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Article

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Tuning the strength of the resonance-assisted hydrogen bond in acenes and phenacenes with two *o*-hydroxyaldehyde groups. The importance of topology

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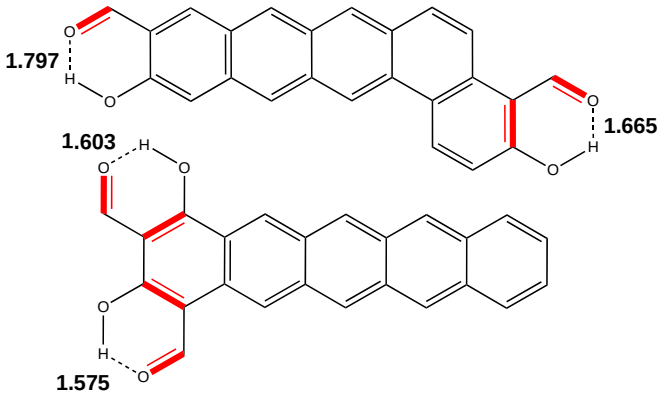
TOC Graphic



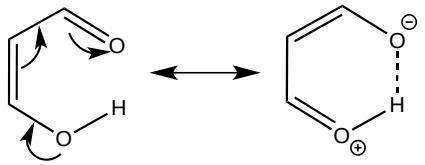
Abstract

The fact that intramolecular resonance-assisted hydrogen bonds (RAHBs) are stronger than conventional ones is attributed to the partial delocalization of the π-electrons within the hydrogen bond (HB) motif, the so-called quasi-ring. If an aromatic ring is involved in the formation of the RAHB, previous studies have shown that there is an interplay between aromaticity and HB strength. Moreover, in 1,3-dihydroxyaryl-2-aldehydes, some of us found that the position of the quasi-ring formed by the substituents interacting through RAHB influences the strength of the H-bonding, the HBs being stronger when a kinked-like structure is generated by formation of the *quasi*-ring. In this work, we explore this concept further by considering a set of acenes and phenacenes of different sizes with two *o*-hydroxyaldehyde substituents. Calculations with the CAM-B3LYP/6-311+G(d,p)+GD3B method show that for long acenes or phenacenes, once the substituent effect loses importance because quasi-rings are pull apart far from each other, the different topologies rule the HB distances. This fact can be explained in most cases using an extended Clar's aromatic π-sextet model. In some kinked systems, however, the justification from the Clar model has to be complemented by taking into account the repulsion between hydrogen atoms. Triphenylene-like compounds with different number of benzene rings have been studied finding out a very good relationship between aromaticity of the *ipso*- and *quasi*-rings with the RAHB distances. This result confirms the importance of the communication of the π-systems of the *ipso*- and *quasi*-rings.

Introduction

Hydrogen bonds (HBs) are one of the strongest non-covalent interactions. They play an important role in many chemical and biological processes; for instance, HBs determine the crystal structure as well as the stabilization of the second-order structure of proteins.[1-4] Because of their directionality and the fact of being strong enough to assemble molecular systems in aggregates, HBs are one of the most important interactions in supramolecular chemistry and molecular engineering.[5] Depending on its bond strength, which can range from 0.2 kcal/mol to 40 kcal/mol, HBs can be classified as weak, moderate or strong.[2]

HBs assisted by additional effects, e.g., resonance-assisted or charge-assisted,[6-9] are among the strongest HBs known. Intramolecular resonance-assisted hydrogen bonds (RAHB) introduced by Gilli *et al.*[6-9] are stronger than conventional HBs because of the extra stabilization connected with the partial delocalization of the π-electrons within the so-called *quasi*-ring containing conjugated formally single and double bonds. A schematic representation of electronic effects proceeding within such cyclic RAHB is shown in Scheme 1 for malonaldehyde. The characteristic elongation of formally double bond and shortening of formally single bonds in the *quasi*-ring together with a strengthening of the HB are fingerprints of RAHBs.

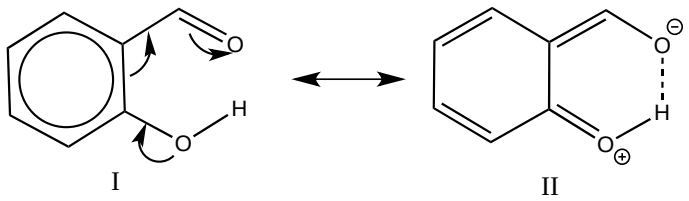


I II

Scheme 1. The two main resonance structures involved in the resonance-assisted hydrogen bond in malonaldehyde.

Many computational studies[10-27] and experimental works[28-31] can be found related to intramolecular and intermolecular RAHBs. The origin of the additional strength of RAHB as compared to conventional HBs is still subject of an ongoing debate.

Gilli *et al*.[6-9] attributed it to the delocalization of the π-electrons. Mo *et al*,[16,18] provided further evidences that the enhanced HB comes from the charge flow from the HB donor to the acceptor through the π-conjugation. Recently, Grosch *et al.*[11] arrived to the conclusion that π polarization and σ charge transfer are the responsible for enhancing RAHB in line with the Gilli *et al*. proposal, although they emphasized that there is no resonance assistance in the sense of an interplay between σ charge transfer and π polarization. Moreover, other researchers, like Sanz *et al*.,[25,26] argued that the characteristics of the σ-skeleton, and not the resonance assistance phenomenon, is the main responsible for the extra stability of RAHB. Also, Guevara-Vela *et al.*[13,14,24] analyzed the nature of the RAHB to conclude that there is an increase in electron localization of π-electrons (not delocalization as expected from Gilli's interpretation) in the *quasi*-ring of RAHB. This localization leads to greater electrostatic, polarization, and charge transfer effects that result in stronger H-bonds. Thus, we can find different interpretations of the basis of the "assistance" in RAHBs.

