complexes of acetylacetone and o-benzoquinonediimine [13]. Among all studied compounds in that paper, aromatic properties

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were reported only in the case of the chelate ring formed by the Ru^{2+} ion with o-benzoquinonediimine.

By chelatoaromaticity, we understand a manifestation of aromatic properties in chelate metal complexes. Chelatoaromaticity can occur in metallocyclic rings formed during metal ion complexation or in rings of the ligand that do not interact directly with metal ions. Consideration of aromatic effects in coordination chemistry is not a common procedure [14]. However, the chelatoaromatic effect may be important for the stability of metal complexes, which influences their potential application. The main feature of the aromatic compounds is their enhanced stability. Thus, by using a proper ligand (the ligand for which chelatoaromatic effect is possible or not) we can change the stability of the chelate metal complexes. That is why we are trying to find ligands that induce strong chelatoaromatic or anti-chelatoaromatic effects. This study is a part of such a survey.

2. Experimental procedure

All calculations have been carried out at the B3LYP [15-17]/6-311++G**[18] level of theory. This combination of the method and basis set previously gave good results in the case of chelate complexes of hydroxypyrones with aluminium and gallium [19], so we believe that this level of calculation is also suitable for this work. Geometries of all studied compounds have been optimized. Frequency calculations confirmed that all geometries calculated in this work are minima with no imaginary frequencies. All these calculations have been performed with the Gaussian'03 program [20].

Values of several aromaticity indices have been estimated for equilibrium geometries of various (neutral molecule, zwitterions, anion and cation) forms of the studied ligand and its chelate complexes with magnesium and aluminium. Aromaticity indicators based on energetic, geometric, magnetic and electronic properties of aromatic compounds have been used. Such comprehensive research is necessary because so far no available index of aromaticity can be accepted as a universal measure of this property [21,22]. In this paper, we have used ten different indices, namely: HOMA (geometric-based) [23], NICS(0), NICS(1) (both represent the magnetic face of aromaticity) [24-28], H [29], PDI [30], FLU [31], I_{ring} [32], MCI [33] and KMCI [34] (all of them belong to the group of so called electronic indices of aromaticity) and ASE (energetic aspect of aromaticity). Theory and computational details of these indices were described in original papers and were the topic of two issues of Chemical Reviews [35,36]. That is why we do not want to present here all details but only the most important facts that are necessary especially for the readers that are not specialists in the field.

HOMA is an index of aromaticity based on a geometric criterion that assumes that in aromatic compounds bond lengths tend to be intermediate between lengths typical for single and double bonds. If bond lengths in the studied system are known, the HOMA index can be easily calculated [23]. Reference values for this method are: real benzene (HOMA equals to 1) and the Kekule structure of benzene with localized single and double bonds (HOMA equals to 0). Larger HOMA values denote stronger aromaticity.

NICS is a magnetic index of aromaticity (magnetic criterion of aromaticity states that an external magnetic field induces a diatropic ring current in aromatic rings). It is probably the most popular measure of aromaticity nowadays. It is defined as the negative value of the absolute magnetic shielding [24]. In this paper, we have calculated this index in two positions: NICS(0) (NICS is calculated in the geometrical center of investigated ring [24]) and NICS(1) (NICS is calculated at the point located 1 Å above the center in perpendicular direction to the ring plane [26]), as this latter has been proven to be a better measure of aromaticity because it reduces the effect of in-plane σ electrons, thus being basically a measure of out of plane π currents. In contrast to HOMA, more negative NICS values indicate stronger aromatic properties of the studied system. Calculations of magnetic properties have been carried out under the GIAO approximation [37] at the same level of theory as geometry optimization.

More recently, electronic indices of aromaticity have been introduced as a new tool in aromaticity research. Several indices from this group have been used in this work. Two of them (PDI [30] and FLU [31]) use delocalization indices (DI) calculated between pairs of atoms in the aromatic ring, while the other three (I_{ring} [32], MCI [33] and KMCI [34]) take into account delocalization (using the same DI values) in the whole ring. For all these indices except FLU (where opposite relationship is valid) larger index values suggest higher aromaticity. Another approach in electronic indices of aromaticity is presented with the H index. In this case, the total energy density at the ring critical point is postulated as a new measure of aromaticity (higher energy density denotes higher aromaticity) [29]. Atoms in Molecules [38] properties (delocalization indices and critical point properties) were obtained using the AIMPAC package [39].

