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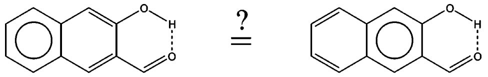
Interplay between Intramolecular Resonance-Assisted Hydrogen Bonding and Aromaticity in *o*-Hydroxyaryl Aldehydes

Marcin Palusiak,[†] Sílvia Simon,[‡] and Miquel Solà[*,‡]

Institut de Química Computacional and Departament de Química, Universitat de Girona,
Campus de Montilivi, 17071 Girona, Catalonia, Spain, and Department of Crystallography and
Crystal Chemistry, University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland

miquel.sola@udg.es

Received March 17, 2006



In this work, we analyze a series of *o*-hydroxyaryl aldehydes to discuss the interrelation between the resonance-assisted hydrogen bond (RAHB) formation and the aromaticity of the adjacent aromatic rings. As compared to the nonaromatic reference species (malonaldehyde), the studied compounds can be separated into two groups: first, the set of systems that have a stronger RAHB than that of the reference species, for which there is a Kekulé structure with a localized double CC bond linking substituted carbon atoms; and second, the systems having a weaker RAHB than that of the reference species, for which only π-electrons coming from a localized Clar π-sextet can be involved in the RAHB. As to aromaticity, there is a clear reduction of aromaticity in the substituted ipso ring for the former group of systems due to the formation of the RAHB, while for the latter group of species only a slight change of local aromaticity is observed in the substituted ipso ring.

1. Introduction

Different types of weak bonding interactions are the subject of numerous investigations in many branches of natural sciences. Among them, the hydrogen bond (H-bond) which plays an important role in many chemical, biochemical, or physical processes, occupies a special place. The special feature of the H-bond arises from the fact that this interaction is significantly directional. For this reason, the H-bond has a crucial impact on phenomena such as crystal packing or stabilization of the second-order structure of proteins as α-helices or β-sheets.[1]

A thorough knowledge of H-bonding phenomena allows for the explanation of many effects taking place not only in the crystal state, but also in solution and living organisms and is indispensable in crystal engineering.[2] Among all the types of H-bonds, the strongest known are those assisted by additional effects, for example, resonance-assisted or charge-assisted H-bonds. Since Gilli et al.[3,4] introduced in 1989 the concept of resonance-assisted hydrogen bonds (RAHBs), it has become one of the most frequently used concepts in structural chemistry. Usually RAHBs are classified as π-conjugated ring or chain motives, for which characteristic changes in geometrical or electronic properties are observed, that is, elongation of formally double bonds and shortening of formally single bonds accompanied by suitable changes in critical points corresponding to these bonds, together with elongation of the X−H (X = proton donor) bond and shortening of the (X)H···Y (Y = proton acceptor) bond within the H-bridge.[5] A schematic representation of electronic effects proceeding within such cyclic RAHB is shown in Figure 1 for malonaldehyde. Different kinds of RAHB have been investigated using experimental and theoretical methods, among them both inter- as well as intramolecular (O)H···O, (N)H···O, (O)H···N, and (O)H···S H-bridges.[6−8] Studies on crystal structures for which such systems have been observed have been reported.[9] For example, it has been found

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[*] To whom correspondence should be addressed. Phone: +34-972.418.912. Fax: +34-972.418.356.

[†] University of Łódź.

[‡] Universitat de Girona.

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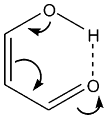

FIGURE 1. Schematic representation of the electronic movement in the cyclic resonance assisted hydrogen bond of malonaldehyde.

for the crystal structures of chromone derivatives[6] that both (N)H···O and (O)H···N intramolecular RAHBs can be observed; however, the existence of (N)H···O bonds is usual for these families of compounds,[10] whereas (O)H···N ones are rather uncommon. The nature of the RAHBs may be explained within the principle of the minimum difference between X and Y proton affinities Δ*P*A within the (X)H···Y H-bond or of the minimum ΔpK_a, where ΔpK_a is the difference between the pK_a values of two interacting groups as measured in a proper polar solvent.[11−14]

The cyclic enolic RAHB structure depicted in Figure 1 contains six delocalized electrons that readily suggest the formation of a pseudoaromatic ring in RAHBs.[15−17] The relation between H-bond strength and the π-electron delocalization in the pseudoaromatic ring has been the subject of different studies[17−19] (for a recent review see ref 20). To our knowledge only two works have analyzed the relation between the RAHB fused to an aromatic ring and the change of aromaticity undergone by this aromatic system.[17,18] The authors of these studies have shown that if the RAHB is fused to an aromatic ring, the RAHB may affect dramatically the π-electron delocalization in the aromatic part of the system. The goal of this work is to extend these initial investigations on the interplay between the intramolecular RAHB and the local aromaticity of six-membered rings (6-MRs) to a series of *o*-hydroxyaryl aldehyde species. To this end, we will analyze not only how the RAHB formation affects aromaticity in the adjacent 6-MR, but also how the different nature of the aromatic 6-MRs modify the strength of the RAHB fused to this aromatic ring. Usually RAHB is considered as mainly a local effect having significant influence only on those parts of molecular systems which are directly involved in this interaction. Yet there are already reports that the formation of a RAHB may have impact on electron distribution also in farther parts of the molecule.[17,21,22] Here we anticipate that our findings prove that intramolecular RAHB has strong impact on electron distribution even in these parts of the molecule which are placed about 10 Å away from the H-bond, and this distance is limited only by the fact that no bigger systems were taken into account in the investigations presented in this work.