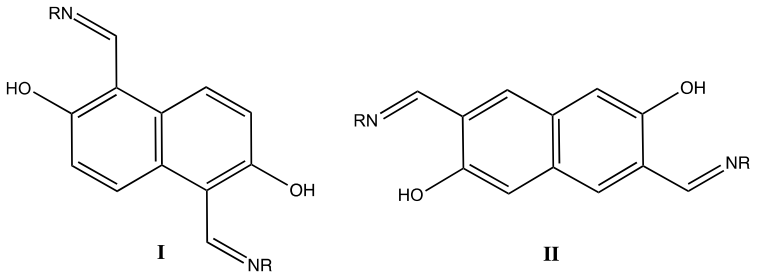


I II

Scheme 2. The two main resonance structures involved in the resonance-assisted hydrogen bond in *o*-hydroxybenzaldehyde.

The first relation between HB formation and aromaticity was reported in a landmark paper by Dewar already in 1945.[32] In his study, Dewar[32] showed that presence of an intramolecular hydrogen bond induces aromatic character at the seven-membered ring (7-MR) of the stipatic acid, thus providing an explanation to the physicochemical properties of this molecule. More recently, studies by our group[33,34] described the interplay between RAHB strength and aromaticity of the *ipso*-ring in a series of *o*-hydroxyarylaldehydes (see Scheme 2). These compounds can separate the π-resonance effect in three different individual

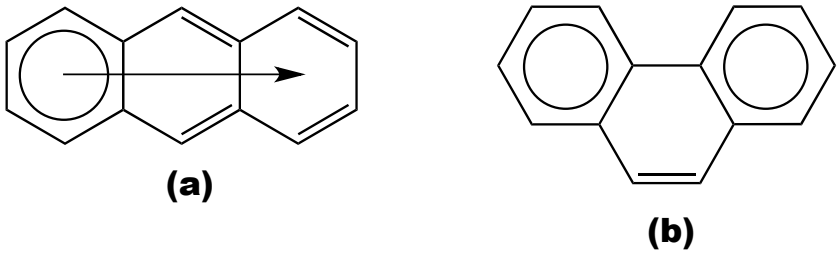
effects, namely, (a) the delocalization within the *quasi*-ring, identified by Gilli *et al*.[8] and already present in malonaldehyde, (b) the effect of the π-electron delocalized within the benzene ring (structure **I** in Scheme 2), and (c) the substituent effect of hydroxyl group (electron-donating group) and carbonyl (electron-withdrawing) that favors the canonical structure with charge separation (structure **II** in Scheme 2). Compared to malonaldehyde, with C=C localized double bond, effects (a) and (c) cooperate with each other, so reinforcing the HB, while (b) goes against HB formation. From the data found in these previous studies, it is clear that RAHB enhancement or weakening can be controlled by changing the substituents[35] and the aromaticity of *ipso*-ring.[33,34] Indeed, in 1,3-dihydroxyaryl-2-aldehydes,[33] we found that the position of the *quasi*-ring formed by the substituents interacting through RAHB influences the strength of the H-bonding, the HBs being stronger when a kinked-like structure is generated by formation of the *quasi*-ring. Similar results were obtained by Houjou *et al*.[28,29] from the analysis of the proton transfer processes in the two systems represented in Scheme 3. These authors showed that HBs are stronger for **I** than **II** irrespective of solvent polarity or crystal packing. According to the authors, the reason is the low distortion of the aromatic rings in **I** as compared to **II**. For the latter, the loss of aromaticity is higher reducing the stability of the HBs formed.



Scheme 3. Structure of the α,α-diimine (**I**) and β,β-diimine (**II**) species.

It is very well-known that aromaticity of condensed benzene rings, the so-called benzenoid hydrocarbons, depends on their number of rings as well as their relative position, that is, their isomeric structure. [*n*]Acenes and [*n*]phenacenes (*n* being the number of rings) are two series of isomeric aligned benzenoid compounds

(Scheme 4). The aromaticity of these compounds has been widely analyzed using different indices.[36] This aromaticity can be explained using Clar's π-sextet model,[37] which states the Kekulé resonance structure with the largest number of disjoint aromatic π-sextets is the most important. Following this rule, the Clar's structures for [3]acene (anthracene) and [3]phenacene (phenanthrene) are the ones represented in Scheme 4. [*n*]Acenes with a migrating π-sextet have similar aromaticity in all rings,[38] whereas in [n]phenacenes the outer rings are more aromatic than the central one. Moreover, [*n*]phenacenes have a larger number of aromatic π-sextets than the corresponding [*n*]acenes and, therefore, are more stable and more aromatic as a result of more stabilizing π-interactions.[39]



Scheme 4. Clar structures for (a) anthracene and (b) phenanthrene.

Following this line of reasoning, one could consider system **II** in Scheme 3 as a part of a *pseudo*-tetracene species formed by a naphthalene attached to two *quasi*-rings in a linear arrangement, whereas compound **I** as a part of *pseudo*-chrysene with two *quasi*-rings in a kinked topology. Given that [*n*]phenacenes are more stable than [n]acenes, one can make the hypothesis than **I** is more stable than **II** due to the better π interactions found in kinked structures as compared to linear ones. The main goal of this work is to prove this hypothesis by analyzing a set of acenes and phenacenes of different sizes with two *o*-hydroxyaldehyde substituents at the outermost rings. We anticipate here that the arrangement of the aromatic rings has a great influence in the RAHB strength and that kinked distribution of rings results in stronger RAHBs.

Results and Discussion

In this section, we will discuss first the changes in RAHB distances when increasing the chain of polycyclic aromatic hydrocarbons (PAHs) in two different topologies, linear and kinked structures. Then we will analyze the effect of including sequentially a new kink starting from a linear topology to finally yield the fully kinked structure. Finally, the design of triphenylene–like compounds will be used to discuss the direct relation between aromaticity and HB strength.

By adding an extra *quasi*-ring to *o*-hydroxybenzaldehyde (Scheme 2) formed by two adjacent OH and HCO substituents, one can generate the five different isomers of dihydroxydibenzaldehyde shown in Figure 1. Two of them present a linear arrangement and resemble anthracene, whereas three of the isomers have a kinked structure and bear a resemblance to phenanthrene.