Probably the most widely accepted aromatic property is the fact that aromatic compounds are more stable than expected. They have some additional

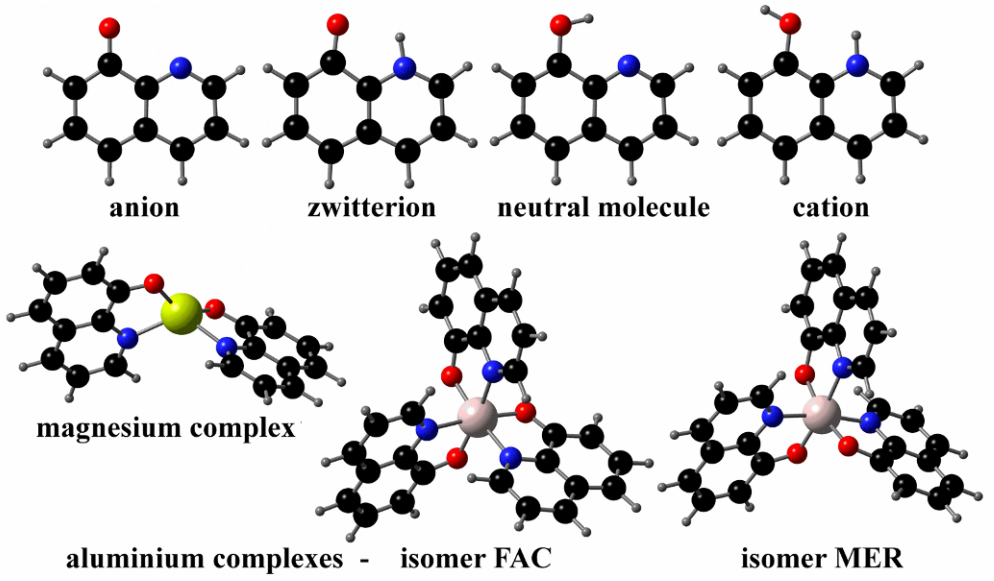

Figure 1. Molecular structures of various forms of 8-hydroxyquinoline and their metal complexes.

"aromatic" energetic stabilization in comparison to the corresponding non-aromatic reference state. Unfortunately, this energetic criterion of aromaticity is difficult to obtain due to the fact that quite often it is really problematic to propose the non-aromatic reference state that is free from drawbacks like strain, topological charge stabilization, changes in hybridization and heteroatom interactions [40]. It looks like one of the best approaches for the calculation of the Aromatic Stabilization Energy (ASE) is an isomerization method [41] where the stabilization energy in the aromatic compound is the difference between energies calculated for a methyl derivative of this system and its non-aromatic exocyclic methylene isomer. Such a method of ASE calculation is applied in this work. Obviously, larger values of aromatic stabilization energies denote higher aromaticity.

Among aromaticity indices used in this work, NICS(0), NICS(1), H, I_{ring}, MCI, and KMCI can determine aromaticity in all types of studied rings (benzene and pyridine ring of ligand and metallocyclic ring in metalcomplexes). On the other hand, PDI, FLU, ASE and HOMA allow to estimate aromaticity only in the rings of ligands. Most aromaticity indices in this study can work as local indicators of the aromaticity strength (they can measure the π-electron delocalization of one ring in the studied compounds). ASE and HOMA have been used here to estimate the total aromaticity of the studied system (aromaticity of the whole π-electronic system instead of the aromaticity of one particular ring). HOMA can measure the local and the total aromaticity (in this case, as total molecule we understand this part of the studied system for which HOMA parameters are available). In addition, the HOMA model can be used for estimation of the electron delocalization in the organic part of the metallocyclic rings. All these possibilities of the HOMA index are used in this study.

3. Results and discussion

Structures of the studied compounds in this work are presented in Fig. 1. We have considered several forms of 8-hydroxyquinoline (HQ) and its metalcomplexes with aluminium (AlQ_3) and magnesium (MgQ_2). In the case of the aluminium complex, two isomers, facial (fac-AlQ_3) and meridional (mer-AlQ_3), are possible. In the case of free ligand, neutral molecule, the zwitterion of 8-hydroxyquinoline (QH), its cation (H_2Q) and anion (Q) are taken into account. The anion is important because deprotonated 8-hydroxyquinoline is an agent that coordinates metal ions, so the difference in the aromaticity strength between free ligand anion and ligand anion coordinated in the metalcomplex should be considered as the measure of the chelatoaromatic effect. On the other hand, the aromatic situation in the cation could be similar to the situation in the complex (the additional proton in the cation is a substitute of the metal ion). In general, the corresponding aromaticities of all forms of the ligand are also important. They should allow us to recognize to what extent electron delocalization can vary in the studied system.

