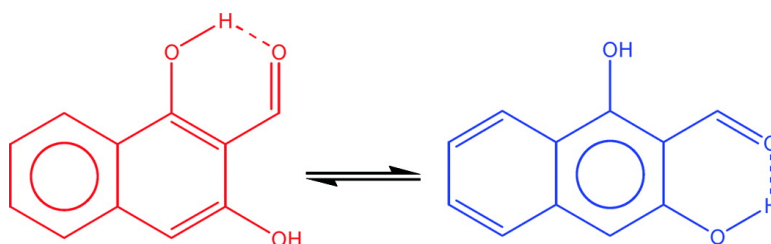Article

# Interplay between Intramolecular Resonance-Assisted Hydrogen Bonding and Local Aromaticity. II. 1,3-Dihydroxyaryl-2-aldehydes

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# Interplay between Intramolecular Resonance-Assisted Hydrogen Bonding and Local Aromaticity. II. 1,3-Dihydroxyaryl-2-aldehydes[†]

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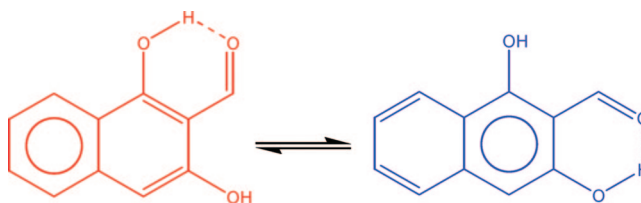
The interplay between aromaticity and hydrogen bonding in 1,3-dihydroxyaryl-2-aldehydes is investigated by means of quantum-chemical calculations. The position of the extra ring formed by substituents interacting through the hydrogen bond (HB) is found to influence both the strength of the HB and the local aromaticity of the polycyclic aromatic hydrocarbon (PAH) skeleton. The HBs are stronger and the entire system is energetically more stable when a kinked-like structure is generated by formation of the *quasi*-ring. Relatively greater loss of aromaticity of the *ipso*-ring can be observed for these kinked-like structures because of the larger participation of π-electrons coming from the *ipso*-ring in the formation of the *quasi*-ring. We conclude that the *quasi*-ring partially adopts the role of a typical aromatic ring, the position of which has a meaningful influence on the aromaticity of the rest of the rings. This makes it possible to explain and modify the properties of 1,3-dihydroxyaryl-2-aldehydes by the planned substitution to the appropriate position of the given PAH.

## Introduction

Since Gilli et al. introduced the concept of the resonance-assisted hydrogen bond (RAHB)[1-7] in 1989, it has become one of the most frequently used concepts in structural chemistry. The fact that these nonconventional hydrogen bonds (HBs) are stronger than conventional ones was explained in terms of the extra stabilization connected with the partial delocalization of the π-electrons within the HB motif containing conjugated formally single and double bonds. Some authors have criticized this interpretation.[8-10] According to them, the characteristics of the σ-skeleton, not the RAHB phenomenon, are the *primary* cause of the extra stability of this interaction. The extra stabilization, it is argued, comes from a shorter distance between the hydrogen donor and the acceptor. These authors do not deny the existence of π-effects, but they consider that they are not the main contributor to the extra stabilization found in RAHBs. However, this is an ongoing debate since the results of numerous investigations show that π-electrons play an important role in strengthening this kind of HBs.[11-15]

[†] For Part I, see ref 11.

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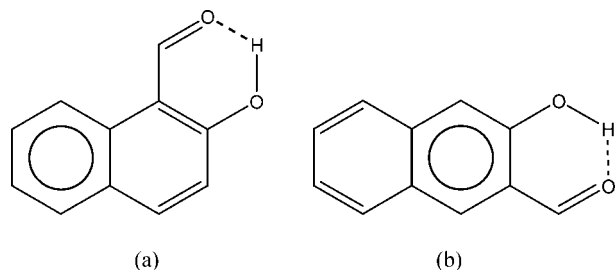
**FIGURE 1.** Examples of systems analyzed in our previous work.[11]

In the first part of this study, we carried out a detailed investigation into a series of *o*-hydroxyaryl aldehydes (see Figure 1 for example systems).[11] Our investigation showed that the set of systems studied could be separated into two groups based on whether the HB was stronger or weaker compared to the malonaldehyde that was taken as the reference species. The findings were explained on the basis of Clar's structures analysis. The case with stronger HBs corresponded to the topological situation shown in Figure 1a, for which there is a Clar's structure with a localized double CC bond linking substituted carbon atoms and a localized Clar's sextet in the unsubstituted six-membered ring (6-MR). The second case, with relatively weaker HBs, corresponded to the topological situation illustrated in Figure 1b, namely, systems for which only $\pi$-electrons coming from a localized Clar's $\pi$-sextet can be involved in the RAHB. Note that the alternative explanation by Sanz et al.[8−10] could also be applied to explain our previous results. The shorter C=C double bond in system **a** as compared to **b** in Figure 1 explains its stronger HB. As far as the aromaticity of the substituted *ipso*-ring was concerned, there was a clear loss of aromaticity due to HB formation with regard to the former group of systems, whereas for the latter group we found only a minor change in local aromaticity in the substituted ring. We also showed that the change in local aromaticity in the substituted *ipso*-ring is linearly related to the strength of the RAHB formed. A further conclusion can be drawn from these studies: both the substituent effect, in fact a $\pi$-electron communication between hydroxyl and carbonyl groups, and the effect of resonance assistance of the HB cooperate against the effect of $\pi$-electron delocalization within the substituted 6-MR. Further results supporting this view have been reported recently.[16] It is worth mentioning here that Lenain et al. have analyzed the cooperativity between aromatic electron delocalization and *intermolecular* HBs using multicenter $\pi$-electron delocalization indices.[17] Finally, experimental studies on 2,6-dihydroxynaphthalene carbaldehydes have been carried out very recently, and the relationship between aromaticity and parameters related with the RAHBs has been confirmed.[18] It is also worth mentioning that compounds containing RAHB moieties also have applications in organometallic synthesis.[19−21]