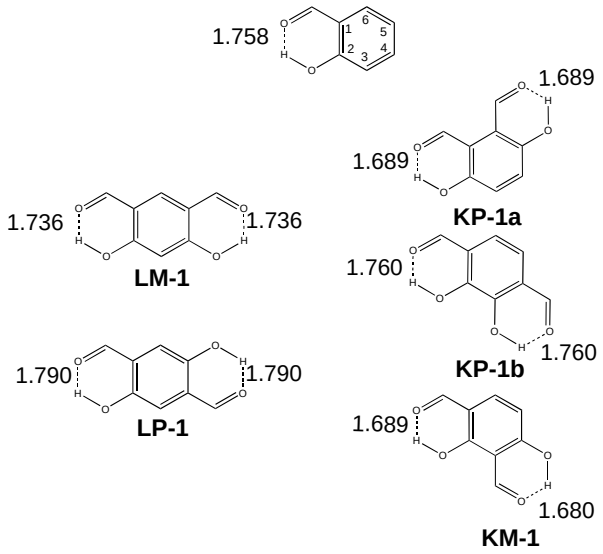
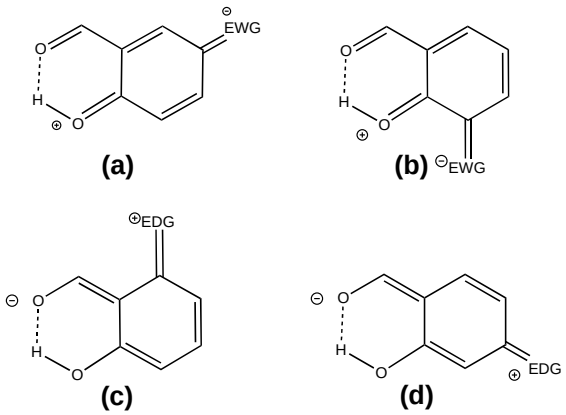


Figure 1. Dihydroxydibenzaldehyde isomers with two *quasi*-rings. RAHB distances in Å.

When the new substituents to build the *quasi*-ring (OH and HCO) are added in positions 4 and 5 of *o*-hydroxybenzaldehyde (see Figure 1 for numbering), one can have two linear conformers, **LM-1** and **LP-1** (L for linear and M and P respect to the relative position of both OH and HCO in the *ipso*-ring, *meta* and *para*

respectively). In a previous work,[35] we dealt with the substituent effect on RAHB distances for substituted *o*-hydroxybenzaldehyde. It was found that depending on the electronic character of the substituents the RAHB is strengthened or weakened. As can be seen in Scheme 5, EDG and EWG in *para* an *ortho* position to each other helps to activate the RAHB. For that reason **LM-1** presents a shorter RAHB distance (1.736 Å) as compared to *o*-hydroxybenzaldehyde (1.758 Å), whereas the RAHB in **LP-1** is deactivated (1.790 Å), as an EWG (CHO) is added to position 4 and an EDG (OH) is attached to position 5. The difference of 0.054 Å in the RAHB bond length of **LM-1** and **LP-1** reflects the substituent effect. As a result of stronger RAHBs, **LM-1** is more stable than its **LP-1** isomer by 8.15 kcal mol^{-1} (see Table 1).



Scheme 5. The resonance structures responsible for the HB strengthening. EWG in positions 3 and 5 and EDG in positions 4 and 6 activate the RAHB (see Figure 1 for numbering). For further details see ref. 35.

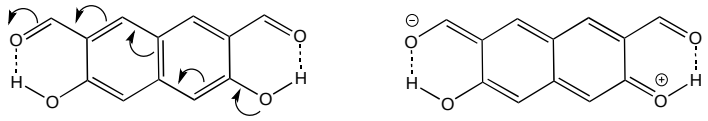
When the second *quasi*-ring is added at the *ortho* positions, we can get three different kinked conformers, named **KP-1a**, **KP-1b**, and **KM-1** (**KP-1a** for OH and **KP-1b** for HCO in *para* positions). As shown in Figure 1, RAHBs in **KP-1a** and **KM-1** become shortened as compared to the *o*-hydroxybenzaldehyde reference, whereas **KP-1b** remains almost unaffected. ~~**KP-1a** is activated because of the presence of an EWG in position 6 (Scheme 5a) and an EDG in position 5 (Scheme 5f) and also because of H···H repulsion between *ortho* substituents.~~ **KM-1** is activated because of the presence of an EWG in position 3 (Scheme 5b) and an

EDG in position 4 (Scheme 5d). **KP-1a** and **KP-1b** are not activated by substituents when forming the RAHB, as EDG and EWG of the *quasi*-rings are, respectively, in positions 5 and 6 in **KP-1a** and 3 and 4 in **KP-1b**. The slight shortening in **KP-1a** can be explained because of a H···H repulsion interaction. Indeed, when one of the HCO groups in **KP-1a** is rotated by 90º through the C_{ring}-C_{CO} bond to place it perpendicular to the 6-MR in such a way that both the RAHB and the H···H repulsion interaction are broken, the RAHB that remains increases its bond length by 0.048 Å. Moreover, we attributed the small deactivating effect in **KP-1b** to the O···O lone pair repulsions between the two OH groups. Table 2 shows that **KM-1** is much more stable than **KP-1a** and **KP-1b** (10.86 kcal mol^{-1} and 9.09 kcal mol^{-1} respectively). The local dipole-dipole repulsions together with H···H and O···O repulsions are the main causes for the destabilization of **KP-1a** and **KP-1b** with respect to **KM-1**. It is worth mentioning that a weak HB (2.423 Å) between aldehyde group and oxygen of the hydroxyl group may also slightly favor the stabilization of the **KM-1** isomer.

