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Theoretical studies on aromaticity of selected hydroxypyrones and their cations and anions. Part 2. Electron delocalisation in the OCCO group[†]

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Electron delocalisation in the OCCO part of hydroxypyrones with two exocyclic oxygens linked by two carbon atoms was studied using well-known aromaticity indices like: HOMA, EN, GEO, NICS(0) and NICS(1). This part of hydroxypyrones is very important due to the fact that the two exocyclic oxygens of deprotonated hydroxypyrone units are responsible for metal ion binding. Values of the aromaticity indices were obtained for geometries calculated by several theoretical methods (HF, SVWN, B3LYP and B1LYP) with 6-311++G(d,p) basis set. Electron delocalisation in the corresponding cations and anions was also considered. The data obtained in this work revealed that the relative delocalisation order in the OCCO group is the same as the aromaticity order determined earlier for the heterocyclic rings of hydroxypyrones (anions $<$ neutral molecule $<$ cation). The problem of quasiaromaticity in neutral hydroxypyrones and their cations is also considered and discussed. Copyright © 2008 John Wiley & Sons, Ltd.

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Keywords: hydroxypyrones; π-electron delocalisation; quasiaromaticity

INTRODUCTION

In a recent publication,[1] the aromaticity of the pyran ring in selected hydroxypyrones (pyromeconic acid – 3-hydroxy-4*H*-pyran-4-one, maltol – 3-hydroxy-2-methyl-4*H*-pyran-4-one and ethylmaltol – 3-hydroxy-2-ethyl-4*H*-pyran-4-one) has been studied theoretically. In this work, the π-electron delocalisation in the OCCO fragment of these compounds (as in Fig. 1) is investigated with meticulous attention. The oxygen atoms of this group are responsible for metal ion binding in many hydroxypyrone–metal complexes with strong biochemical and pharmacological activity.[2] This is why our attention is focused on the problem of how physicochemical properties of the OCCO group can influence the properties and stabilities of formed chelate compounds. In order to expand our studies, the charged forms of the studied ligands have also been taken into account. Hydroxypyrone anions are created by deprotonation of the hydroxyl group, while cations result from protonation of the keto group.[3]

Aromaticity, introduced by Kekule,[4] is a very important concept in chemistry. It is a milestone in the explanation of structure, stability and reactivity of many groups of chemical compounds. Unfortunately, aromaticity is not an observable quantity (that means it cannot be measured directly). Thus, it is difficult to elaborate its strict definition. Therefore, during past years many criteria were used for the aromaticity description. The aromaticity definition proposed by Schleyer and Jiao[5] stated that: 'Compounds which exhibit exalted diamagnetic susceptibility are aromatic. Cyclic electron delocalisation also may result in bond length equalisation, abnormal chemical shifts and magnetic anisotropies, as well as chemical and physical properties which reflect energetic stabilisation'. In other words, aromaticity originates from cyclic π-electron delocalisation (ring current) that generates some so-called aromatic properties. These specific magnetic, geometric and energetic properties are the base for defining many aromaticity indices.[6] They are widely used in quantitative studies of this phenomenon. Aromaticity indices used in this work are described in the Section 'Computational Details'.

Aromatic rings can be built from different kinds of elements. First of all, aromaticity can exist in unsaturated rings consisting in carbon atoms only. On the other hand, in heterocyclic rings where at least one carbon atom is replaced by another suitable element (O, N, S or others), heteroaromaticity is expected. Metalloaromaticity is the manifestation of aromatic properties in chelates where a metal ion is the essential part of the ring

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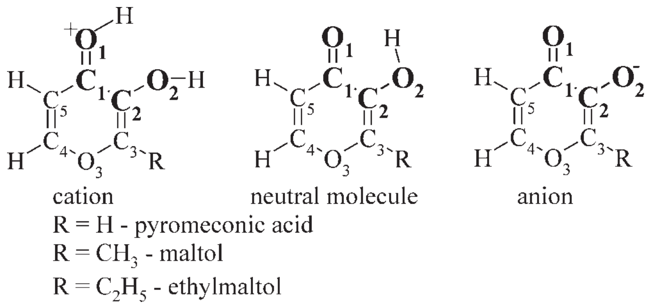

Figure 1. Molecular structures of the investigated compounds. Atoms building up the OCCO fragment are bolded

as introduced by Calvin and Wilson in 1945.[7] Nowadays, the importance of understanding metalloaromaticity increases because it is very useful in the explanation of many essential properties of metal complexes with organic ligands.[8] Metalloaromaticity of oxovanadyl complexes with maltol and kojic acid has been recently documented.[9] In this work, the attention is focused on the phenomenon of quasiaromaticity. Quasiaromatic pseudo-rings with hydrogen bonds (H-bonds) can appear in cyclic systems in which the C═C—C fragment (or analogical fragment including heteroatoms) has been formally replaced by the A. . .H—D group (A and H—D are the proton donor and acceptor, respectively).[10]