2. Methodology

Geometries of all analyzed systems shown in Figures 2 and 3 were optimized without any symmetry constraints using DFT methods in the Gaussian 03 set of codes.[23] The B3LYP functional[24−27] was applied in conjunction with the 6-311+G(d,p) basis set[28,29] for all atoms. The frequency analysis at the same level of theory has been used to verify that the optimized geometries correspond to stationary points. For each system (**I** to **XIII**) in Figure 2, we have analyzed three possible conformers (see Figure 3), namely, the closed cis (a), open cis (b), and trans (c) species. The energy difference (E_{diff}) between optimized closed cis and open cis conformers has been taken as an indication of RAHB strength. In this work, we discuss only the results of the cis isomers since they are the most relevant as far as the RAHB is concerned. However, the Cartesian coordinates, energies, and aromaticity descriptors of the optimized B3LYP/6-311+G(d,p) structures of all these isomers (closed cis, open cis, and trans) are given in the Supporting Information.

The harmonic oscillator model of aromaticity (HOMA) index has been employed as a geometrical criterion of local aromaticity. According to the definition proposed by Kruszewski and Krygowski[30,31] the applied formula is as follows:

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{\mathrm{opt}} - R_{\mathrm{i}})^2 \qquad (1)$$

where *n* corresponds to the number of bonds within the analyzed ring, in the case of the present study *n* equals 6, α being a constant fitted to give a value of HOMA = 1 for ideally aromatic systems with all bonds lengths equal to optimal value R_{opt} and HOMA = 0 for nonaromatic species (for CC bonds α =257.7 and R_{opt} =1.388 Å).

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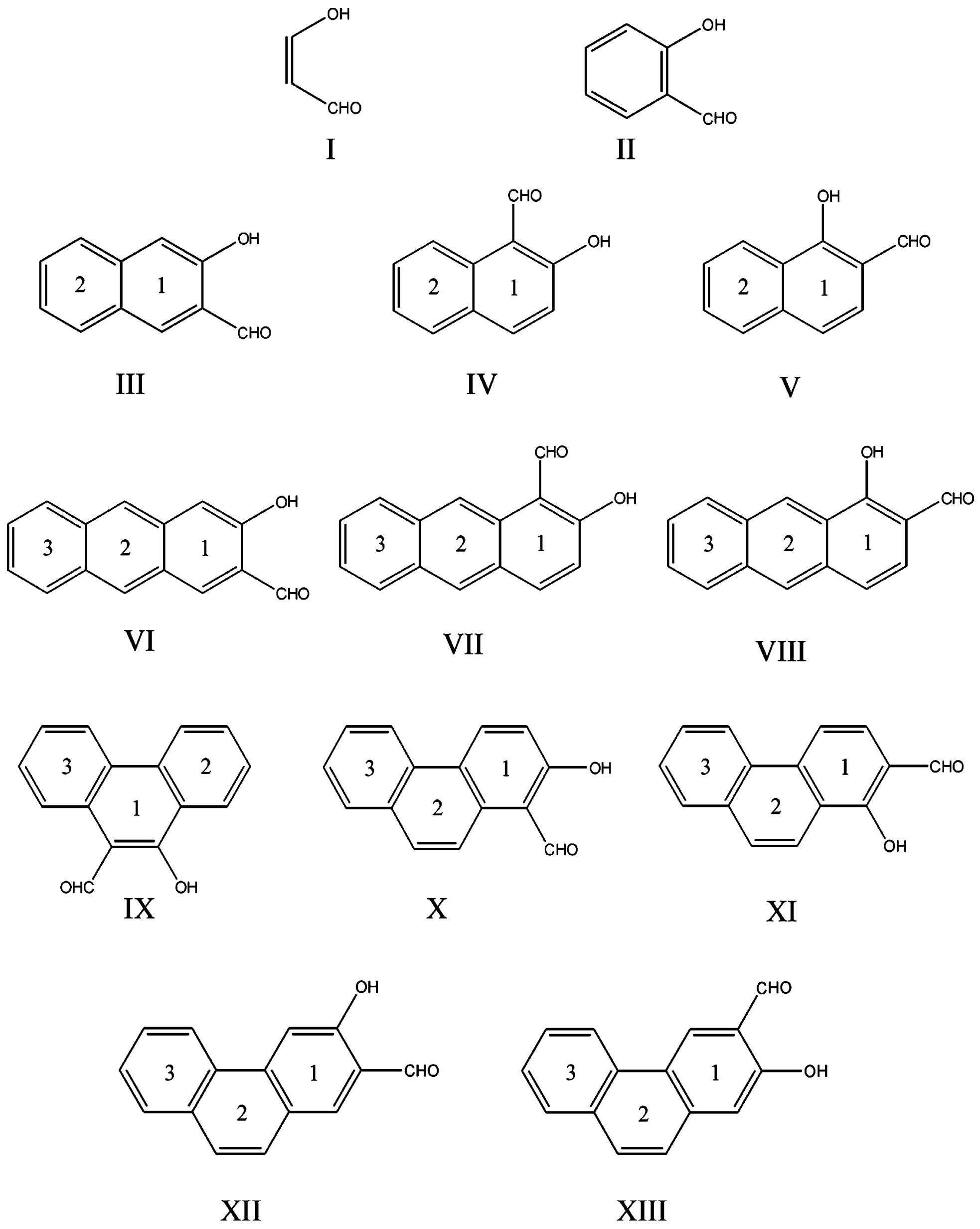