If we now focus on aromaticities of the *ipso*-rings, which are collected in Table 1 and Table 2 for linear and kinked compounds respectively, we can state that there is not a direct relation between the aromaticity of the *ipso*-ring and the HB distances, although the systems with stronger RAHBs are the ones having the less aromatic *ipso*-rings. Thus, from these data one can observe that different effects are the responsible of the RAHB length in the *quasi*-ring, being not always very easy to be predicted the main factor ruling the change in the HB distance. To decrease substituent effects, one can increase the distance between them by adding extra benzene rings and building PAHs with two o-hydroxyaldehyde substituents with two different topologies, namely, linear (named **LM-n** and **LP-n**, where **n** is the number of benzene rings) and kinked (**KM-na**, **KM-nb**, and **KP-n** following the nomenclature of Figure 1 and being n the number of benzene rings). All these new compounds resemble [*n*]acenes (linear) and [*n*]phenanthrenes (kinked). It is worth mentioning that the maximum number of added benzene rings

in this work is 5, as it was found that for [*n*]acenes with larger *n* values, open-shell biradical singlet state can be more stable that closed-shell singlet state.[40,41]

Figure 2 depicts the linear structures studied with the corresponding RAHB distances and the labels of the 6-MRs. Aromaticity of the different 6-MRs and *quasi*-rings are collected in Table 1. Let's start adding one ring to both **LP-1** and **LM-1** systems, so giving **LP-2** and **LM-2**. The addition of a first ring brings to a reduction of the strength of RAHBs that have longer HB distances. There are two electronic effects that explain the weakening of RAHBs in **LP-2** and **LM-2**. First, the substituent effect decreases as the number of benzene rings increases. This is especially important in the case of **LP-2** for which it is not possible to find monoionic resonance structures that favor the RAHB. For **LM-2**, the monoionic resonance structure in Scheme 6 (and its symmetric counterpart not depicted) indicates that substituent effects favor both RAHBs as shown already by Krygowski *et al*.,[42] but the effect is not as important as in **LM-1** due to the increased distance between substituents.



LM-2

Scheme 6. Substituted naphthalene resonance structure responsible for the HB strengthening in **LM-2**.

Second, the aromaticity of the 6-MRs when going from **LP-1** or **LM-1** to **LP-2** or **LM-2** compounds decreases and the π-density is partially localized in the C2–C3, C4–C5, and C6–C1 bonds (see Figure 1 for labels). Then, the C1–C2 bond having the two substituents has less π-electrons available for resonance assistance (C1–C2 bond distances are 1.425 Å for **LM-1** and 1.435 Å for **LM-2**) and, consequently, the HB is weakened. The same trend is also followed when adding more benzene rings, showing a convergence of hydrogen bond distances and aromaticities for *n* > 3. Linear PAHs present a migrating π-sextet (see Scheme 4), with similar

aromaticities for the different rings. The convergence between **LP** and **LM** aromaticities can be seen in Table 1. **LM-1** and **LP-1** start with very different aromaticities (0.0563 and 0.0817 respectively) and they converge to similar values (0.0435 and 0.0442 for *ipso*-rings in **LM-5** and **LP-5** respectively).

Table 1. PDI values (in e) for the benzene rings and *quasi*-rings (PDI_Q) of the linear systems. ΔE_{rel} is the relative energy between **LMn** and **LPn** isomers (kcal mol^{-1}). See Figure 2 for labels of the rings.

	PDI			PDI_Q		ΔE_{rel}
Systems	**A**	**B**	**C**	**A'**	**B'**	
LM-1	0.0563			0.0107	0.0107	-
LP-1	0.0817			0.0134	0.0134	8.15
LM-2	0.0553	0.0553		0.0080	0.0080	-
LP-2	0.0649	0.0649		0.0086	0.0086	3.20
LM-3	0.0503	0.0616	0.0503	0.0064	0.0064	-
LP-3	0.0540	0.0670	0.0540	0.0066	0.0066	1.37
LM-4	0.0462	0.0599	0.0599	0.0055	0.0055	-
LP-4	0.0477	0.0619	0.0619	0.0056	0.0056	0.62
LM-5	0.0435	0.0577	0.0631	0.0050	0.0050	-
LP-5	0.0442	0.0588	0.0648	0.0050	0.0050	0.28

Table 1 also collects the relative energy between **LM** and **LP** isomers, with **LM** being always the most stable one. When only one benzene ring is separating both *quasi*-rings (**LP-1** and **LM-1**) the energy difference is quite large (8.15 kcal mol^{-1}). When the number of 6-MR is increasing, the relative stability of **LP-n** with respect to **LM-n** decreases to 0.28 kcal mol^{-1}, the two isomers being almost degenerated for $n = 5$. Not only relative energies and aromaticities converge with the increase of n, but also HB lengths as shown in Figure 2. Then, despite the substituent effect favors the RAHB in **LM-n** systems and disfavors it in **LP-n** species, there is a convergence in the relative energies, aromaticities, and HB lengths of this two series of compounds, indicating that substituent effects becomes negligible for systems with $n > 3$.

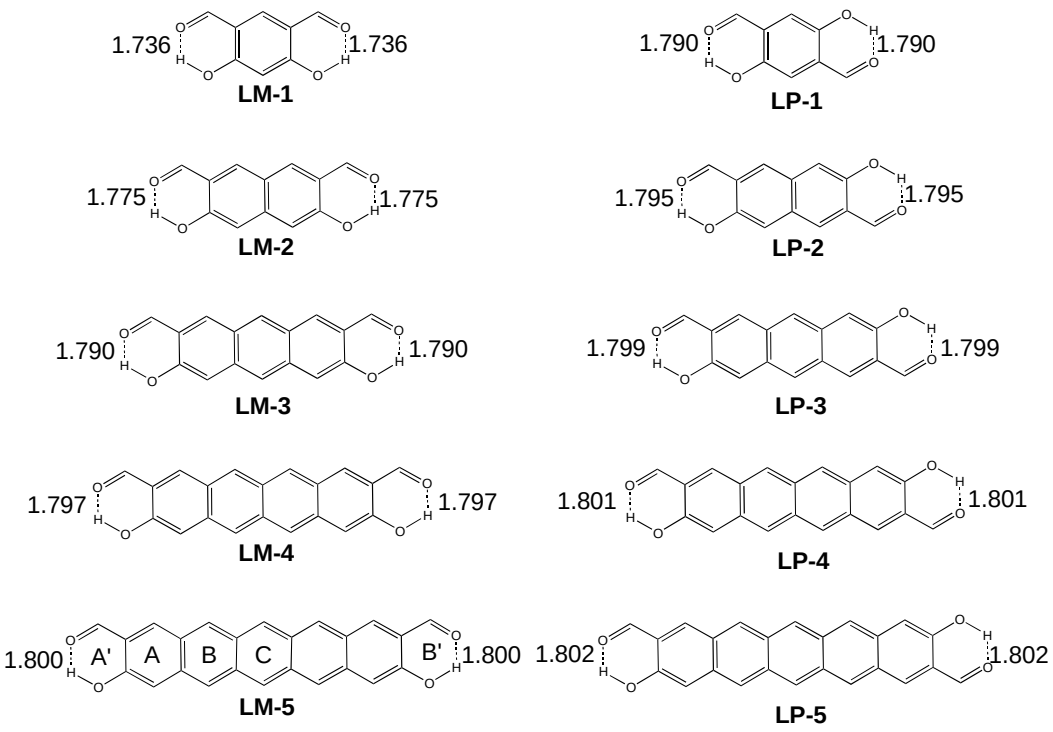


Figure 2. [*n*]Acene-like isomers (*n* = 1–5). Bond lengths in Å.