HOMA data for all studied forms of 8-hydroxyquinoline are presented in Fig. 2. In general, differences in aromaticities between the two isomers of the aluminium complex are negligible, in spite of the fact that the MER isomer is more stable by about 25 kJ mol^{-1}. For this

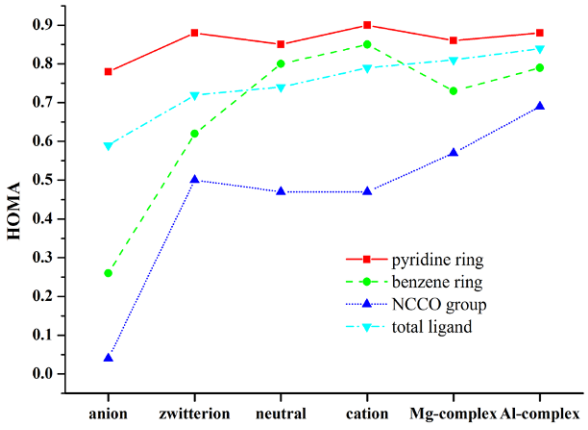

Figure 2. Local and total HOMA values for different forms of 8-hydroxyquinoline.

reason, values obtained for MER and FAC isomers are sometimes represented in this study by one value. The data calculated using the HOMA model suggest that each ring in the 8-hydroxyquinoline system presents different aromatic properties. For all studied forms of 8-hydroxyquinoline is always the highest HOMA value is observed for the pyridine ring. Aromaticity of this ring is high (HOMA values about 0.85) and only slightly varies from one form to another. This means that aromaticity of the pyridine ring in the studied compounds is a bit lower than that of the pyridine alone (HOMA index of pyridine, calculated for the geometry obtained as a mean of four experimental geometries, is 0.998 [42]). This is justified by one of the most characteristic properties of highly aromatic compounds - their tendency to retain their high delocalization level [43]. Thus, aromaticity of this ring in all studied forms is high and more or less stable. Quite a different behaviour is observed for the benzene ring of the molecular system under consideration. The change in aromaticity is connected with the influence of the oxygen atom on the electron delocalization in the benzene ring. It is known that an exocyclic group connected with the ring by a double bond can efficiently disturb the ring aromaticity [44]. This disturbance (benzene's HOMA index is usually reported as 0.99) depends on the bond order of the double bonded substituent. If the exocyclic double bond is elongated by any effect, the exocyclic bond is going toward a single one and aromaticity of the ring increases [45]. This effect can be clearly observed in Fig. 2. Low aromaticity is obtained for the anion, where the C–O bond joined to the ring has a somewhat larger double bond is character. In the zwitterionic structure of 8-hydroxyquinoline, the C=O double bond character is slightly weakened by the intramolecular hydrogen bond formed by the carbonyl moiety with the NH group. This slight C=O elongation is reflected in the moderate aromaticity of the benzene ring in this form of 8-hydroxyquinoline (HOMA about 0.6). In the structures of neutral 8-hydroxyquinoline and its cation, the C=O double bond character is clearly reduced. Automatically, aromaticity of the benzene ring increases to values of aromatic compounds (HOMA higher than 0.8). In the case of metal complexes, the carbon-oxygen double bond from the 8-hydroxyquinoline anion is elongated by interactions with the metal ion. The length of the carbon-oxygen bond is longer than in the case of the zwitterion (QH) structure, but shorter than the single C-O bond in neutral (HQ) and cation (H_2Q). For this reason, aromaticity of the benzene ring in metal complexes is in between that of the zwitterion and neutral molecules.