Several phenomena, crucial for electron delocalisation in studied compounds, are considered in this work. First of all, the determination of the π-electron delocalisation levels of the OCCO group in various hydroxypyrone forms is calculated and discussed. These data are necessary (i) for future studies of metal-induced aromaticity in chelates of investigated ligands (ii) to know whether the π-electron delocalisation levels in the OCCO spacer of hydroxypyrones follow the order established previously for their heterocyclic pyran rings[1] and (iii) finally, to discuss the problem of quasiaromaticity as a proper term to describe such H-bonded 'five'-membered OCCO—H . . . pseudo- rings.

COMPUTATIONAL DETAILS

The geometries used for the evaluation of quasiaromaticity/π-electron delocalisation in the OCCO group of hydroxypyrones are the same as determined in previous work[1] considering heteroaromaticity of their pyran rings. These geometries were calculated at HF,[11] SVWN,[12] B3LYP[13] and B1LYP[14] levels. The 6-311++G(d,p) basis set[15] was used in all cases.

Aromaticity indices, employed in the previous study (NICS(0),[16] HOMA,[17] EN[18] and GEO[18]) are used also in this work. The only exception is the I_6 index.[19] It can be calculated for full rings with carbon and hetero atoms only. Thus, it cannot be employed for evaluating the aromaticity of a quasi-ring including a H-bond. Instead of it, another index from the NICS family, NICS(1) is used.[20]

NICS indices are defined as theoretically computed negative values of the absolute magnetic shielding. The difference between NICS(0) and NICS(1) is in the point where the magnetic shielding is calculated. NICS(0) value is determined in the geometrical centre of the (potentially) aromatic system while NICS(1) value is obtained 1 Å above the centre of the mean aromatic plane (in order to avoid the influence of sigma electrons). In this work, NICS(0) values are calculated in the geometric centre of the four heavy atoms (two oxygen and two carbon atoms) that form the studied pseudo-ring while NICS(1) values are obtained 1 Å above the plane of these atoms. In order to compare the values obtained for the anions and cations to those of neutral molecules, NICS values have to be determined for (more or less) the same point in the molecular space. Due to the fact that there is no H-bond in the hydroxypyrone anions (since the proton dissociates from the hydroxypyrone molecule when the anion is formed, as in Fig. 1), the hydrogen atom involved in the intra-ring H-bond is neglected in the determination of the point where NICS values are calculated. The NICS(0) value for the aromatic reference molecule, that is benzene, is about −10, and for antiaromatic reference system, cyclobutadiene, it is about 28. In general, the more negative the NICS (both NICS(0) and NICS(1)) value is observed, the stronger the aromaticity is expected. For magnetic property calculations, the gauge independent atomic orbitals (GIAO) method is used.[21]

Indices of aromaticity based on the geometric criterion depend solely on bond lengths in the studied systems that are relatively easy to obtain from experiment or theory. Among them, HOMA index is the best method. Several years ago,[18] two different ways of dearomatisation were discovered inside HOMA index: bond elongation (sub-index EN) and bond alternation (sub-index GEO). The HOMA, EN and GEO indices were defined as follows:

$$\begin{aligned}\mathrm{HOMA} &= 1 - \alpha(R_{\mathrm{opt}} - R_{\mathrm{ave}})^2 - \alpha/N\Sigma(R_{\mathrm{ave}} - R_{\mathrm{i}})^2 \\ &= 1 - \mathrm{EN} - \mathrm{GEO}\end{aligned}$$

In this equation, R_{opt}, R_{i} and R_{ave} are optimal bond length, bond length in the real system and average bond length in the studied system, respectively. N is the number of bonds taken into the summation while α is an empirical constant fixed to provide HOMA = 0 for a model system (Kekule structure of benzene with bond lengths equal to the reference single and double bonds used for R_{opt} determination).