Now let's focus on kinked systems, which are built from **KP-1a**, **KP-1b**, and **KM-1**, by adding extra 6-MRs to generate the different [*n*]phenacene-like compounds depicted in Figure 3. **KM** has been used to name systems with the same substituent building the *quasi*-rings located in "*meta"* position one with respect the other, i.e., not connected by a straight axis containing the two most separated C atoms. Similar to the linear set, we build kinked PAHs up to five benzene rings. The main difference with respect to linear conformers is that, for each system, we can have two different *quasi*-rings with RAHB distance. When one ring is added, the hydrogen bond distances increase or decrease depending on aromaticity of the *ipso*-ring and the substituent effect. However, again, the substituent effect is partially neutralized due to the existence of different π-delocalization paths. As before, the RAHB distances tend to converge while increasing the number of benzene rings. Relative energies between kinked and linear (**LM**-n as reference) are collected in Table 2, $\Delta E_{K\text{-}L}$. As the number of kinked rings increase, they are much more stable than the linear isomers, in agreement with previous studies of

Poater *et al*.[38] It is worth noting that the relative energy of the different kinked isomers for n ≥ 2 depends mainly on the number of H···H repulsion interactions (2HRIs) between the H atoms located in the bay regions of the kinked species. The higher the number of 2HRI, the lower the stability of the isomer. For instance, **KM-2b** (two 2HRI) is less stable than **KP-2** (one 2HRI) and this in turn is less stable than **KM-2a** (no 2HRI). Or the order of stability for *n* = 3 is **KP-3a** (three 3HRI) < **KM-3** (two 2HRI) < **KP-3b** (one 2HRI). And the same for *n* = 4 and 5 (see Figure 4).

Table 2. PDI values (in e) for the benzene rings and *quasi*-rings (PDI_Q) of the kinked systems. $E_{(K-L)}$ is the relative energy to LM-n while E_{rel} is the relative energy between **KM-n** and **KP-n** isomers (kcal mol^{-1})

	PDI					PDI_Q		ΔE_{K-L}[a]	ΔE_{rel}[b]
Systems	**A**	**B**	**C**	**D**	**E**	**A'**	**B'**		
KM-1	0.0586					0.0149	0.0138	0.00	
KP-1a	0.0668					0.0202	0.0202	10.86	10.86
KP-1b	0.0704					0.0170	0.0170	9.09	9.09
KM-2a	0.0609	0.0609				0.0192	0.0192	-3.56	
KM-2b	0.0592	0.0592				0.0195	0.0195	2.75	6.30
KP-2	0.0539	0.0575				0.0179	0.0178	-3.13	0.42
KM-3	0.0611	0.0509	0.0599			0.0179	0.0179	-9.15	2.21
KP-3a	0.0608	0.0540	0.0608			0.0187	0.0187	-5.00	6.36
KP-3b	0.0632	0.0519	0.0632			0.0182	0.0182	-11.36	
KM-4a	0.0613	0.0551	0.0551	0.0613		0.0840	0.0184	-19.39	
KM-4b	0.0600	0.0557	0.0557	0.0600		0.0186	0.0186	-13.02	6.37
KP-4	0.0591	0.0563	0.0542	0.0609		0.0184	0.0182	-16.53	2.86
KM-5	0.0610	0.0540	0.0585	0.0546	0.0597	0.0182	0.0184	-24.79	3.00
KP-5a	0.0599	0.0553	0.0589	0.0553	0.0599	0.0185	0.0185	-21.47	6.33
KP-5b	0.0614	0.0535	0.0600	0.0535	0.0614	0.0183	0.0183	-27.79	

[a] **LM-n** is the reference system for energy difference
[b] The most stable systems between **KM-n** and **KP-n** is taken as the reference system