Due to the lack of HOMA parameters for the oxygen-metal and nitrogen-metal bonds it is not possible to calculate this index for the ring containing metal ions. We can only employ the HOMA method for estimation of the electron delocalization in the NCCO group, which is directly involved in the metal ion binding. For this group, low aromaticity in the anion (again the influence of the exocyclic C=O double bond) increases to moderate levels of electron delocalization in QH, HQ and H_2Q structures (HOMA about 0.5). The ring formed due to H-bonding in QH, HQ and H_2Q structures can be considered a quasi-aromatic ring [46].The highest (but not very high) HOMA values for this group are observed in the cases of magnesium and aluminium metal complexes (about 0.6). Of course, such relatively intermediate electron delocalization values of this group in metal complexes do not denote that the whole metallocyclic rings are aromatic (see below). HOMA indices can also be applied to calculate total aromaticities for the whole π-electronic part of the investigated ligand. This total aromaticity varies between about 0.6 and 0.8 HOMA values, and increases monotonously from the anion through neutral (QH and HQ) and cationic (H_2Q) forms of 8-hydroxyquinoline till 8-hydroxyquinoline metal complexes. This means that during complexation aromaticity of every 8-hydroxyquinoline ligand anion gains about 20% of its aromaticity.

Once having discussed the results of the HOMA index, we proceed with other aromaticity criteria. The results of the NICS, PDI and FLU calculations are presented in Fig. 3. Results of NICS(0) calculations suggest for both rings (pyridine and benzene) similar aromaticity variations. From anion to cation, the aromaticity increases (NICS values getting more negative) and slightly decreases from cation to metal complexes. Changes of NICS(0) values are much bigger for the benzene ring (from -4 to -10 ppm) than for the pyridine ring (from about -5.5 to -7.0 ppm). In all cases except the anion, NICS(0) model predicts higher aromaticity for the benzene ring.

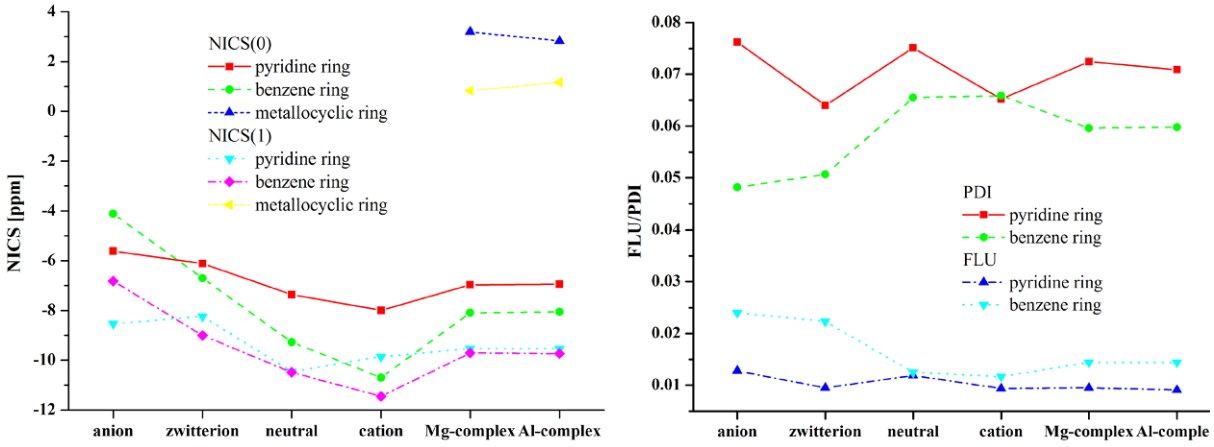

Figure 3. Magnetic (NICS(0) and NICS(1)) and electronic (PDI and FLU) data for studied forms of 8-hydroxyquinoline. Corresponding values for benzene, pyridine and cyclohexane are: -8.07, -6.87, -2.02, (NICS(0)) and 10.24, -10.16, -1.94 (NICS(1), respectively.

So, NICS(0) provides different conclusions about the relative aromaticities of the ligand rings in comparison with the HOMA model. The similarity between NICS and HOMA predictions is bigger in the case of NICS(1) data. For this index there is no clear trend in aromaticity for the pyridine ring, with NICS(1) values oscillating around -9.0 ppm. The trends in the relative aromaticities predicted for the benzene ring by the NICS(1) model follow those estimated by the NICS(0) (and HOMA). By means of NICS it is possible to determine the electron delocalization in the metallocyclic rings too. One can see that both NICS indices describe these rings as non-aromatic. Thus, compared to HOMA, that means that the high electron delocalization expected for this ring by HOMA, is only restricted to the NCCO fragment, not to the whole metallocyclic ring. This could justify why the changes in aromaticity between the FAC and MER isomers of the aluminium complex are always negligible. Breaking of the electron delocalization between 8-hydroxyquinoline anions and the metal ion results in π-electronic separation of 8-hydroxyquinoline's units in the complex. That is why different relative geometrical positions of anion units in the facial and meridional isomers do not modify their aromaticities.