In the neutral molecules and cations of the investigated compounds, there is an intramolecular H-bond. Several methods of estimation of H-bond strength based on Quantum Theory of Atoms in Molecules (QTAIM)[22] are used in this work. They are: charge density (ρ), its curvature perpendicular to the molecular plane (λ_3), Laplacian of the charge density ($\nabla^2\rho$) and energy density (H) determined for the intramolecular H-bond critical point[23,24] or the critical point of the ring formed by intramolecular hydrogen bonding.[25] It was found that weak HBs show both $\nabla^2\rho$ and $H > 0$, medium HBs show positive Laplacian values connected with negative energy density and finally strong HBs are characterized by negative $\nabla^2\rho$ and H values. All AIM properties presented here have been calculated using the AIMPAC package.[26] Additionally, in papers mentioned above enthalpy of some reactions were employed to evaluate the H-bond strength. After small modifications, they are used in this paper, as in Fig. 2. The simplest choice is the enthalpy difference between two rotamers, one in which the intramolecular H-bond is present and the second in which the intramolecular H-bond is destroyed by the proton rotation of about 180° along the carbon oxygen bond (as in reactions 1 and 2). However, on going from one rotamer to another, we do not only eliminate the intramolecular H-bond, but we also introduce the O. . .O non-bonded interaction. Therefore, the energy gap between both rotamers is not a strict measure of the H-bond strength. Consequently, more complicated reaction types (3–5) are preferred. Another method used for the HB energy determination is the Lippincott–Schroeder (L–S) model.[27] With this empirical

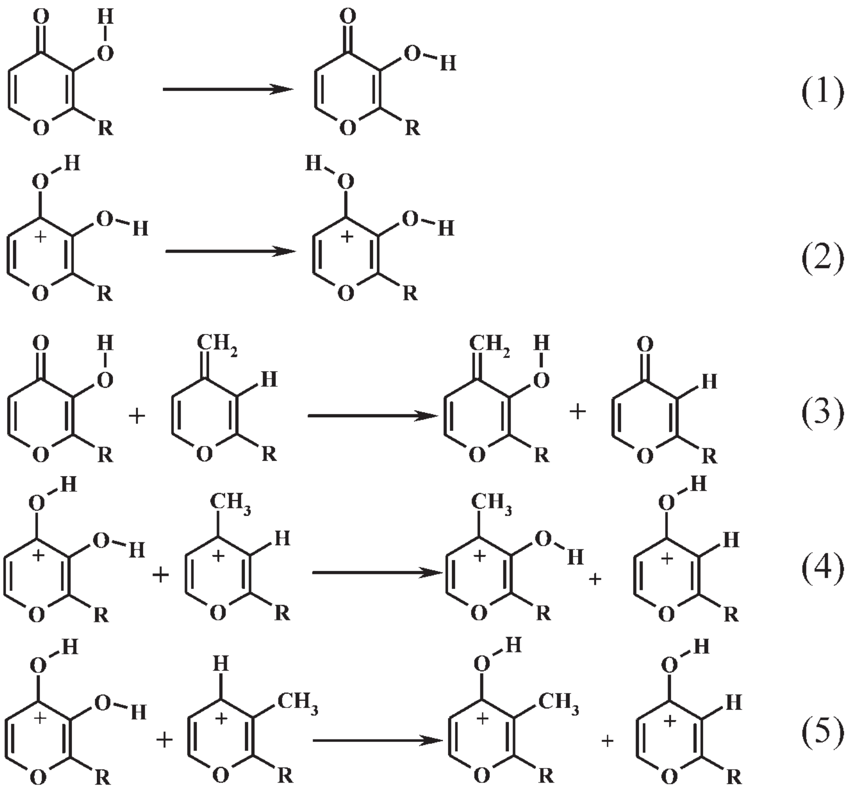

Figure 2. Reaction schemes used for estimation of hydrogen bond strengths

model (modified later by Reid[28]), the HB energy can be computed if the position of the hydrogen atom is known.

RESULTS AND DISCUSSION

Aromaticity/π-electron delocalisation data for the OCCO part of pyromeconic acid, maltol and ethylmaltol (neutral molecules, cations and anions) are shown in Tables 1–3, respectively. Values obtained for different ligands are very similar comparing the same ligand form at the same computational level. It is not surprising since independence of the aromaticity level on the substituent effect was also observed in the previous study where the aromaticity of hydroxypyrone-pyran rings were examined.[1] That is why electron delocalisation properties are graphically

Table 1. Aromaticity data for pyromeconic acid (6-311++G(d,p) basis set)

Aromaticity index	HF	SVWN	B3LYP	B1LYP
Neutral molecule				
HOMA	−0.09	0.43	0.05	0.04
GEO	0.87	0.35	0.55	0.57
EN	0.22	0.22	0.40	0.39
NICS(0)	−4.66	−4.85	−4.21	−4.22
NICS(1)	−3.14	−3.57	−3.17	−3.17
Cation				
HOMA	0.63	0.67	0.46	0.39
GEO	0.07	0.03	0.04	0.08
EN	0.30	0.30	0.50	0.52
NICS(0)	−7.94	−7.67	−7.61	−7.61
NICS(1)	−3.51	−3.92	−3.31	−3.31
Anion				
HOMA	−0.70	−0.15	−0.51	−0.50
GEO	1.59	0.97	1.22	1.22
EN	0.11	0.18	0.29	0.28
NICS(0)	−0.79	−0.54	−0.47	−0.45
NICS(1)	−2.24	−2.14	−2.01	−2.00