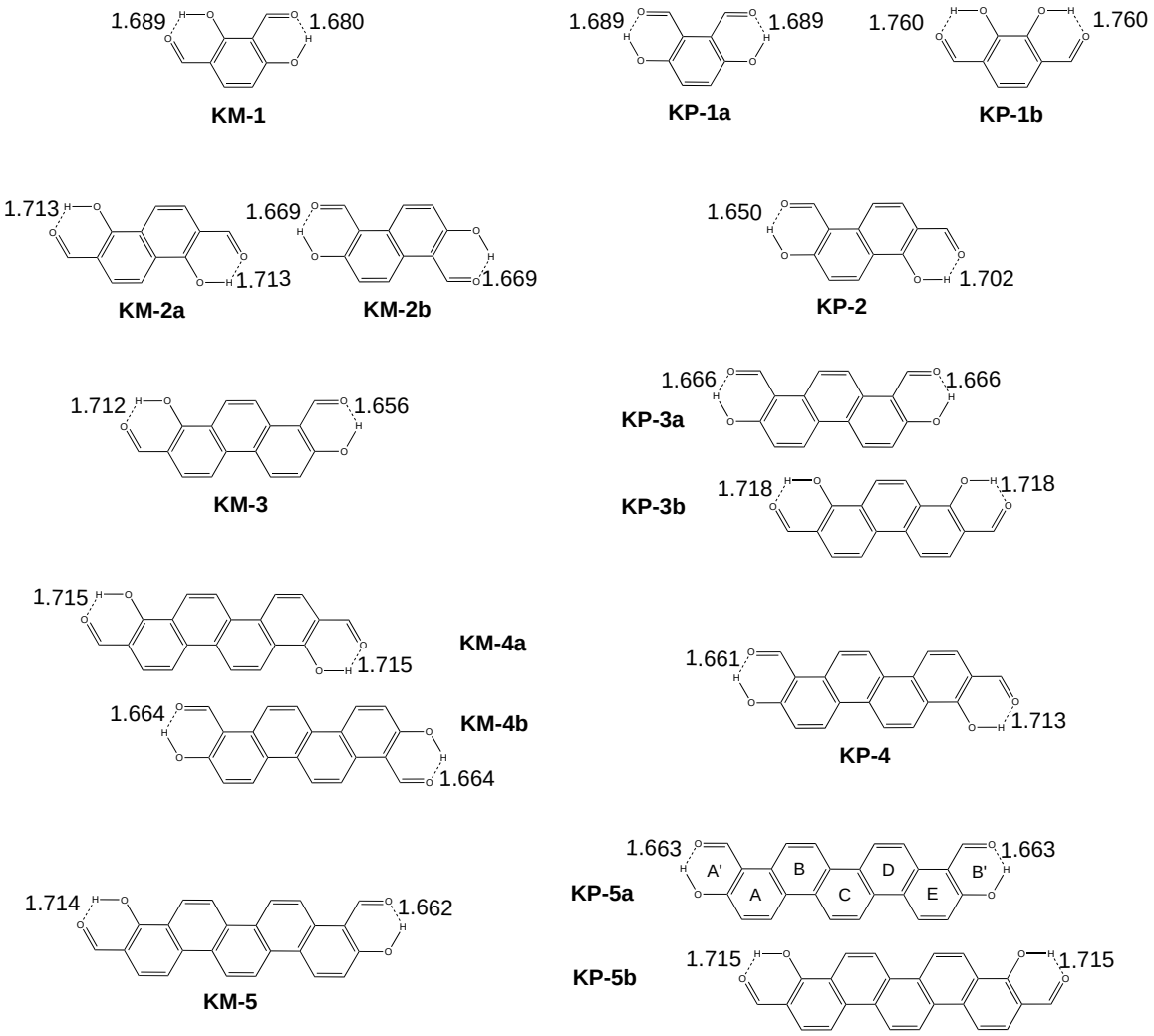


Figure 3. [n]Phenacene-like isomers (n = 1–5). Bond lengths in Å.

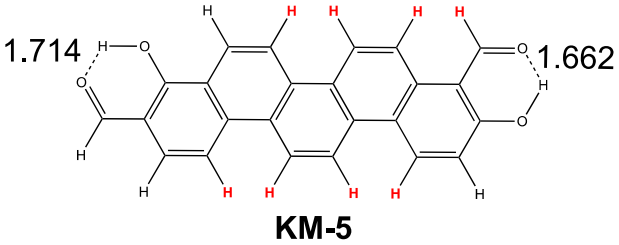


Figure 4. The four H···H repulsion interactions in **KM-5** molecule indicated in red color. Bond lengths in Å.

Previous studies[36] reported that, in [*n*]phenacenes, the aromaticity is larger in the external rings than in the central ones, while in [*n*]acenes external rings are slightly

aromatic than inner ones. For our systems, this fact should be translated in more aromatic *quasi*-rings for **KP** and **KM** compounds as compared to **LP** and **LM** systems. Indeed, this is what is found and, for instance, PDI_Q is 0.005 e in **LM-5** and four time higher (0.0182 e) in **KM-5**. This is in agreement with the HB strength of *quasi*-rings, being stronger, with shorter RAHB distance, in kinked compounds (with larger aromaticity for the *quasi*-ring) than in their linear counterparts. In addition, kinked PAHs have an alternation of the aromaticity from the external to the central rings. This alternation can easily be predicted by Clar's aromatic π-sextet model (Scheme 4).

When adding one more ring to **KP-1a** to build **KP-2**, we can see that *quasi*-rings in **KP-2** have quite different HB distances (1.650 Å and 1.702 Å for **A'** and **B'** respectively) but similar aromaticities (0.0179 and 0.0178 e). This change on the HB distances is neither related to the aromaticity of the *ipso*-ring (0.0539 e for **A** and 0.0575 e for **B**) nor to the double bond character of the shared C1–C2 (1.403 Å for **A'** and 1.395 Å for **B'** ring). The difference in these distances can be understood if we take into account that *quasi*-ring **A'** is affected by a 2HRI that "artificially" makes the RAHB shorter, whereas quasi-ring B' is free of this type of interactions. The same behavior is found for the rest of isomers (*e.g.* 1.713 Å for **KM-2a** with no 2HRI and 1.669 Å for **KM-2b** with two 2HRI). To validate the decrease of the HB distance due to the presence of 2HRI, we have removed one of the hydrogen atoms involved in the repulsion to generate a radical structure without 2HRI. In the case of radical **KM-5** generated after removal of a single hydrogen (the one close to the CHO group), the HB length increases from 1.662 Å to 1.719 Å, which is very close to the HB length in the second quasi-ring (1.715 Å) i.e. the one without H···H repulsion. So, indeed, the repulsion seems to be responsible for shortening the HB distance for about 0.06 Å. Moreover, in the case of **KP-5a**, removal of the repulsion between two H on both sites (the ones on phenyl rings close to the quasi-ring) leads to the increase of HB length from 1.663 Å in **KP-5a** (with H···H repulsion) to 1.720 Å in the biradical system with no H··H

repulsion affecting the RAHB. Finally, let us note that at variance with the linear species, the RAHB distances converge already for *n* = 2.

From our results, we can see that RAHB distance can be tuned by adding a set of 6-MRs between *quasi*-rings. When a linear chain is built, the RAHB distance increases, whereas for kinked chains the lenght of RAHB remains quite constant. Clar's aromatic π-sextet model extended to *quasi*-rings helps to explain the different RAHB lenght and aromaticity of the *ipso* and *quasi*-rings in linear and kinked compounds. Nevertheless, the two different RAHB lengths found in some kinked systems and the fact that the most stable isomers have, in some cases, larger RAHB distances cannot be explained with the Clar model. To explain these results one needs to resort to H···H repulsive interactions.