As an extension of our previous work,[11] we have considered in this paper the complete series of closed-shell 1,3-dihy-droxyaryl-2-aldehydes (see Figure 2) with one, two, and three fused phenyl rings. Thanks to the particular properties of these chemical species, it is possible to analyze the effect of the different topological distributions of the aromatic rings and the *quasi*-ring. The formation of a *quasi*-ring within one of the systems analyzed can be achieved by means of a linear topology (as in system **IIa**) or in a kinked way (as in system **IIc**). In addition, the skeleton of the polycyclic aromatic hydrocarbon (PAH) can be either linear (like anthracene, system **III**) or kinked (like phenanthrene, system **IV** or **V**). By these means, one can obtain all possible topological situations for the PAHs studied, namely, linear PAH and linear *quasi*-ring, linear PAH and kinked *quasi*-ring, kinked PAH and linear *quasi*-ring, and kinked PAH and kinked *quasi*-ring. In the last case, one can have both kinks in the same clockwise direction (as in **IVc**) or in clockwise and anticlockwise directions (as in **Vc**). It is worth mentioning that any further extension of the modeled systems would provide few new topological situations (consider, for instance, pyrene), and basically topological motifs already considered would only be repeated in more complicated models. Of course, the diverse motifs lead to HBs of different strengths. The main goal of this paper is to calculate the different possibilities and to provide an explanation of the differences observed. As the change in aromaticity of the *ipso*-ring was found to be related to the strength of the HB,[11] special attention is devoted to how the formation of different topological cases affects the aromaticity of the *ipso*-ring. It will be shown that $\pi$-electronic effects play an important role in the stabilization of the molecular structure of these chemical species and additionally that the *quasi*-ring formed through the H-bridge can partially adopt the role of a typical aromatic ring.

## Methods

The geometries of all systems analyzed and shown in Figure 2 were optimized without any symmetry constraints, using DFT methods in the Gaussian03 set of codes.[22] The B3LYP functional[23−26] was applied in conjunction with the 6-311+G(d,p) basis set[27,28] for all atoms. Frequency analysis at the same level of theory was used to verify that the optimized geometries corresponded to stationary points. No imaginary frequencies were found. The energy difference ($E_{diff}$) between optimized closed and open conformers was taken as an indication of RAHB strength. We are aware that $E_{diff}$ may contain energy contributions not directly related to HB formation. However, this is the most common method of defining the strength of an intramolecular HB[29−33] and is used as such in the present work.

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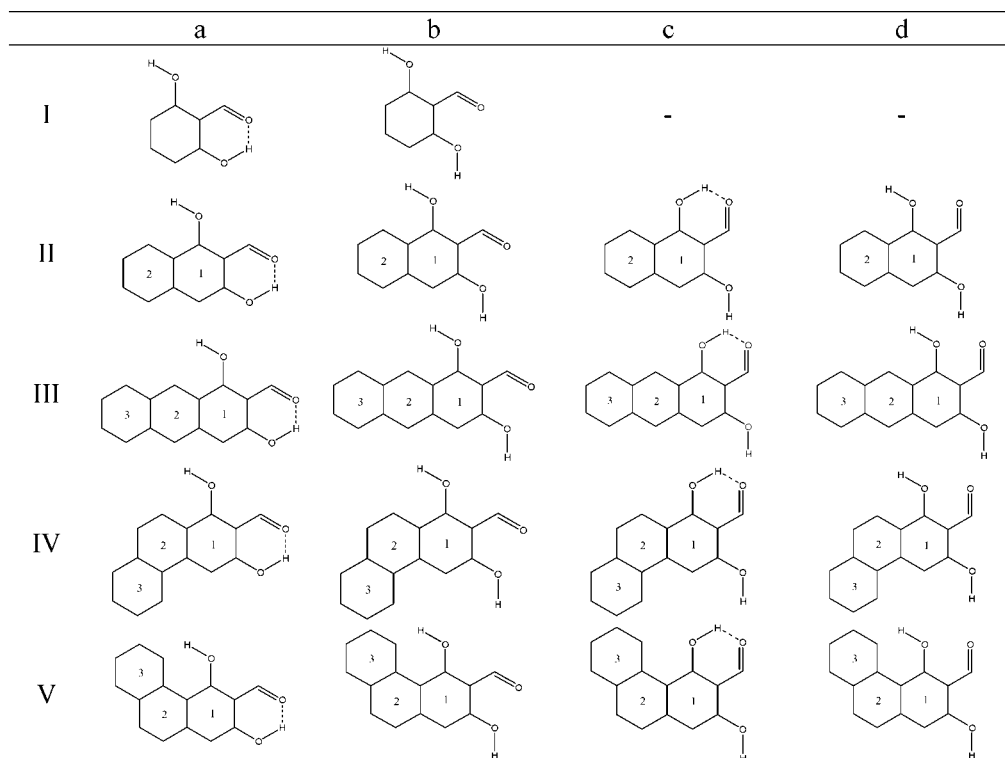(28) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

**FIGURE 2.** Diagrams of the systems considered. All carbonic rings are formally aromatic, and the representation of a given Kekulé structure has been omitted for clarity.