FIGURE 2. Labels for the molecules and rings studied.

As a magnetic indicator of local aromaticity, the nucleus-independent chemical shift (NICS) index as defined by Schleyer et al.[32] has been used. This is one of the most widely employed indicators of aromaticity. NICS(0) is defined as the negative value of the absolute shielding computed at a ring center determined by the nonweighted average of the heavy atoms' coordinates in the ring. Rings with large negative NICS(0) values are considered aromatic. The more negative the NICS(0) value is, the more aromatic the ring is. As it has been shown by Lazzeretti and Aihara,[33−35] the NICS(0) values may contain important spurious contributions from the in-plane tensor components that are not related to aromaticity. So, to complement the NICS analysis, NICS(1) values have been also calculated as the negative values of absolute shielding measured 1 Å above the center of the ring. It has been postulated that NICS(1) better reflects aromaticity patterns because at 1 Å the effects of the π-electron ring current are dominant and local σ-bonding contributions are diminished.[33,36,37]

As electronic-based descriptors of aromaticity, we have used the para-delocalization (PDI) and the aromatic fluctuation (FLU) indexes. The PDI is the average of all delocalization indexes (DIs)[38] of para related carbon atoms in a given 6-MR.[39] The DI value between atoms A and B, δ(A,B), as defined in the framework of the atoms-in-molecules theory (AIM) of Bader,[40] is obtained by double integration of the exchange-correlation density,[41] $\Gamma_{XC}(\vec{r}_1,\vec{r}_2)$,

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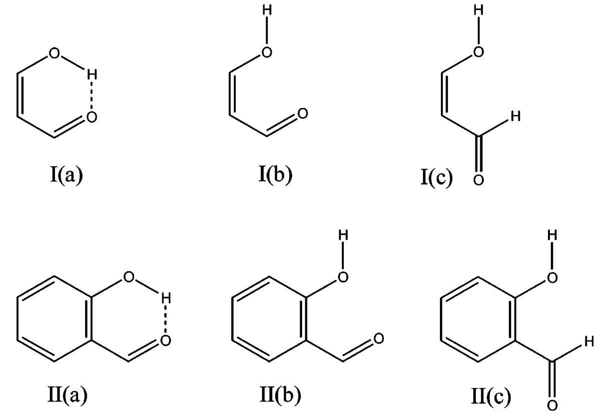
I(a) I(b) I(c)

II(a) II(b) II(c)

FIGURE 3. Schematic representation of the closed cis (a), open cis (b), and trans (c) conformers of malonaldehyde and *o*-hydroxybenzaldehyde.

over the basins of atoms A and B, which are defined from the zero-flux gradient condition applied to the one-electron density, $\rho(r)$:

$$\delta(\mathrm{A,B}) = -\int_{\mathrm{A}}\int_{\mathrm{B}} \Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 - \int_{\mathrm{B}}\int_{\mathrm{A}} \Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 = -2\int_{\mathrm{A}}\int_{\mathrm{B}} \Gamma_{\mathrm{XC}}(\vec{r}_1,\vec{r}_2)\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 \quad (2)$$

$\delta(\mathrm{A,B})$ provides a quantitative idea of the number of electrons delocalized or shared between atoms A and B. Aromatic 6-MRs have larger PDI values than nonaromatic ones. Finally, the FLU index[42] is based on the fact that aromaticity is related to the cyclic delocalized circulation of π-electrons, and it is thus constructed not only considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also taking into account the similarity of electron sharing between adjacent atoms. It is defined as

$$\mathrm{FLU} = \frac{1}{n}\sum_{\mathrm{A-B}}^{\mathrm{RING}}\left[\left(\frac{V(\mathrm{B})}{V(\mathrm{A})}\right)^{\alpha}\left(\frac{\delta(\mathrm{A,B}) - \delta_{\mathrm{ref}}(\mathrm{A,B})}{\delta_{\mathrm{ref}}(\mathrm{A,B})}\right)\right]^2 \quad (3)$$