Table 2. Aromaticity data for maltol (6-311 ++ G(d,p) basis set)

Aromaticity index	HF	SVWN	B3LYP	B1LYP
Neutral molecule				
HOMA	−0.08	0.48	0.17	0.05
GEO	0.85	0.30	0.48	0.55
EN	0.24	0.22	0.35	0.40
NICS(0)	−4.80	−4.95	−4.35	−4.37
NICS(1)	−3.15	−3.53	−3.23	−3.20
Cation				
HOMA	0.68	0.71	0.47	0.45
GEO	0.06	0.03	0.04	0.07
EN	0.26	0.26	0.49	0.48
NICS(0)	−8.14	−7.96	−7.83	−7.83
NICS(1)	−4.27	−3.93	−3.37	−3.38
Anion				
HOMA	−0.58	−0.01	−0.41	−0.40
GEO	1.46	0.84	1.12	1.12
EN	0.12	0.17	0.29	0.28
NICS(0)	−0.94	−0.77	−0.54	−0.55
NICS(1)	−2.26	−2.19	−2.03	−2.04

presented for the pyromeconic acid only, as in Fig. 3(a) (NICS(0)), (b) (NICS(1)) and (c) (HOMA). From the present data, one very important conclusion can be simply evaluated. The order of the electron delocalisation in the OCCO group is exactly the same as the aromaticity order determined previously for pyran ring in studied compounds.[1] As previously observed, the π-electron delocalisation is the highest, moderate or the lowest for the cations, neutral molecules or anions, respectively.

Inside the HOMA model, the tendencies of EN and GEO sub-indices are completely different (as in Fig. 3(d)). The EN part decreases from cations to neutral molecules and anions while the GEO part increases in the same order. The lowest (close to zero) GEO values are predicted for cations while the highest are calculated for anions. If the same computational level is considered, calculated GEO values are always larger than EN for neutral molecules and anions. In the case of cations, the EN part dominates.

Table 3. Aromaticity data for ethylmaltol (6-311 ++ G(d,p) basis set)

Aromaticity index	HF	SVWN	B3LYP	B1LYP
Neutral molecule				
HOMA	−0.07	0.47	0.03	0.05
GEO	0.84	0.31	0.54	0.55
EN	0.23	0.22	0.43	0.40
NICS(0)	−4.45	−4.39	−4.23	−4.24
NICS(1)	−3.08	−3.48	−3.22	−3.23
Cation				
HOMA	0.56	0.66	0.43	0.44
GEO	0.14	0.04	0.06	0.06
EN	0.30	0.30	0.51	0.50
NICS(0)	−8.10	−7.74	−7.75	−7.75
NICS(1)	−3.83	−3.62	−3.27	−3.29
Anion				
HOMA	−0.59	−0.02	−0.39	−0.39
GEO	1.48	0.85	1.11	1.12
EN	0.11	0.17	0.28	0.27
NICS(0)	−0.87	−0.52	−0.47	−0.52
NICS(1)	−2.18	−2.12	−1.94	−2.00

It is easy to note that the NICS values do not depend very significantly upon the method used for calculation. Nevertheless, some non-negligible dissimilarities are observed. A different situation is obtained for the HOMA index. In general, it seems that the values of HOMA index are highly sensitive to rather subtle geometry changes predicted by different levels of theory. In particular, HOMA values calculated using the SVWN geometries are very different from the others. Data provided by this computational scheme for hydroxypyrone anions are close to the values estimated by other methods for neutral molecule. A similar behaviour was observed previously for the heterocyclic rings of the studied compounds.[1] Such a large dependence of the HOMA values on the method of calculation reveals that if anyone wants to use HOMA indexes for comparing the aromaticity levels of different compounds, the same method of calculations must be rigorously used for all of them.

Aromaticity in the pyran ring is compared with the π-electron delocalisation level in the OCCO group in Fig. 4. Again, only the pyromeconic acid molecule is presented. The levels of aromaticity in the heterocyclic ring and in the π-electron delocalisation in the OCCO spacer determined by HOMA method are comparable for all hydroxypyrone forms. In the case of NICS(0), a small deviation (a slightly higher aromaticity is suggested in the pyran ring) is observed for neutral molecule. NICS(1) calculations predict always larger electron delocalisation in the pyran ring than in the OCCO part.