Electronic indices (PDI and FLU) give relative aromaticities for the studied molecules similar to the predictions based on HOMA values. Variations of aromaticity for the pyridine ring are small and this ring is more aromatic than the benzene ring (please note that higher PDI and lower FLU values denote higher aromaticity). Larger changes of electron delocalization among the different forms are observed for the benzene ring. The order of relative aromaticities is the same, but the aromaticities in pairs anion-zwitterion, neutral-cation. Mg and Al metal complexes are very close, much closer than for other presented indices. Aromaticity data provided by other electronic indices of aromaticity are collected in Table 1. In general, data gathered in this Table follows observations given by almost all previously discussed indices (except NICS(0)) for both benzene- and pyridine-like rings. There are two exceptions. The first is the index H (which is quite constant). The second are aromaticities of the anion obtained for the pyridine ring. Unexpectedly, aromaticities of the anionic form in this ring is the highest one. But we know, from the previous data, that changes of aromaticity in the pyridine ring are lower than in the benzene ring. That's why, aromaticity changes in the benzene ring are more important and decisive for the trends observed in the whole system. Next, let us look at the data provided by I_{ring}, MCI, KMCI and H indices for the metallocycllic rings of metal complexes. Again we can notice that aromaticities of metallocyclic rings are very poor, much lower than for other parts of studied compounds.

The last method used in this report for aromaticity estimations is the energy-based ASE index. Calculations of ASEs have been performed for the whole π-electronic system of studied compounds. Due to the fact that previous calculations indicated a non-aromatic character of the chelate's rings, only pyridine and benzene rings of ligand were involved in these calculations The reaction used for ASE evaluation is presented in Fig. 4, while the results of calculations are collected in Table 2. The compound presented on the right side of the reaction scheme represents the 8-hydroxyquinoline molecule modified by two methyl substituents that should not disturb the electron delocalization in the molecular system under investigation. On the left we see the corresponding tautomer in which one hydrogen from every methyl group is moved to the neighboring carbon atom. As a result, the continuity of the delocalized

Table 1. Numerical values of some electronic indices of aromaticity.

Molecular system	I_{ring}	MCI	KMCI	H
		Pyridine ring		
Anion	0.0274	0.0382	0.0103	0.0074
Zwitterion	0.0187	0.0234	0.0070	0.0054
Neutral molecule	0.0262	0.0363	0.0098	0.0075
Cation	0.0191	0.0244	0.0072	0.0079
Magnesium complex	0.0242	0.0331	0.0091	0.0075
Aluminium complex - FAC, MER	0.0235, 0.0241	0.0321, 0.0329	0.0088, 0.0090	0.0073, 0.0074
		Benzene ring		
Anion	0.0137	0.0174	0.0051	0.0068
Zwitterion	0.0146	0.0181	0.0055	0.0070
Neutral molecule	0.0228	0.0314	0.0086	0.0073
Cation	0.0237	0.0322	0.0089	0.0074
Magnesium complex	0.0199	0.0266	0.0075	0.0075
Aluminium complex - FAC, MER	0.0200, 0.0201	0.0267, 0.0269	0.0075, 0.0075	0.0071, 0.0072
		Metallocyclic ring		
Magnesium complex	0.0008	0.0008	0.0005	0.0007
Aluminium complex - FAC, MER	0.0006, 0.0006	0.0005, 0.0006	0.0004, 0.0004	0.0037, 0.0038

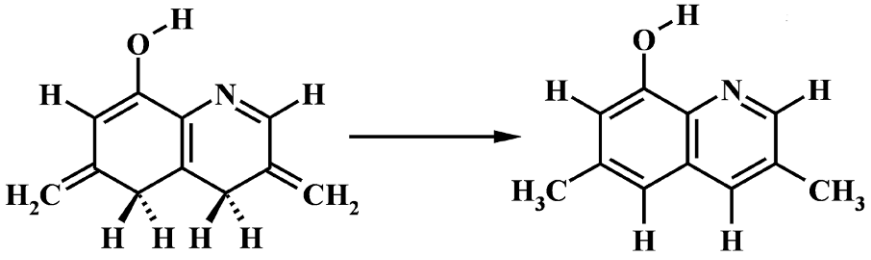

Figure 4. Reaction scheme used for Aromatic Stabilization Energies evaluation.