where $\delta(\mathrm{A,B})$ is the DI between basins of atoms A and B and $V(\mathrm{A})$ is the valence of atom A, with the sum running over all adjacent pairs of atoms around the ring, n being equal to the number of members in the ring, and $\delta_{\mathrm{ref}}(\mathrm{C,C}) = 1.4$ e (the DI between two adjacent C atoms in benzene[42]). α in eq 3 is a simple function to ensure that the enclosed term is always greater or equal to 1; accordingly it reads

$$\alpha = \begin{cases} 1 & V(\mathrm{B}) > V(\mathrm{A}) \\ -1 & V(\mathrm{B}) \leq V(\mathrm{A}) \end{cases} \quad (4)$$

with the valence of atom A, $V(\mathrm{A})$, reading as follows:

$$V(\mathrm{A}) = \sum_{\mathrm{B}\neq\mathrm{A}} \delta(\mathrm{A,B}) \quad (5)$$

Consequently, FLU is close to 0 in aromatic species; the higher the FLU values, the lower the aromaticity. The AIMPAC package[43] was employed for the topological characterization of electron density distribution and for the DI calculations.

3. Results and Discussion

For all systems analyzed the closed cis form is more stable than the open cis conformer. The energy difference (E_{diff}) between these two forms together with the geometric parameters that are more related to the RAHB strength are given in Table 1. E_{diff} is the most common recipe to define the strength of an intramolecular HB.[5,44-47] However, it should be emphasized that in the case of systems investigated here E_{diff} is not the exact H-bond binding energy, but the energy of stabilization arising from the formation of the extra ring in the closed cis form as compared to the open cis structure. Thus E_{diff} may contain also energetic contributions resulting from side effects, which can take place in both closed cis as well as open cis conformers. For example, the steric repulsions between the hydroxyl H atom and the nearest H atoms of the aromatic system affect the total energy of some of the open conformers and, consequently, their E_{diff} values (vide infra). However, as one can see in Table 1, in general, an increase in E_{diff} goes with a decrease of the (O)H···O and O···O distances and an increase in the O−H bond length, the ∠O−H···O angle, and the DI between H···O atoms, thus giving support to the use of E_{diff} as an indicator of RAHB strength. As to this $\delta(\mathrm{O,H})$ value, in a previous study[48] a linear relation between the H-bond strength and H-bond DIs ($\delta(\mathrm{X,H})$, with X being the proton acceptor atom) was already found. A similar relationship can be observed in the systems investigated here between E_{diff} and $\delta(\mathrm{O,H})$ values in Table 1, the correlation coefficient r^2 being equal to 0.92.

TABLE 1. B3LYP/6-311+G(d,p) Selected Geometrical Parameters Usually Considered as Indicators of H-bond Strength for the Closed cis Form and Energy Difference between the Closed cis and the Open cis Forms

	E_{diff} [kcal mol^{-1}]	$d_{\mathrm{O-H}}$ [Å]	$d_{\mathrm{(O)H\cdots O}}$ [Å]	$d_{\mathrm{O\cdots O}}$ [Å]	∠O−H···O [deg]	$\delta(\mathrm{H,O})$ [e]
I	12.96	0.996	1.705	2.590	145.77	0.120
II	11.07	0.984	1.765	2.638	145.84	0.102
III	10.07	0.980	1.793	2.661	145.78	0.095
IV	13.84	0.993	1.662	2.555	147.36	0.123
V	13.89	0.990	1.710	2.598	147.20	0.115
VI	9.66	0.979	1.802	2.670	145.91	0.093
VII	14.51	0.996	1.647	2.545	147.72	0.128
VIII	14.55	0.993	1.687	2.582	147.73	0.121
IX	16.10	0.999	1.613	2.520	148.75	0.136
X	13.38	0.991	1.665	2.555	147.13	0.121
XI	13.72	0.988	1.723	2.609	147.10	0.111
XII	10.55	0.982	1.787	2.656	145.75	0.098
XIII	10.50	0.982	1.783	2.653	145.78	0.099

We use malonaldehyde species **I** as a reference compound since for this system there is no interaction of the RAHB with an aromatic ring. For this system, the E_{diff} value is 13.0 kcal·mol^{-1}, which is not far from the 12.5 kcal·mol^{-1} obtained at the MP2/D95** level for the parent *cis*-2-enol of acetylacetone species.[15] Taking compound **I** as the reference, we can separate the systems studied into two groups. The first one includes species **II**, **III**, **VI**, **XII**, and **XIII** for which the RAHB is weaker than that of compound **I** according to the smaller E_{diff} values and longer (O)H···O H-bond distances. The second one contains all species (**IV**, **V**, **VII**, **VIII**, **IX**, **X**, and **XI**) having a stronger RAHB than that of the system of reference (larger E_{diff} values and generally shorter (O)H···O H-bond

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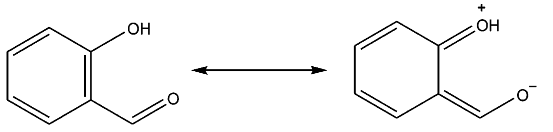

FIGURE 4. Schematic representation of the electronic interaction between the aromatic ring and the substituents.

distances). We will see in the next paragraphs that this separation is governed by the interaction between the RAHB and the aromatic moiety.