Finally, we want to analyse if the discussed pseudo-rings can be classified as quasiaromatic systems. This group fulfils the formal definition presented in the Introduction. But there is an additional criterion for quasiaromatic compounds: the π-electron delocalisation in the quasiaromatic system should depend on the strength of the H-bond in the quasi-ring.[29] It means that the appearance of a ring current (essential for the aromaticity definition), is possible and the π-electron delocalisation is not restricted to the heavy atoms of the discussed group only.

As it was mentioned in the Computational Details, some AIM properties and enthalpies of reactions are useful for the determination of the intramolecular H-bond energies. Results of such calculations are juxtaposed in Table 4 (enthalpies) and Table 5 (AIM properties). Calculated enthalpies strongly suggest that the strength of the intramolecular H-bond in the neutral molecules is much higher than that in the studied cations. This result is supported by the electron density analysis of the investigated neutral and positively charged species. In all neutral molecules, intramolecular H-bond critical points and critical points of the ring closed by this bond have been found. Collected properties of these critical points show that the energy of the intramolecular HB in neutral hydroxypyrones is not strong. For cations, intramolecular H-bond interactions are so weak that no critical point connected with them are observed.

In order to know whether there is any dependence between the H-bond strength and electron delocalisation level in the OCCO group, we have checked structures of all these types of hydroxypyrones that are deposited in the Cambridge Structural Database (CSD).[30] Twenty-one experimental structures of

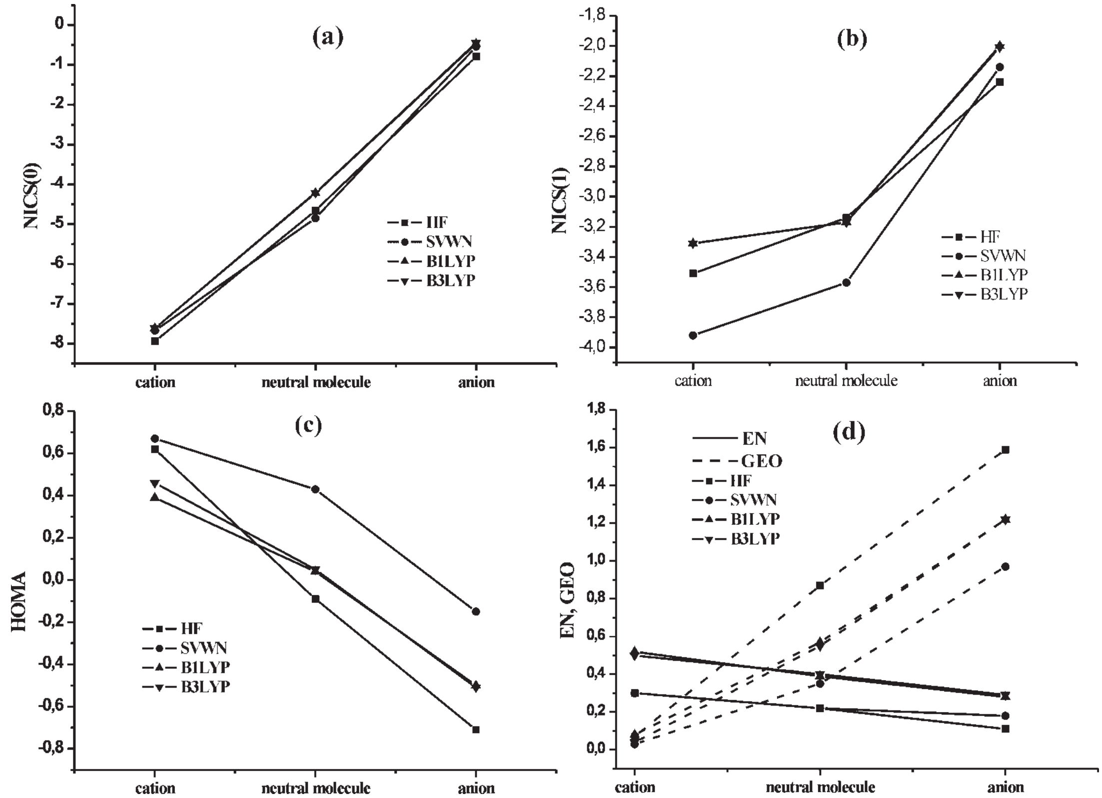

Figure 3. PI-electron delocalisation properties of the OCCO group (pyromeconic acid, 6-311 ++ G(d,p) basis set)