The HOMA index was applied as a geometry-based indicator of local aromaticity. According to its definition[34,35] HOMA can be expressed by the following equation:

$$\text{HOMA} = 1 - \frac{1}{n}\sum_{j=1}^{n} \alpha_i (R_{\text{opt},i} - R_j)^2 \tag{1}$$

where $n$ represents the total number of bonds in the molecule and $\alpha_i$ is a normalization constant (for C−C and C−O bonds, $R_{\text{opt,CC}} = 1.388$ Å, $R_{\text{opt,CO}} = 1.265$ Å, $\alpha_{\text{C−C}} = 257.7$, and $\alpha_{\text{C−O}} = 157.38$) fixed to give HOMA = 0 for a model nonaromatic system, e.g., the Kekulé structure of benzene, and HOMA = 1 for the system in which all bonds are equal to the optimal value $R_{\text{opt},i}$, assumed to be realized for fully aromatic systems.[36] The higher the HOMA value, the more "aromatic" is the ring in question and, hence, the more delocalized the system's $\pi$-electrons.

Different aromaticity criteria based on electron delocalization measures were employed.[37,38] These indices try to measure the cyclic electron delocalization of mobile electrons in aromatic rings. First was the *para*-delocalization index (PDI),[39] which is an average of all delocalization indices (DI)[40,41] of *para*-related carbon atoms

in a given 6-MR. The DI value between atoms $A$ and $B$, $\delta(A,B)$, is obtained by the double integration of the exchange-correlation density ($\Gamma_{XC}(\vec{r}_1,\vec{r}_2)$) over the space occupied by atoms $A$ and $B$:

$$\delta(A, B) = -2\int_A \int_B \Gamma_{XC}(\vec{\mathbf{r}}_1, \vec{\mathbf{r}}_2) d\vec{\mathbf{r}}_1 d\vec{\mathbf{r}}_2 \tag{2}$$

For single-determinant closed-shell wave functions one obtains

$$\delta(A, B) = 4\sum_{i,j}^{N/2} S_{ij}(A)S_{ij}(B) \tag{3}$$

The sums in eq 3 run over all the $N/2$ occupied molecular orbitals. $S_{ij}(A)$ is the overlap between molecular orbitals $i$ and $j$ within the basin of atom $A$. It should be pointed out that no direct usage of Bader's atoms in molecules (AIM) theory[42,43] has been applied in this work, although we make use of the AIM atomic partition defined from the condition of zero-flux gradient in one-electron density[42,43] $\rho(\mathbf{r})$ to compute $S_{ij}(A)$ values. However, as shown previously,[37,44,45] other partitions of the molecular space can also be used. $\delta(A,B)$ provides a quantitative idea of the number of electron pairs delocalized or shared between atoms $A$ and $B$. The PDI is, therefore, clearly related to the idea of electron delocalization so often found in textbook definitions of aromaticity.

The second index employed was the aromatic fluctuation index (FLU),[46] which describes the fluctuation of electronic charge between adjacent atoms in a given ring. The FLU index is based on the fact that aromaticity is related to the *cyclic* delocalized

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circulation of $\pi$-electrons and is constructed considering not only the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also the similarity in terms of electron sharing between adjacent atoms. It is defined as

$$\text{FLU} = \frac{1}{n} \sum_{A-B}^{\text{ring}} \left[ \left( \frac{V(B)}{V(A)} \right)^\alpha \left( \frac{\delta(A, B) - \delta_{\text{ref}}(A, B)}{\delta_{\text{ref}}(A, B)} \right) \right]^2 \quad (4)$$

with the sum running over all adjacent pairs of atoms around the ring, $n$ being equal to the number of members in the ring, $\delta_{\text{ref}}(C,C) = 1.389e$ (the $\delta(C,C)$ value in benzene at the B3LYP/6-311++G(d,p) level), and $V(A)$ being the global delocalization of atom $A$ given by

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

Finally, $\alpha$ is a simple function to make sure that the first term in eq 4 is always greater than or equal to 1, so it takes the values

$$\alpha = \begin{cases} 1 & V(B) > V(A) \\ -1 & V(B) \leq V(A) \end{cases} \quad (6)$$

FLU is close to 0 in aromatic species, and differs from it in nonaromatic ones.