It is worth noting that there are three simultaneous π-electron delocalization effects taking place within the analyzed systems **II**−**XIII**. The first one is the global effect of delocalization of π-electrons proceeding inside the aromatic rings, leading to stabilization of aromatic species. In the Clar's model,[49−51] an aromatic π-sextet in a Kekulé resonance structure is defined as six π-electrons localized in a single benzene ring separated from adjacent rings by formal CC single bonds. In this model, the Kekulé resonance structure with the largest number of disjoint aromatic π-sextets is the so-called Clar structure. According to Clar's model, it is possible to divide our analyzed systems into two subgroups. In the first group there are those systems for which only one Clar structure can be found. It is the case of derivatives of benzene and phenanthrene. In the case of **II,** the situation does not need special comment, since only one ring is present in the molecule and the π-sextet of electrons has to be localized within this ring. In the case of phenanthrene, two Clar π-sextets are localized within the lateral rings, while the inner ring is significantly less aromatic, with a single pair of π-electrons localized in the bond linking carbon atoms placed in positions 9 and 10.[52] In these systems, rings having a localized π-sextet in the Clar structure are the most aromatic centers.[52,53] The second group contains all species having more that a single Clar structure, namely, all derivatives of naphthalene and anthracene. For these latter, Clar's model cannot differentiate which of the Clar structures contributes more to the aromaticity of the system. In this case, the so-called "migrating Clar π-sextet" can be considered according to Clar's concept. The idea of the migrating Clar π-sextet may explain relatively small differences in values of parameters reflecting local aromaticity of the rings. In other words, the observed local aromaticity is a result of superposition of all Clar structures acting for a given molecule.

The second effect is the one due to the interaction between the substituents. A schematic representation of this effect is shown in Figure 4. As one can see, the substituent effect (also known as mesomeric effect) is involving π-electrons of an aromatic system as a result of communication between both of the substituents.[54] Therefore, it is possible to postulate that this effect proceeds, so to say, against the process of delocalization of π-electrons in the ring, perturbing the uniform distribution of electrons within the aromatic system. One can expect that in the case of investigated systems the substituted ring should be less aromatic than the corresponding ring within the unsubstituted species. Indeed, all aromaticity indices indicate less aromatic character of the benzene ring in **II** as compared to the unsubstituted molecule of benzene (see aromaticity descriptors of Tables 2 and 3). Both the effect of delocalization of π-electrons and the substituent effect are present in all investigated systems and are mutually competitive.

The last effect is strictly connected with the existence of the intramolecular RAHB and can be considered only in the case of closed cis conformers. As one can see in Figure 1, the effect of resonance within the extra pseudoaromatic ring formed by the RAHB is proceeding in the same direction as it takes place in the substituent effect (Figure 4). Therefore, both these effects should mutually cooperate. One can even postulate, that both the effect of communication between the substituents and the resonance accompanying H-bonding are in fact the same phenomenon which can be considered as a mesomeric effect amplified with the process of formation of the extra pseudoaromatic RAHB ring.

Comparing the aromaticity indicators of Tables 2 and 3, a decrease of aromaticity of the 6-MR in closed cis **II** is observed in comparison with the unsubstitued benzene molecule as a consequence of the substituent effect and RAHB formation leading to changes in π-electron delocalization.[54] Substituents are disturbing regular distribution of π-electrons within their carrier ring. On the other side, the aromatic system of π-electrons in closed cis **II** is relatively stable, which makes the communication between both substituents difficult, also reducing the effect of resonance in H-bonding in **II**. This is the reason why the RAHB is relatively weaker in **II** as compared to in **I**.

Applying these conclusions to compound **III**, one can expect that the substituted ring 1 (see Figure 2) should be the less aromatic of both, while unsubstituted one should have a larger aromatic character, as it is less influenced by additional effects. Nevertheless, aromaticity indices do not indicate such a situation. On the contrary, it seems that both rings have relatively similar aromatic character, with the substituted one appearing to be even more aromatic. The explanation can be found in the diagram shown in Figure 5. Two Clar structures are possible for **III**. In structure **a** of Figure 5, the Clar π-sextet is localized within the unsubstituted ring. This implies localization of four π-electrons within the substituted ring and leads to a decrease of π-electrons available in the bond linking substituted carbon atoms which are those that contribute to the RAHB. In the case of Clar structure **b,** this bond is significantly richer with π-electrons. This allows for supplying both the substituent effect and resonance assistance of H-bond with π-electrons from the substituted ring, even if it will partially disturb the local aromaticity of this ring. So the Clar structure **b** is favored over structure **a** in the closed cis form of **III**, because the former helps the formation of the RAHB. However, π-electrons available for the RAHB in **III** are less than those in reference compound **I** and, as a consequence, the RAHB in this species is also weaker than in species **I**. As far as the aromaticity of ring 1 is concerned, there are two effects that counteract: first, by increasing the weight of the resonance structure **b** with a π-sextet localized in ring 1, the aromaticity of this ring is increased; and second, the assistance of the π-sextet in the formation of the H-bond partially destroys the aromaticity of ring 1. As a consequence, for **III** we find a minor loss of aromaticity in ring 1 as compared to unsubstituted species. This is confirmed by