neutral hydroxypyrones have been found (sometimes one compound is represented by its several polimorphs observed in the solid state). There is only one cationic structure (maltol cation) and no anionic one. Thus, using experimental data there is no possibility to perform such a study for charged hydroxypyrone species. Here arises a new problem, whether experimental geometries are the best choice to study such a relationship. They are affected by solid-state effects, which can disturb and hide the potential dependence of electron delocalisation and H-bond strength. Lattice forces may modify the O...O distances quite easily since the modifications of the hydrogen bridged geometries require much less energy than stretching or lengthening of normal molecular bonds. In addition, creation of the intermolecular H-bonds is familiar in the crystal structures of the studied compounds. Because of that, we decided to perform some theoretical calculations for isolated neutral molecule, cation and (additionally) anion of pyromeconic acid. Usually, during such calculations, the intramolecular H-bond interactions are changed by setting an O...O distance slightly shorter or longer than that in equilibrium and optimising all the other geometrical parameteters. Aromaticity indices are calculated for all theoretical and experimental structures. Unfortunately, in our case the data derived from above-discussed methods of HB strength estimation cannot be correlated with aromaticity data calculated for theoretical structures with various O...O distances. Enthalpies can be calculated for geometrical minima only. On the other hand, no critical point can be found for cations and in the case of neutral molecules they are present only in equilibria and for theoretical structures with O...O distances shorter than those in equilibria. As an alternative, we decided to

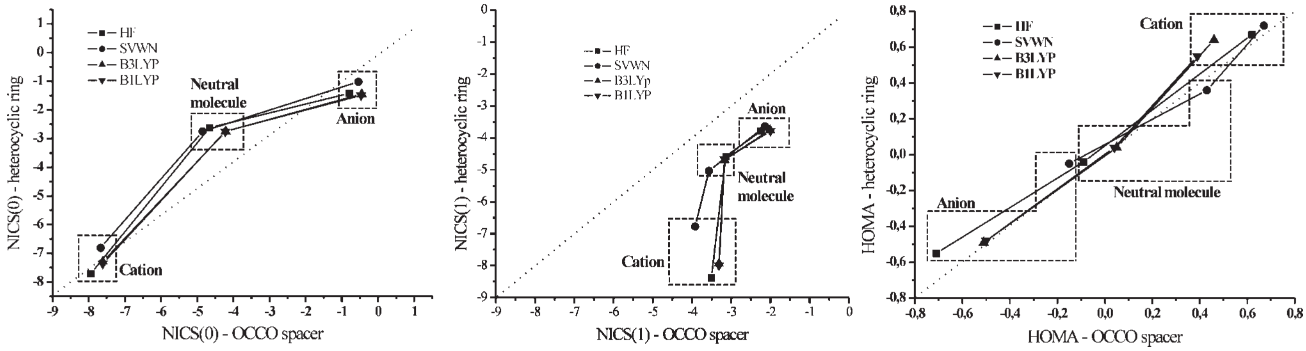

Figure 4. Comparison of aromaticity in the heterocyclic ring and π-electron delocalisation in the OCCO group for various forms of the pyromeconic acid molecule (6-311 ++ G(d,p) basis set)

Table 4. Enthalpies (B3LYP/6-311++G(d,p), kJ/mol) of reactions presented in Fig. 2

Reaction	Pyromeconic acid	Maltol	Ethylmaltol
(1)	37.74	44.45	43.48
(2)	16.46	16.90	17.83
(3)	24.58	25.64	25.77
(4)	2.17	1.92	2.90
(5)	5.48	8.46	8.71

Table 5. AIM properties calculated at bond and ring critical points connected with intramolecular hydrogen bond (B3LYP/6-311++G(d,p) level)

	ρ	$\nabla^2\rho$	λ_3	H
Bond critical point				
Pyromeconic acid	0.0237	0.0947	0.1336	0.0024
Maltol	0.0246	0.0967	0.1398	0.0023
Ethylmaltol	0.0247	0.0970	0.1407	0.0023
Ring critical point				
Pyromeconic acid	0.0235	0.1159	0.1279	0.0038
Maltol	0.0242	0.1226	0.1316	0.0041
Ethylmaltol	0.0243	0.1236	0.1321	0.0041

use the L–S model. As it was proved,[31] the energy of the —O…H—O— H-bond estimated in the frame of the L–S method depends solely on the distance between the hydrogen donor and acceptor (the O…O distance). Due to these reasons, the O…O distance is employed as a convenient measure of the HB interactions suitable to compare with aromaticity data. In order to be sure that the O…O distance is a good indicator of the H-bond strength, we have correlated the AIM properties and O…O distances for the equilibrated geometry of neutral pyromeconic acid and in the structures in which the O…O distance is shorter than that at equilibrium (as it was mentioned above, only in these cases, necessary bond and ring critical points are observed). Calculations reveal that the O…O distances pretty correlate with AIM properties (the lowest correlation coefficient is 0.9283, as in the Supplementary Material).