Third were the multicenter indices recently defined by Giambiagi and co-workers. For a closed-shell single-determinant wave function of a 6-MR molecule, Giambiagi's proposal of aromaticity index reads[47]

$$\text{KSCI} = 24 \sum_{i,j,k,l,m,n} S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) S_{mn}(E) S_{ni}(F) \quad (7)$$

A particular extension of this last index has been devised by Bultinck, Ponec, and co-workers.[17,48] According to these authors, totaling all of the KSCI resulting from the permutations of indices $A$, $B$,..., $F$ defines a new index of aromaticity; in the case of a 6-MR, this is the so-called six-center index (SCI).[48] The particular expression of SCI for a decomposition of the molecular space into atomic basins, in the case of a single-determinant closed-shell wave function, reads as follows:

$$\text{SCI} = \frac{16}{3} \sum_{\alpha} \sum_{i,j,k,l,m,n} \Gamma_\alpha [S_{ij}(A) S_{jk}(B) S_{kl}(C) S_{lm}(D) S_{mn}(E) S_{ni}(F)] \quad (8)$$

where $\Gamma_\alpha$ stands for a permutation operator that interchanges the atomic labels $A$, $B$,..., $F$ to generate up to 6! combinations. Generally the values of SCI and KSCI are in close correlation because the dominant contribution to SCI is the Kekulé structure, although some exceptions may arise.

Finally, we used the nucleus-independent chemical shift (NICS) index as defined by Schleyer et al.[49] as a magnetic indicator of local aromaticity. This is one of the most widely employed indicators of aromaticity. NICS(0) is defined as the negative value of 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, the more aromatic the ring is. As has been shown by Lazzeretti and Aihara,[50-52] the NICS(0) values may contain important spurious contributions from the in-

**TABLE 1. Correlation Matrix Estimated for All Aromaticity Indices Used**

|  | HOMA | PDI | FLU | SCI | KSCI | NICS(0) | NICS(1) |
|---|---|---|---|---|---|---|---|
| HOMA | 1.000 | | | | | | |
| PDI | 0.836 | 1.000 | | | | | |
| FLU | −0.915 | −0.951 | 1.000 | | | | |
| SCI | 0.838 | 0.982 | −0.943 | 1.000 | | | |
| KSCI | 0.839 | 0.983 | −0.942 | 1.000 | 1.000 | | |
| NICS(0) | −0.752 | −0.443 | 0.584 | −0.403 | −0.402 | 1.000 | |
| NICS(1) | −0.641 | −0.767 | 0.776 | −0.685 | −0.683 | 0.645 | 1.000 |

plane tensor components that are not related to aromaticity. Therefore, to complement the NICS analysis, we also calculated NICS(1) values 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 $\pi$-electron ring current are dominant and local $\sigma$-bonding contributions are diminished.[53-55]

It is worth mentioning that all indices of aromaticity are generally well intercorrelated, as can be concluded on the basis of the correlation coefficients collected in Table 1. The only exception may be the case of NICS indices. In this case it is possible to observe two sets of data that have the same trend but shift between each other. This arises from the fact that NICS values estimated for the inner ring of anthracene or phenanthrene are overestimated (one of the trends corresponds to the inner rings of systems under consideration, whereas the second trend corresponds to the lateral rings). This effect is connected with the influence of ring currents present within the lateral rings of this molecular system.[56-61] The worse NICS correlations may also result from the fact that, in general, NICS reflects the magnetic features of a molecular system perturbed in an external magnetic field, whereas both HOMA and all electron density based indices correspond to ground-state properties of the given molecular system.[51,62]

## Results and Discussion

Table 2 gathers together some selected aromaticity indices for the different aromatic rings of the polycyclic aromatic hydrocarbons (PAHs) that we analyzed. A full set of data estimated for all indices of aromaticity can be found in Table S1 in the Supporting Information. Energetic and geometric parameters of the intramolecular HBs as well as aromaticity indicators for the *quasi*-ring formed are collected in Table 3. Aromaticity indices estimated for the unsubstituted species can be found in ref 11. The presentation of the results is centered on two main interrelated goals. First, the strength of the HB and its relation with the $\pi$-electron delocalization within the

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**TABLE 2.    Values of Selected Aromaticity Indices Used[a]**