On the way from linear to kinked structures

As said in the previous section, the general trend of the bond lengths in RAHBs of kinked and linear PAHs can be explained using the extended Clar's model that relates aromaticity of the *ipso*- and *quasi*-rings with the RAHB distance. To get deeper insight into the different behavior of linear **LM-5** and kinked **KP-5a** species, we transformed **LM-5** compound to **KP-5a** by kinking one by one the different rings, so going through **LM-5'** (one kink), **KP-5'** (two kinks) and finally **KP-5a** (three kinks). Figure 5 schematically draws the four different compounds that brings to the kinked **KP-5a** from linear **LP-5**. Starting from one kink in right side (**LM-5'**), there is an important decrease of the HB distance (from 1.800 Å to 1.665 Å), while the HB distance of the *quasi*-ring that keeps in a linear topology remains almost unchanged. As it can be seen in Table 3, this change in the topology goes together with important change in the aromaticity of the different rings. Following expectations from Clar's model, there is a decrease of aromaticity in the **D** ring (phenanthrene-like topology) in favor of an increase in **E** ring. As pointed out before, the kinked *quasi*-ring (**B'**) with shorter HB distance becomes much more aromatic.

Table 3. PDI values (in e) of the benzene rings and *quasi*-rings (PDI_Q) of the systems studied along the change from linear **LM-5** to kinked **KP-5a** structure. Relative energies referred to **LM-5** (kcal mol^{-1})

	PDI					PDI_Q		E_{rel}
System	**A**	**B**	**C**	**D**	**E**	**A'**	**B'**	
LM-5	0.0435	0.0577	0.0631	0.0577	0.0435	0.0050	0.0050	0.00
LM-5'	0.0495	0.0634	0.0613	0.0309	0.0665	0.0060	0.0170	-11.42
KP-5'	0.0654	0.0387	0.0731	0.0401	0.0638	0.0172	0.0176	-23.44
KP-5a	0.0599	0.0553	0.0589	0.0553	0.0599	0.0185	0.0185	-21.47

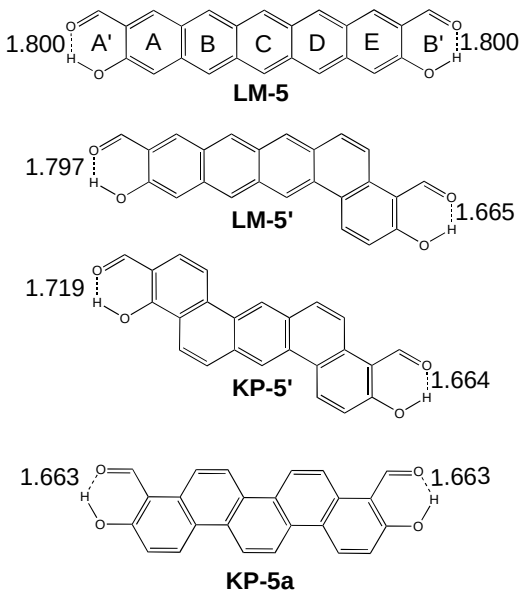


Figure 5. From linear to kinked PAHs. Bond lengths in Å.

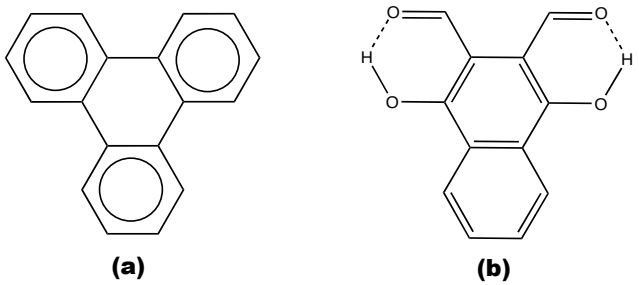
Now we can proceed kinking the other side of the chain, obtaining the **KP-5'** compound. We observed a decrease of the HB distance to 1.719 Å, but not as large as in the previous kink (1.665 Å). The difference again the presence of a 2HRI in the first kink and not in the second one. As seen in the previous kink, there is an important lost of aromaticity in ring **B** and an increase in rings **A** and **A'**. To get the total kinked compound **KP-5a**, we proceed to twist the central part of the chain. Aromaticity of the central rings becomes more similar to each other, with larger values for **A**, **C**, and **E**, as it was expected from Clar's model. *Quasi*-ring aromaticities present no important changes, as their kinked topology do not change when kinking the central part of the chain. The C1–C2 bonds bearing the

substituents in the two outer aromatic rings changes from 1.451 Å in **LM-5** to 1.399 Å in **KP-5a**, thus indicating an increase in the double character of this bond when going from linear to kinked structures. As before, the aromaticity of the *ipso*- and *quasi*-rings increases when going from the linear to the kinked topology.

Finally, Table 3 also collects the relative energies of the different conformers with respect to the linear one (**LM-5**). As it was expected, when kinking only one site, there is an important stabilization (-11.42 kcal mol^{-1}). This agrees with previous work showing that phenanthrene is more stable than anthracene because of better π-interactions.[39] When the other site of the chain is kinked, the stabilization energy increases up to -23.44 kcal mol^{-1}, so reinforcing the stabilization because of phenanthrene-like topology being more stable. In the last conformer, where all the chain is kinked, the relative energy decreases to -21.47 kcal mol^{-1} but because there is an increase of hydrogen repulsion through the whole chain, five 2HRI in **KP-5a** to be compared to three 2HRI for **KP-5'**.

Triphenylene-like RAHB

Let us move one step further and consider a set of compounds with two *quasi*-rings that resemble triphenylene (see Scheme 7). Starting from **KP-1a**, **KP-1b**, and **KM-1**, one can add successive benzene rings in the *ipso*-ring keeping the original two *quasi*-rings to generate the compounds depicted in Figure 6 named **KP-Lna**, **KP-Lnb**, and **KM-Ln**, with *n* being the number of benzene rings.