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TABLE 2. B3LYP/6-311+G(d,p) Aromaticity Indices for the Closed cis Form of the Investigated Systems[a]

	HOMA			NICS(0)			NICS(1)			PDI			FLU		
	ring 1	ring 2	ring 3	ring 1	ring 2	ring 3	ring 1	ring 2	ring 3	ring 1	ring 2	ring 3	ring 1	ring 2	ring 3
I															
II	0.925			−7.985			−9.026			0.081			0.006		
III	0.756	0.738		−8.993	−6.968		−9.728	−9.348		0.062	0.070		0.012	0.012	
IV	0.642	0.832		−7.114	−8.192		−8.442	−10.319		0.054	0.078		0.017	0.007	
V	0.693	0.830		−7.713	−7.997		−8.855	−10.340		0.054	0.077		0.017	0.008	
VI	0.615	0.693	0.613	−8.301	−9.682	−6.643	−9.033	−11.479	−8.961	0.054	0.062	0.064	0.017	0.012	0.017
VII	0.487	0.743	0.688	−5.975	−10.615	−7.576	−7.562	−12.279	−9.959	0.045	0.065	0.067	0.022	0.010	0.014
VIII	0.544	0.740	0.667	−6.788	−10.588	−7.409	−7.960	−12.333	−9.864	0.045	0.064	0.066	0.023	0.010	0.015
IX	0.339	0.896	0.883	−4.701	−7.647	−7.752	−6.582	−10.115	−9.973	0.032	0.082	0.083	0.025	0.005	0.004
X	0.731	0.529	0.862	−7.395	−5.915	−8.477	−8.600	−8.606	−10.818	0.060	0.050	0.080	0.013	0.018	0.006
XI	0.785	0.513	0.855	−7.518	−5.607	−8.313	−8.708	−8.313	−10.686	0.060	0.049	0.079	0.013	0.019	0.006
XII	0.832	0.405	0.875	−8.818	−4.340	−8.025	−9.866	−7.396	−10.396	0.065	0.042	0.081	0.009	0.022	0.005
XIII	0.828	0.421	0.884	−9.007	−4.327	−8.372	−10.007	−7.493	−10.535	0.065	0.043	0.081	0.009	0.022	0.005

[a] NICS in ppm and PDI in electrons.

TABLE 3. B3LYP/6-311+G(d,p) Aromaticity Indices for Unsubstituted Polycyclic Aromatic Hydrocarbons Related to Substituted Investigated Species[a]

	HOMA		NICS(0)		NICS(1)		PDI		FLU	
	ring 1	ring 2	ring 1	ring 2	ring 1	ring 2	ring 1	ring 2	ring 1	ring 2
benzene	0.990		−8.039		−10.217		0.103		0.000	
naphthalene	0.784		−8.407		−10.482		0.075		0.009	
anthracene	0.629	0.720	−7.481	−11.152	−9.722	−12.792	0.065	0.065	0.016	0.010
phenanthrene	0.868	0.460	−8.513	−5.412	−10.680	−8.205	0.081	0.046	0.005	0.081

[a] NICS in ppm and PDI in electrons.

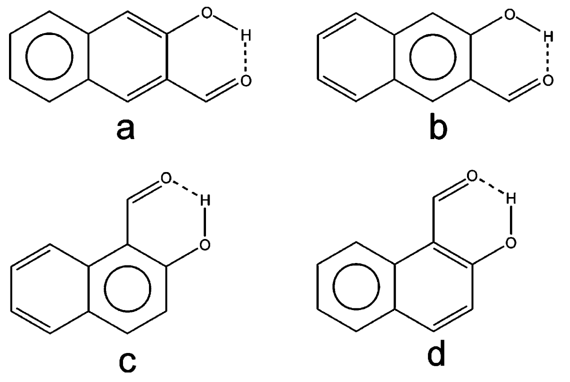

FIGURE 5. Clar structures for species **III** and **IV**.

the values of local aromaticity indices which in general indicate a slight reduction of the aromaticity for the two rings.

In the case of **IV**, aromaticity indices clearly indicate the substituted ring as the less aromatic and the unsubstituted ring as the one with the localized Clar π-sextet. This seems to be in excellent agreement with observations made for **III**. There is now a localized double CC bond linking substituted carbon atoms for structure **d**. Structure **d** is now favored as compared to **c** in the closed cis form since in the former the H-bond is assisted by the two π-electrons localized in the double CC bond linking substituted carbon atoms, while in the latter the H-bond is assisted by the six π-electrons which are delocalized over the whole ring and less available for assisting the H-bond. In this case, π-electrons accessible for the RAHB are similar to those in reference compound **I** and the RAHB in this species, measured both by E_{diff} as well as geometrical parameters of H-bridge, seems to be stronger than in species **I**.