| | HOMA | | | PDI × 10² | | | FLU × 10² | | | SCI × 10² | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ring 1 | ring 2 | ring 3 | ring 1 | ring 2 | ring 3 | ring 1 | ring 2 | ring 3 | ring 1 | ring 2 | ring 3 |
| Ia | 0.906 | | | 7.265 | | | 0.786 | | | 3.945 | | |
| Ib | 0.936 | | | 7.727 | | | 0.569 | | | 4.472 | | |
| IIa | 0.716 | 0.754 | | 5.359 | 7.103 | | 1.543 | 1.080 | | 2.271 | 3.546 | |
| IIb | 0.738 | 0.800 | | 5.459 | 7.355 | | 1.500 | 0.927 | | 2.407 | 3.810 | |
| IIc | 0.690 | 0.838 | | 4.817 | 7.616 | | 1.861 | 0.775 | | 1.985 | 4.091 | |
| IId | 0.711 | 0.809 | | 5.380 | 7.461 | | 1.553 | 0.874 | | 2.356 | 3.919 | |
| IIIa | 0.562 | 0.712 | 0.633 | 4.603 | 6.220 | 6.418 | 2.064 | 1.126 | 1.624 | 1.735 | 2.491 | 2.841 |
| IIIb | 0.581 | 0.743 | 0.654 | 4.624 | 6.323 | 6.529 | 2.081 | 1.069 | 1.542 | 1.798 | 2.603 | 2.950 |
| IIIc | 0.540 | 0.748 | 0.674 | 3.956 | 6.322 | 6.656 | 2.433 | 1.025 | 1.429 | 1.463 | 2.686 | 3.083 |
| IIId | 0.548 | 0.746 | 0.662 | 4.554 | 6.369 | 6.565 | 2.132 | 1.044 | 1.517 | 1.753 | 2.653 | 2.983 |
| IVa | 0.799 | 0.424 | 0.877 | 5.722 | 4.324 | 8.077 | 1.251 | 2.133 | 0.524 | 2.659 | 1.627 | 4.666 |
| IVb | 0.824 | 0.479 | 0.870 | 5.946 | 4.567 | 8.035 | 1.145 | 1.993 | 0.554 | 2.886 | 1.764 | 4.603 |
| IVc | 0.784 | 0.520 | 0.855 | 5.350 | 4.819 | 7.938 | 1.468 | 1.880 | 0.602 | 2.427 | 1.921 | 4.496 |
| IVd | 0.804 | 0.490 | 0.868 | 5.899 | 4.657 | 8.020 | 1.178 | 1.942 | 0.567 | 2.844 | 1.823 | 4.576 |
| Va | 0.786 | 0.374 | 0.866 | 5.336 | 4.706 | 7.986 | 1.454 | 1.901 | 0.547 | 2.652 | 1.566 | 4.631 |
| Vb | 0.815 | 0.419 | 0.855 | 5.955 | 4.565 | 8.001 | 1.137 | 2.060 | 0.514 | 2.910 | 1.697 | 4.571 |
| Vc | 0.730 | 0.436 | 0.845 | 5.752 | 4.237 | 8.055 | 1.234 | 2.251 | 0.468 | 2.411 | 1.879 | 4.540 |
| Vd | 0.798 | 0.430 | 0.853 | 6.008 | 4.471 | 8.013 | 1.100 | 2.111 | 0.501 | 2.876 | 1.751 | 4.552 |

[a] The first ring is the substituted one, and the rest are numbered in natural order (see Figure 2 for ring numbering). PDI and SCI are given in electrons.

**TABLE 3.    Selected Parameters of the Systems with a *quasi* Ring Formed as a Result of H-Bond Formation[a]**

| | $d(H\cdots O)$ [Å] | $d(O-H)$ [Å] | $d(O\cdots O)$ [Å] | $\angle(O-H\cdots O)$ [deg] | $E_{diff}$ [kcal/mol] | PDI × 10² | SCI × 10³ | KSCI × 10³ | $NICS_Q(0)$ | $\Delta PDI_{ipso}$ × 10³ | $\Delta NICS_{ipso}(0)$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 1.711 | 0.988 | 2.598 | 147.2 | 12.57 | 2.33 | 0.78 | 0.24 | 2.12 | 4.62 | 0.80 |
| IIa | 1.728 | 0.985 | 2.611 | 147.2 | 11.73 | 1.70 | 0.64 | 0.19 | 2.21 | 1.00 | 0.38 |
| IIc | 1.660 | 0.996 | 2.561 | 148.4 | 15.31 | 2.87 | 0.93 | 0.29 | 2.50 | 5.64 | 1.41 |
| IIIa | 1.735 | 0.984 | 2.618 | 147.4 | 11.38 | 1.45 | 0.59 | 0.18 | 2.36 | 0.20 | 0.08 |
| IIIc | 1.642 | 0.999 | 2.549 | 148.8 | 15.97 | 3.06 | 1.00 | 0.31 | 2.69 | 5.98 | 1.61 |
| IVa | 1.723 | 0.986 | 2.607 | 147.2 | 12.25 | 1.90 | 0.68 | 0.21 | 2.43 | 2.23 | 0.52 |
| IVc | 1.672 | 0.993 | 2.571 | 148.3 | 15.12 | 2.68 | 0.89 | 0.27 | 2.55 | 5.49 | 1.14 |
| Va | 1.715 | 0.987 | 2.600 | 147.1 | 12.42 | 1.95 | 0.70 | 0.21 | 2.58 | 2.56 | 0.73 |
| Vc | 1.611 | 1.000 | 2.533 | 151.2 | 16.23 | 2.67 | 0.95 | 0.29 | 2.78 | 6.19 | 1.28 |

[a] Values of PDI, SCI, KSCI, and $NICS_Q$ correspond to *quasi*-rings. $\Delta PDI_{ipso}$ and $\Delta NICS_{ipso}$ have been estimated for the *ipso*-ring as the difference between $PDI_{ipso}$ and $NICS_{ipso}$ values estimated for H-bonded and non-H-bonded isomers, respectively. PDI, KSCI, and SCI are given in electrons, and NICS values in ppm.

*ipso*-ring is discussed. Second, an analysis of the aromaticity of the *quasi*-ring is performed in relation to the strength of the intramolecular HB that is formed.