Experimental O…O distances measured for the crystal structures and corresponding (HOMA, NICS(0) and NICS(1)) data are compared in Fig. 5(a). (Values of aromaticity indices for these structures are available as Supplementary Data.) This Figure suggests that there is no, or very poor, correlation between delocalisation of π-electrons in the pseudo-ring and O…O distance of its hydrogen bridge. Determined linear correlation coefficients are 0.037 for HOMA, 0.069 for NICS(1) and (a bit higher but also not significant) 0.200 for NICS(0). Similar results were obtained by Krygowski *et al.* for the pseudo-rings of Schiff bases constructed with five[32] or six[33] heavy atoms. From this point of view, the pseudo-ring in hydroxypyrones cannot be described as a quasiaromatic system.

On the other hand in Fig. 5(b)–(d), one can observe successful correlations between the H-bond strength and the π-electron

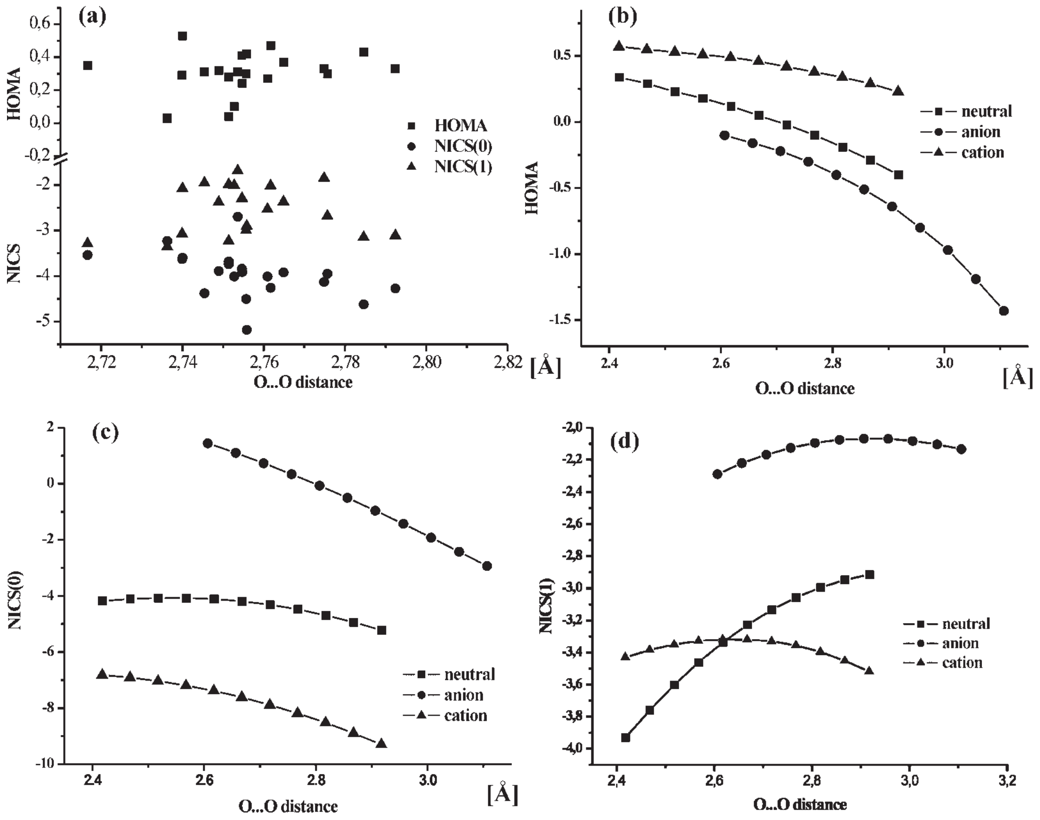

Figure 5. Correlation between values of different aromaticity indices (HOMA, NICS(0) and NICS(1)) and O…O distances in the OCCO fragment

delocalisation (HOMA and NICS data presented, numerical results are stored as Supplementary Materials) in calculated structures with fixed O...O distances. Therefore, when the theoretical geometries are considered, the OCCO group can be classified as a quasiaromatic system. However, unexpectedly, the relationships between the HB strength and the π-electron delocalisation observed for HOMA and NICS indices are different. The HOMA index behaviour is reasonable. For both neutral and cationic forms of pyromeconic acid during shortening of the O...O distance (simulation of the stronger H-bond) HOMA values increase. So, as it is expected for quasiaromatic systems, the stronger the H-bond, the stronger the aromaticity is. The same relationship (a shorter O...O distance results in a bit less negative HOMA value) is observed for the anion. Although the correlation coefficients are 0.983, 0.953 and 0.963 for the neutral molecule, cation and anion of pyromeconic acid, respectively, this relationship is parabolic rather than linear (parabolic correlation coefficients for neutral molecule, cation and anion are 0.999, 0.997 and 0.998, respectively).