This philosophy has application for all of the systems with a migrating Clar π-sextet, that is, for systems from **III** to **VIII**. All the compounds which belong to the first group, that is, those with a RAHB weaker than compound **I** (**II**, **III**, and **VI**), present a similar behavior in the aromatic character change. For these systems, there is weakly differentiated aromatic character of all rings. In selected cases, the substituted rings seem to be even more aromatic than unsubstituted ones, which confirms that both substituent effect and resonance effect within the extra ring formed because of the RAHB formation are mutually cooperating. Compounds belonging to the second group, that is, those with a stronger RAHB than that of the reference compound (**IV**, **V**, **VII**, and **VIII**), present the substituted rings significantly less aromatic than unsubstituted ones. This fact again indicates the same direction of both mesomeric effects. It is worth mentioning that the HOMA results for **V** are in line with those obtained for 2-hydroxyacetonaphthone by Filarowski et al.[17]

Let us also note the slightly larger E_{diff} value for **V** and **VIII** as compared to those for **IV** and **VII**, respectively, despite the slightly shorter (O)H···O and O···O distances and somewhat larger δ(O,H) in **IV** and **VII** (see Table 1), which support the formation of a stronger HB for these species as compared to **V** and **VIII**, respectively. We attribute this fact to the larger H···H repulsive interactions present in the open cis conformer when the hydroxyl substituent is in β position with respect to a C atom of a C−C bridge (as in **V**, **VIII**, **IX**, and **XI** isomers), which is translated into larger E_{diff} values because of the open cis conformer destabilization and not because of stronger H-bonding. This effect will also explain the larger E_{diff} value of **XI** in comparison with **X**. We note in passing that the differences caused by these H···H repulsive interactions are minor (compare E_{diff} values of **IV** vs **V**, **VII** vs **VIII**, or **X** vs **XI**) as expected from the fact that, for instance, in biphenyl the difference between the planar structure (with two H···H contacts separated by about 2 Å) and the most stable conformer is only 1.4 kcal mol^{-1}.[55,56]

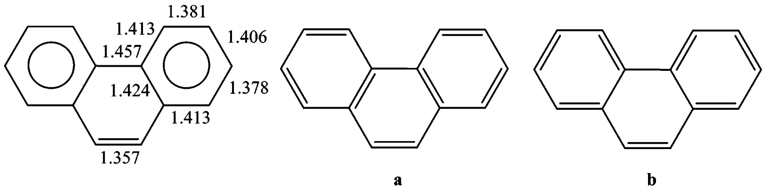

FIGURE 6. Most important resonance structures and Clar structure for phenanthrene together with its B3LYP/6-311+G(d,p) C−C bond lengths (in Å).

An interesting situation occurs in the case of all phenanthrene derivatives. As was previously mentioned, phenanthrene is an example of a hydrocarbon with a single stable Clar structure where the inner ring is significantly less aromatic than the lateral ones. Moreover it has strongly localized double bond linking carbon atoms placed in positions 9 and 10. According to previous observations, if the inner ring is substituted (the case of **IX**) then both the substituent effect and the effect of the resonance within the extra ring are additionally stabilizing the only Clar structure. It is worth noting that, among the species analyzed, **IX** shows the greatest E_{diff} value in agreement with the fact that the two π electrons of the double C(9)C(10) bond linking substituted carbon atoms in this system are particularly well localized and that formation of extra ring additionally stabilizes the only possible Clar structure. However, if one of the lateral rings is substituted, additional effects disturb the aromatic character of this ring, analogously as it takes place in benzene derivatives, leading to a decrease of aromaticity of this ring in comparison with the next lateral ring. Nevertheless, this ring is still more aromatic than the inner one. In other words, influence of both resonance effects is mainly limited to the substituted ring, since the stability of the only Clar structure is making the transfer of these effects to adjacent rings difficult. For these phenanthrene derivatives substituted in the outer rings we have two different situations. On one hand, one is represented by **XII** and **XIII** for which the RAHB is weaker than in compound **I**, and, on the other hand, compounds **X** and **XI** have a RAHB stronger than that of malonaldehyde. The difference can be explained by taking into account that the two resonance structures that lead to the Clar structure are not equally important. From the B3LYP/6-311+G(d,p) bond lengths of phenanthrene in Figure 6, it is clear that structure **a** has a larger contribution than structure **b** in the final wave function. Taking structure **a** as the most important in phenanthrene, we have that for **XII** and **XIII** we need the six π-electrons delocalized in ring 1 to assist the formation of the H-bond as in compound **III**. Thus, for these systems, aromaticity in ring 1 remains the same as in the unsubstituted phenanthrene or even increases slightly. On the other hand, in species **X** and **XI** the RAHB can be assisted by the two π-electrons localized in the double CC bond linking substituted carbon atoms. This leads to a stronger RAHB than in the reference compound and to a significant loss and gain of aromaticity in rings 1 and 2, respectively.