As is well-known, π-electron delocalization plays a crucial role in shaping the chemical and physical properties of the chemical species analyzed in this work. In the case of the systems studied here it is possible to separate this π-electron delocalization into three different π-electronic effects that cooperate or compete among themselves:

(i) The first is an effect of π-electron delocalization taking place within aromatic parts of the PAHs. This effect leads to the formation of stable π-aromatic systems typical of the electronic structures of PAHs. π-Electrons involved in this effect should, in general, be relatively less available in the other π-electronic effects. Therefore, their participation in HB formation should lead to the partial destabilization of the aromatic system.

(ii) The second effect is due to the formation of the H-bonded *quasi*-ring, which leads to partial delocalization of π-electrons within this ring.[11] The π-electronic effect responsible for this delocalization should generally compete with the first effect. As already mentioned, however, this competition does not always lead to energetic destabilization of the entire molecular system, since H-bonded systems are in general more stable in relation to non-H-bonded ones.

(iii) The third effect is connected with the substituent effect characteristic of aromatic substituted molecules. Both hydroxyl and carbonyl groups attached to a phenyl ring interact between themselves through the resonance (mesomeric) effect. The hydroxyl group, with two lone electron pairs located on the oxygen atom, is known as an electron-donating substituent. This is reflected in the negative value of Hammett's substituent constants, for instance, $\sigma_p = -0.37$.[63] At the same time, the carbonyl group has electron-withdrawing properties, with $\sigma_p = 0.42$. In the systems considered, these substituents are placed in the *ortho* position, and thus communication through the resonance (mesomeric) effect will undoubtedly proceed, aside from the formation of the H-bridge. Nevertheless, both the second and third effects follow the same direction and combine against the first effect (see ref 11 for more details, including chemical diagrams). In fact, aromaticity indices clearly indicate the loss of aromaticity in substituted 6-MRs (see ref 11 and Supporting Information).

One of the basic ideas of this study was to eliminate from our considerations the effect of the communication between substituents in order to estimate the direct π-electronic interaction between the HB motif and the aromatic part of the molecules. As can be seen from the data collected in Table 3, the differences in local aromaticity of the *ipso* 6-MR are

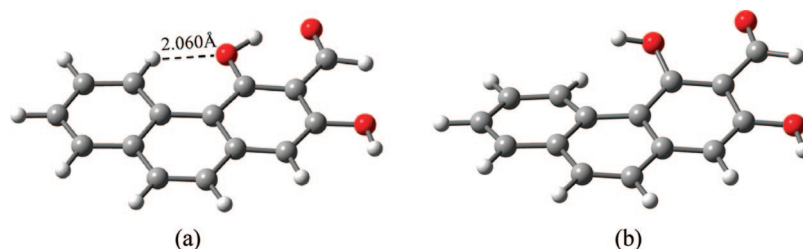(63) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

**FIGURE 3.** Graphical representation of the fully optimized geometry of systems **Vc** (a) and **Vd** (b). The H···H repulsion in **Vd** leads to distortion of the hydrocarbon skeleton, which becomes nonplanar.

relatively small when compared with systems **b** and **d**. This proves that when the $\pi$-electronic effect of H-bridge formation is eliminated (both **b** and **d** are open conformers), the effect of communication between substituents is practically the same. By comparing systems **a** and **c** in this way, it is possible to estimate the almost pure influence of HB formation on the $\pi$-electronic structure of the aromatic part of the systems.

As previously stated, the difference between the closed and open conformers of a given system, $E_{diff}$, gives an approximate value of the energy of intramolecular RAHB.[29−33] For malonaldehyde $E_{diff}$ this energy was calculated to be 12.96 kcal·mol$^{-1}$, whereas for $o$-hydroxybenzaldehyde it was 11.07 kcal·mol$^{-1}$, both computed at the same B3LYP/6-311+G(d,p) level as used in the present work. Interestingly, in 1,3-dihydroxybenz-2-aldehyde $E_{diff}$ it is 12.57 kcal·mol$^{-1}$. We can take the latter system as the reference species. The reason for the reduction in $E_{diff}$ when going from malonaldehyde to $o$-hydroxybenzaldehyde was attributed to the fact that in the latter the $\pi$-electrons are less available for participation in the $\pi$-electronic delocalization within the *quasi*-ring.[11] The increase in $E_{diff}$ of 1.5 kcal·mol$^{-1}$ when going from $o$-hydroxybenzaldehyde to 1,3-dihydroxybenz-2-aldehyde (**Ia**) can be explained by taking into account that the $\pi$-electron delocalization within the *ipso*-ring and the $\pi$-electronic effect assisting RAHB formation are two competing effects. The presence of three substituents in 1,3-dihydroxybenz-2-aldehyde leads to a bigger decrease in the aromaticity of the substituted *ipso*-ring (e.g., PDI = 0.073) than in the case of $o$-hydroxybenzaldehyde substituted by only two substituents (e.g., PDI = 0.081).[11] As a result of the $\pi$-electrons being more localized and more available in 1,3-dihydroxybenz-2-aldehyde, the HB formation leads to relatively greater stabilization of the whole system in these species than in the case of $o$-hydroxybenzaldehyde. It is worth noting here that the C=C bond length between the two C atoms involved in the formation of the *quasi*-ring is slightly longer in 1,3-dihydroxybenz-2-aldehyde (1.422 Å) than for $o$-hydroxybenzaldehyde (1.419 Å), despite the HB being stronger for the former. This suggests that $\pi$-electron communication could be more significant than C=C bond lengths in the formation of RAHBs.