π-electronic system is destroyed by the presence of methylene groups in the ring. In addition, with this tautomeric transformation exocyclic $=CH_2$ groups force additional bond localization. Consequently, no aromaticity should be possible in the compound on the left and the energetic difference (the change of the enthalpy of presented reaction) between these two compounds can be considered as the measure of the ASE of 8-hydroxyquinoline. The neutral structure of 8-hydroxyquinoline is presented in Fig. 4, but analogous reactions have been used for the ASE estimation of all its other forms. In the case of AlQ_3 and MgQ_2 only one from two/three anionic units of 8-hydroxyquinoline was modified.

The relative ASE values (ASE of the anion is taken as the zero level) are included in the third column of Table 2. As ASE measures the total aromaticity, it should be compared to HOMA values for the whole π-electronic system of studied ligand in Fig. 2. It is easy to observe that $HOMA_{total}$ and ASE lead to similar results. The only exception is the neutral from of the ligand, which presents quite a large ASE value. This drawback may be attributed to the influence of the intramolecular hydrogen bond, which is potentially stronger in the original structure than in the structure with exocyclic CH_2 groups. It is expected that small folding of the cumulated benzene and pyridine rings, forced by the exocyclic and endocyclic methylene groups in the dearomatized structure from the left side of the reaction scheme can also disturb the strength of the intramolecular hydrogen bond. For this reason, the ASE value of the neutral 8-hydroxyquinoline does not only represent the effect of dearomatization but also accounts changes in the strength of the intramolecular hydrogen bond.

In addition, we can try to compare the strength of the chelatoaromatic effect in the 8-hydroxyquinoline metal

Table 2. Calculated ASE values (enthalpies of reaction from Fig. 4, kJ mol^{-1}) and relative differences in ASE for different 8-hydroxyquinoline forms.

Molecular system	ASE	ASE (relative)
Anion	229.1	0.0
Zwitterion	234.2	5.1
Neutral molecule	253.8	24.7
Cation	241.6	12.5
Magnesium complex	243.9	14.8
Aluminium complex - FAC, MER	243.1, 241.3	14.0, 12.1

**corresponding ASE energies for pyridine and benzene are 138.9 and 138.7 kJ mol^{-1}, respectively.*

complexes with the strength of this property in previously studied by us metal complexes of hydroxypyrones, like maltol, ethylmaltol and pyromeconic acid. The aromatic and chelatoaromatic properties of these compounds are reported in our previous paper [19]. The most important point is the fact that the aromaticity difference between the free anionic ligand structure and anionic unit in the metal complexes is significantly bigger for hydroxypyrones than for the 8-hydroxyquinoline. That is why we expect the chelatoaromatic effect to be more important for hydroxypyrones than for the presented compounds.

Finally, we can conclude that the series of aromaticity indices employed in this paper show a quite consistent picture of aromaticity changes in the 8-hydroxyquinoline system; even though, they do not agree in all cases. This fact can be justified from the so-called multidimensional character of this property [47,48], in the sense that one can argue that it is understandable that different indices afford divergent ordering since the compound may be more aromatic than other in one dimension and less aromatic in another [21,43,49]. This explains why many authors advise to use a set of indices based on different physical properties, as it has been done in the present manuscript.

4. Conclusions

The 8-hydroxyquinoline ligand and its metal complexes constitute a new example of the changes in aromaticity connected with the formation of chelate complexes. Due to the ligand structure, the situation of 8-hydroxyquinoline metal complexes is complicated by the fact that this ligand consists of two rings with quite different aromatic properties. Five different forms of the 8-hydroxyquinoline system have been studied: anion, zwitterion, neutral, cation and ligand in the metal complex (three examples). When we move from one ligand form to another, the aromaticity of the pyridine ring oscillates (in rather stochastic manner) around one (high) level of aromaticity. At the same time, aromaticity of the benzene ring (connected with the exocyclic oxygen substituent) increases monotonically in the order anion < zwitterion < metal complex < neutral < cation. In summary, the total aromaticity increases in the order anion < zwitterion < neutral < cation < metal complex. Aromaticity of the ligand's anion is always low while the aromaticity of this anion in the metal complex is much higher. That means that metal complex is stabilized by the aromatic effect. Such a result allows us to incorporate the metal complexes of 8-hydroxyquinoline into the group of chelatoaromatic compounds. NICS and some electronic indices of aromaticity show that electron delocalization in chelate rings with the metal ions is very poor. Thus, 8-hydroxyquinoline units in metal complexes constitute (as it was observed in the case of hydroxypyrones) separate π-electronic systems.

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