In summary, the closed cis conformer stabilizes the RAHB by increasing the weight of the Kekulé structures with a localized double CC bond linking substituted carbon atoms. If this is possible (as in **IV**, **V**, **VII**, **VIII**, **IX**, **X**, and **XI**) then the RAHB is stronger than that of the reference compound **I**. If this is not possible (as in **II**, **III**, **VI**, **XII**, and **XIII**), then the closed cis conformer favors the RAHB by increasing the weight of the resonance structures with a π-sextet localized in the ipso ring 1. As a consequence, the RAHB is weaker than that of the reference compound **I**. Thus the mesomeric effect is operative in all cases, but its magnitude is larger when the substituents interact with a localized double CC bond linking substituted carbon atoms. As far as the aromaticity of ring 1 is concerned, there is a clear loss of local aromaticity for the former group of systems, while for the latter there is a small gain or a minor loss of local aromaticity in ring 1 as compared to unsubstituted species.

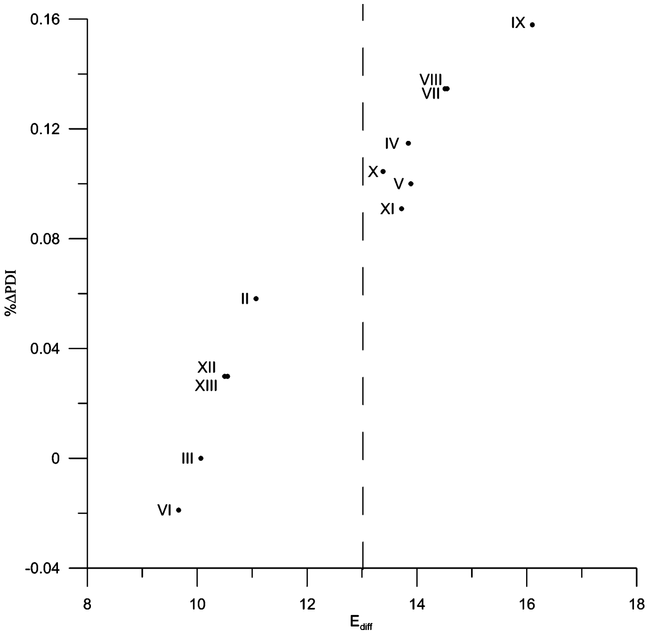

FIGURE 7. Plot of %ΔPDI vs E_{diff} values for all species studied. Units of energy are kcal mol^{-1}.

In the previous paragraphs, we have based our analysis on the influence of the local aromaticity of the ipso ring over the RAHB strength on qualitative arguments based on Clar structures. Figure 7 shows that this relation is indeed quantitative. As an energetic measure of the RAHB formation we use the energy difference between the closed cis form and the open cis structure (E_{diff}), while as an indication of the change of local aromaticity of ring 1 we consider the percentage of the PDI reduction when going from open cis to closed cis form (PDI values for the open cis form can be found in the Supporting Information). Such a relation (with a linear correlation coefficient of $r^2 = 0.95$) is shown in Figure 7, where again a clear separation into two groups can be noticed.

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4. Conclusions

It has been shown that mesomeric (resonance) effects proceeding in molecules of the investigated series of substituted polycyclic hydrocarbons has a large impact on electron distribution within the entire group of molecules. This impact is clearly stronger for those species for which the resonance assisted hydrogen bond can be considered. It is worth mentioning that, except for a few reports, usually the resonance assisted hydrogen bonds are considered as mainly a local phenomenon limited for atoms directly involved in H-bonding. From the presented materials, the conclusion arises that both the substituent effect and the effect of resonance assistance of the hydrogen bond are mutually cooperating, and it is even possible to state that both these effects can be treated as a component of the same phenomenon.

As compared to the nonaromatic reference species, the studied compounds can be separated into two groups: first, the set of systems for which the effect of stabilization resulting from the formation of a resonance-assisted hydrogen bond is greater than that of the reference species (the well-known and intensively investigated molecule of malonaldehyde), for which we show that there is a Kekulé structure with a localized double CC bond linking substituted carbon atoms; and second, the systems for which this effect of stabilization is relatively weaker than in the case of reference species, for which only π-electrons coming from a localized Clar π-sextet can be involved in the resonance-assisted hydrogen bond. As far as the aromaticity of substituted ipso ring 1 is concerned, there is a clear loss of aromaticity for the former group of systems, while for the latter group we find a minor change of local aromaticity in ring 1. It has been also shown that the change in local aromaticity of the substituted ipso ring 1 is linearly related to the strength of the RAHB formed.

Acknowledgment. Financial help has been furnished by the Spanish Ministerio de Educación y Ciencia (MEC) Project No. CTQ2005-08797-C02-01/BQU and by the Departament d'Universitats, Recerca i Societat de la Informació (DURSI) Project No. 2005SGR-00238. The visit of M.P. to the University of Girona was supported financially by a HPC-Europa project. We thank the Centre de Supercomputació de Catalunya (CESCA) for partial funding of computer time.

Supporting Information Available: Cartesian coordinates, energies, and aromaticity descriptors. This material is available free of charge via the Internet at http://pubs.acs.org.

JO060591X