As can be observed in Table 3, HBs are relatively stronger in systems **c** than systems **a**. For systems **a**, $E_{diff}$ is quite close to the value found for 1,3-dihydroxybenz-2-aldehyde (the differences are smaller than 1 kcal·mol$^{-1}$). On the other hand, systems **c** have an HB energy that is about 3−4 kcal·mol$^{-1}$ higher than in reference system **Ia**. The stronger HBs found in systems **c** are also corroborated by shorter $d(H···O)$ and $d(O···O)$ bond distances as compared to those corresponding to systems **a** (see Table 3).

Comparison between the $E_{diff}$ values (and also of $d(O-H)$ and $d(O···O)$ bond distances) of **IIIc**, **IVc**, and **Vc** leads to the
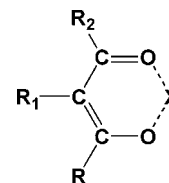


**FIGURE 4.** Diagram of the systems considered as *quasi*-aromatic. According to definition X may be a hydrogen atom or a metal ion.

conclusion that the presence or absence of one or two kinks in the molecule has little influence on the final HB strength. Somewhat unexpectedly, HB strength increases in the order **Vc** > **IIIc** > **IVc**. The fact that $E_{diff}$ is bigger for **IIIc** than **IVc** is in line with the higher aromaticity of the outer rings in phenanthrene as compared to anthracene.[64] A more aromatic ring makes it more difficult for the $\pi$-electrons to participate in HB formation. On the other hand, the $E_{diff}$ value in **Vc** is likely overestimated because of both the $(C_{ring3})H···O(H)$ stabilizing interaction in **Vc** and H···H short repulsive contact in **Vd** between the H atom of the hydroxyl group that participates in the HB in **Vc** and one of the H atoms of the kinked ring 3 ($d(H···H)$ = 1.181 Å). See Figure 3 for graphical representations of the **Vc** and **Vd** molecular structures.

Let us now discuss the $\pi$-electron delocalization within the *quasi*-ring in terms of *quasi*-aromaticity and its relationship with HB strength. The term *quasi*-aromaticity was coined in 1970[65] and is used for systems related to that shown in Figure 4. Recently, it was reported in relation to malonaldehyde and its simple derivatives that the *quasi*-ring formed due to HB formation may reflect some properties similar to these observed for typical aromatic rings.[12] It has also been shown that under certain conditions the *quasi*-ring may imitate a benzene ring fused to benzenoid hydrocarbons. The topological aspects of this situation were investigated by Krygowski and his co-workers[66] and since then have been complemented by the analysis of ring currents induced within related systems.[67] Therefore, this extra ring can be considered as *quasi*-aromatic, and in line with this, its *quasi*-aromaticity may be quantified in a way similar to that employed in the case of typical aromatic systems, namely, by the use of aromaticity indices. Table 3 contains values of selected aromaticity indices used in this work, calculated for the *quasi*-ring present in a given system. There

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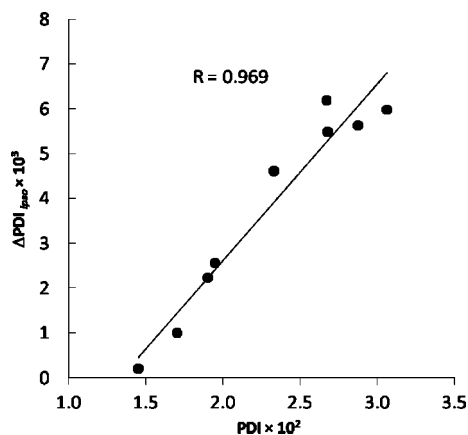
**FIGURE 5.** Interrelation between the absolute values of the $\Delta$PDI$_{ipso}$ and PDI of the *quasi*-rings. $\Delta$PDI$_{ipso}$ has been estimated for the *ipso*-ring as the difference between PDI$_{ipso}$ values corresponding to closed and open isomers, respectively.

is a direct relationship between the strength of the HB and the *quasi*-aromatic character of the *quasi*-ring: the stronger the HB, the more aromatic the *quasi*-ring clearly is. A linear relationship between values of $E_{diff}$ and aromaticity indices can be set up, with a correlation coefficient of $R = 0.938$ for $E_{diff}$ versus PDI. For SCI and KSCI, the values of $R$ are even closer to 1. Thus, it is possible to conclude that the strengthening of the HB within the *quasi*-ring is directly connected with the $\pi$-electronic effect or more accurately the effect of the delocalization of $\pi$-electrons within this ring. It is worthwhile noting here that there is no correlation between NICS$_Q$ and the other indices of aromaticity used or between $E_{diff}$ and NICS$_Q$. In fact, NICS$_Q$ values indicate that *quasi*-rings are not aromatic. In our opinion, NICS is not the best index for systems that are very dissimilar to typical aromatic systems. In connection with this, Krygowski and co-workers have shown recently that the typical diatropic ring current found around aromatic rings is not present in the *quasi*-ring of RAHBs.[16]