In this context, the behaviour of the NICS(0) index is somehow surprisingly different. The π-electron delocalisation decreases (more positive value of the NICS index denotes lower delocalisation!) while H-bond becomes stronger. What can be responsible for such a behaviour? It should be mentioned that the NICS(0) value depends on the size of the examined ring.[34] For example five-membered rings with the same level of aromaticity have more negative NICS values than those in six-membered ones. It is obvious that five-membered rings are smaller, so the distances from the middle of the ring (this is the point usually used for NICS index calculations) to the electron cloud of the ring is shorter. In Fig. 6, the NICS(0) together with NICS(1) values in the neutral pyromeconic acid are drawn as a function of the distance from the middle of the carbon–carbon bond of the OCCO group moving outside the ring, to the ring plane. It is clearly indicated that the factor, which mainly determines the NICS(0) value, is the distance of the carbon–carbon bond in the OCCO group. NICS values in this work are calculated in the geometric centre of the four atoms that built the OCCO fragment. It is obvious that if the O...O distance is getting longer the point used for NICS(0) value calculations is positioned closer to the carbon–carbon bond (the OCCO group is planar) and calculated NICS(0) values are 'artificially' decreased. This is the origin of the obtained artefact, the longer the O...O distance, the more negative the NICS(0) value is. The curve of the relationship between NICS(1) value and the proximity to the centre of the C—C bond is the same but the dependency is weaker, as in Fig. 6. As a result, the NICS(1) behaviour is between these observed for NICS(0) and HOMA. In conclusion, we can say that HOMA results obtained for theoretical geometries with various O...O distances make clear that the stronger H-bond in studied hydroxypyrones, the more efficient the π-electron delocalisation is. Hence, this system may be considered as quasiaromatic. NICS calculations are not reliable at this point because especially NICS(0) index values strongly depend on the proximity of the carbon–carbon bond of the OCCO group to the point where NICS values are calculated.

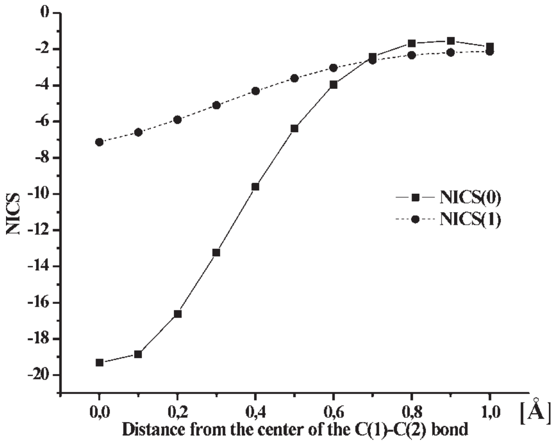

Figure 6. NICS values as a function of the distance from the middle of the C–C bond in the OCCO molecular fragment

CONCLUSIONS

The order of the π-electron delocalisation in the studied OCCO group is the same as the aromaticity order reported earlier for the heterocyclic pyran rings of the studied compounds. The delocalisation level in this group is always the highest for the protonated hydroxypyrones (cations) and the lowest for their deprotonated form (anions). The level of the electron delocalisation in the neutral molecules is between the values calculated for the charged species. Differences among the studied hydroxypyrones are negligible if the same form (anion, neutral molecule or cation) and computational level is analysed. It is observed that the EN sub-index decreases from the cation to the neutral molecule and the anion, while the GEO part of the HOMA index increases strongly in the same order. Delocalisations of the π-electrons in pyran rings and in the OCCO group are similar.

HOMA values obtained by HF, B1LYP or B3LYP methods are more or less comparable for the same form of hydroxypyrones. In contrary, HOMA values based on the SVWN results are very different from those provided by other methods. It should be stressed that HOMA data can be compared only if the same computational scheme is used. On the other hand, values of the NICS index are less sensitive to the level of theory used for calculations.

The strength of the intramolecular H-bond in the neutral form of the studied ligands is not large but it is even smaller in their cations.

Data obtained for experimental geometries show no significant correlation between the H-bond strength and the π-electron delocalisation. On the other hand, for theoretical structures with fixed O...O distances such a relationship appears. Experimental geometries, measured in crystals, are not the best choice in the quasiaromaticity research since they are strongly affected by lattice forces that can deform the less stable H-bonded quasi-rings. For this reason, experimental data reveal no relationship between H-bond strength and electron delocalisation. However, our theoretical results show that the studied compounds fulfil the conditions required for quasiaromatic systems.

SUPPLEMENTARY MATERIAL

AIM and aromaticity properties for experimental and experimental hydroxypyrones structures are freely available in *Wiley Interscience*.

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