We have already mentioned that the effect of resonance proceeding within the *quasi*-ring competes with the effect of $\pi$-electron delocalization within the substituted 6-MR. This means we can expect there to be some link between the substituted *ipso*-ring's loss of local aromaticity and the *quasi*-aromaticity of the *quasi*-ring. This link is illustrated in the diagram in Figure 5. Numerical values are collected in Table 2. ($\Delta$PDI$_{ipso}$ and $\Delta$NICS$_{ipso}$ have been estimated for the *ipso*-ring as the differences between values of a given aromaticity index corresponding to closed and open isomers, respectively.) As can be seen, there is a close-to-linear relationship, which indicates that the increase in the *quasi*-aromatic character of the *quasi*-ring proceeds at the cost of loss of aromaticity in the *ipso*-ring. As expected, such a relationship cannot be found for the NICS$_Q$ index, for the reasons already discussed. It is worth pointing out, however, that the loss of aromaticity in the *ipso*-ring is reflected by NICS to the same degree as in the case of electron-based indices. For instance, the correlation coefficient for the linear relationship between $\Delta$PDI$_{ipso}$ and $\Delta$NICS$_{ipso}$ values is close to 1 ($R = 0.95$).

In line with the idea of the *quasi*-ring partially adopting the role of a typical aromatic ring, it is possible to attribute to each of the systems investigated a related unsubstituted hydrocarbon with $N + 1$ aromatic rings, as compared to the original hydrocarbon with $N$ aromatic rings. For example, for two

substituted naphthalene derivatives **IIa** and **IIc**, one can consider two PAHs, namely, anthracene and phenanthrene, as corresponding to **IIa** and **IIc**, respectively. It is well-known that phenanthrene is relatively more stable than anthracene. It was explained recently by one of us through energy decomposition analyses performed on several PAHs that the greater stability of the kinked hydrocarbons in comparison with their straight counterparts is connected with the relatively more effective stabilizing interactions in their $\pi$-electronic systems.[68] In another paper it has been shown that for models of infinite chains of benzenoid rings, kinked PAHs are in general more stable than straight ones.[69] Thus, it is worth taking a closer look at systems with *quasi*-rings. From the differences in the total energies of the **a** and **c** systems we can obtain the energy parameter $\Delta E^{a,c} = E_{total}(\mathbf{a}) - E_{total}(\mathbf{c})$, which will numerically reflect differences in energy stability between linear and kinked systems. $\Delta E^{a,c}$ adopts values of 3.81, 5.17, 2.92, and 3.73 kcal/mol for **II**, **III**, **IV**, and **V**, respectively. In all cases the **c** isomer, as the kinked one, is more stable than the linear one. As stated previously, this is the result of the stronger HBs found in species **c**. Moreover, $\Delta E^{a,c}$ has the greatest value in system **III**, with the longest straight topology, while the lowest values can be observed for the derivatives of phenanthrene, **IV** and **V**, the systems which already had a kinked topology. What is also worth pointing out is that the energy difference between **IVc** and **Vc** is about 2.15 kcal·mol$^{-1}$, with **IVc** being the most stable. Thus, the most stable double kinked systems are those with two clockwise kinks (with chrysene being better than tetrahelicene topology). The chrysene-like system (**IVc**) is more stable because of the steric repulsions between lateral parts of the tetrahelicene-like system (**Vc**) (see Figure 3). Therefore, comparing our systems with $N + 1$ PAHs, we can conclude that the *quasi*-ring partially adopts properties of a typical aromatic ring, which emphasizes the importance of $\pi$-electronic effects on the stabilization of the systems studied in this work.

Another important conclusion can be drawn when the comparison between $N$ PAHs and $N + 1$ is considered. It is well-known that the reactivity of a given PAH is related to the aromaticity of a particular ring within this PAH. Consequently, the reactivity of the series of 1,3-dihydroxyaryl-2-aldehydes may depend on the position of the *quasi*-ring within the given system. As argued above, the aromaticity of the *ipso*-ring depends on the conformer that is taken into account. Thus, it is possible to conclude that the reactivity of 1,3-dihydroxyaryl-2-aldehydes depends on which HB is formed. HB formation can therefore be used to control the aromaticity of the *ipso*-ring, and in consequence the reactivity of different PAHs.

## Conclusions

It can be concluded from our studies of 1,3-dihydroxyaryl-2-aldehydes that the position of the extra *quasi*-aromatic ring formed by substituents interacting through RAHB influences both the strength of the H-bonding and the local aromaticity of the PAH skeleton. HBs are relatively stronger and the entire system is energetically more stable when a kinked-like structure is generated by the addition of the *quasi*-aromatic ring. Systems with a straight-line topology are relatively less stable and have weaker HBs. What is particularly interesting is that relatively

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greater loss of aromaticity in the *ipso*-ring can be observed for kinked-like structures. Since the local aromaticity of the given PAH may be responsible for the reactivity of the molecule, the possibility of formation of two *quasi*-rings in two different topological positions for the same chemical species may, in some way, serve to control the reactivity of 1,3-dihydroxyaryl-2-aldehydes. Clearly, the communication between the *quasi*-ring and the PAH skeleton proceeds through $\pi$-electronic effects, which may indicate the importance of this kind of phenomena in the case of the HBs analyzed in this work.

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

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