Scheme 7. (a) Clar's structure for triphenylene (b) triphenylene-like double-headed *quasi*-ring compound

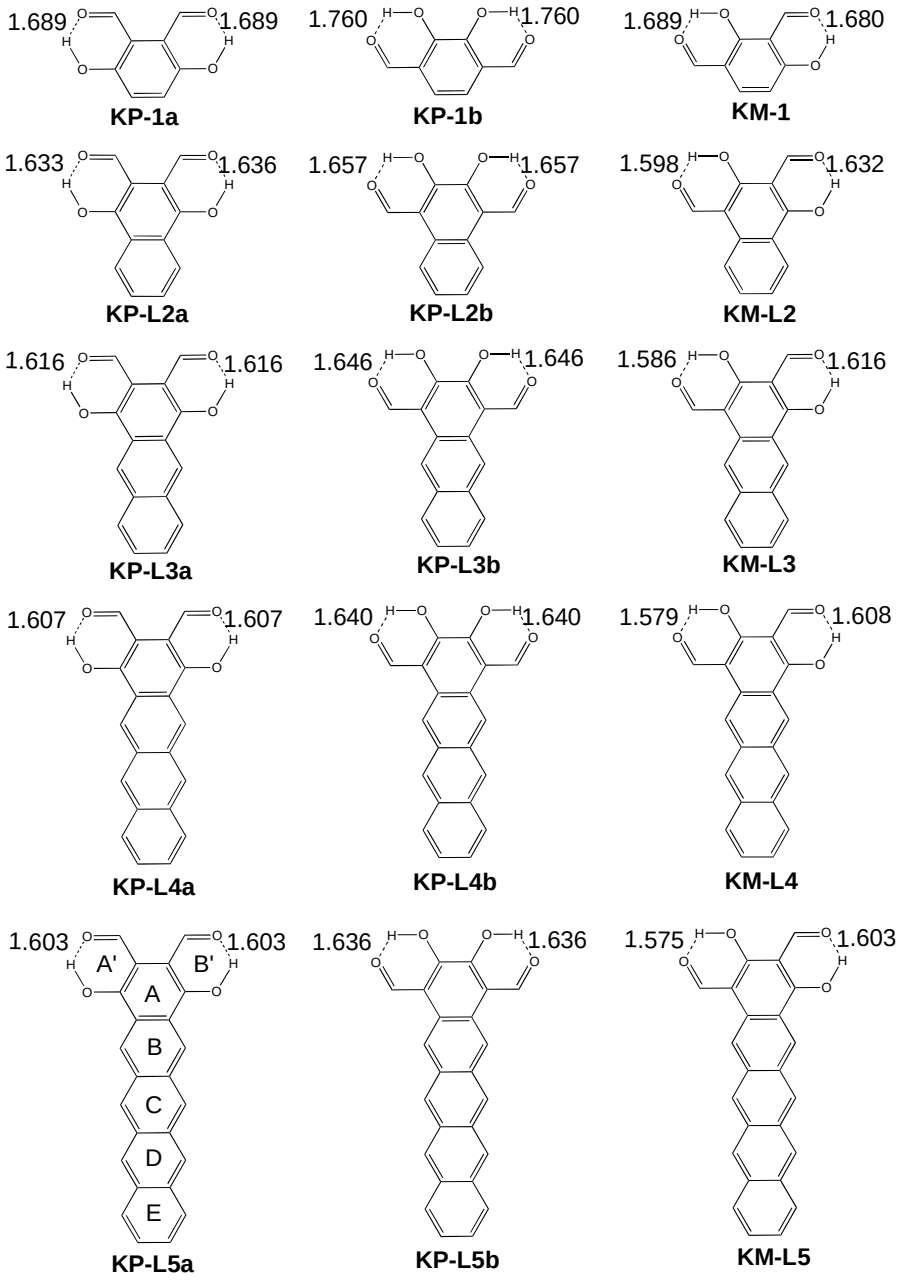


Figure 6. Triphenylene-like studied structures. Bond lengths in Å.

For systems with triphenylene-like structures, substituent effects on the RAHB of the *quasi*-rings remain the same in each series of compounds (for each column in Figure 6). After adding one ring (**KP-L2a**, **KP-L2b**, and **KM-L2**) an important shortening of the RAHB distances are observed. According to Clar's π-sextet model (Scheme 6), the central ring in triphenylene is an "empty ring" while the

outer rings are the most aromatic ones. Analyzing data collected in Table 4, one can observe the *ipso*-rings have much smaller aromaticities than the added benzene ring (e.g. for **KP-L2a** 0.0344 e for ring **A** and 0.0860 e for ring **B**). For these compounds it is expected that aromaticity of all external ring being large, so *quasi*-ring also increase their aromaticity when adding a benzene ring (from 0.0170 e for **KP-1b** to 0.0217 e for **KP-L2b**).

Table 4. PDI values (in e) of benzene rings and *quasi*-rings (PDI_Q) of the different triphenylene-like systems. Relative energies respect to KM-Ln (kcal mol^{-1}).

	PDI					PDI_Q		E_{rel}
Systems	**A**	**B**	**C**	**D**	**E**	**A'**	**B'**	
KP-1a	0.0668					0.0202	0.0202	10.86
KP-1b	0.0704					0.0170	0.0170	9.09
KM-1	0.0586					0.0149	0.0138	
KP-L2a	0.0344	0.0860				0.0242	0.0242	6.22
KP-L2b	0.0383	0.0870				0.0217	0.0217	12.31
KM-L2	0.0329	0.0843				0.0197	0.0175	
KP-L3a	0.0243	0.0682	0.0699			0.0259	0.0259	5.68
KP-L3b	0.0287	0.0703	0.0699			0.0230	0.0230	12.49
KM-L3	0.0238	0.0689	0.0691			0.0212	0.0183	
KP-L4a	0.0206	0.0590	0.0660	0.0613		0.0267	0.0267	5.47
KP-L4b	0.0249	0.0617	0.0670	0.0609		0.0237	0.0237	12.61
KM-L4	0.0201	0.0595	0.0667	0.0610		0.0218	0.0191	
KP-L5a	0.0189	0.0552	0.0633	0.0628	0.0564	0.0268	0.0268	5.47
KP-L5b	0.0227	0.0563	0.0658	0.0627	0.0561	0.0239	0.0239	12.72
KM-L5	0.0181	0.0545	0.0635	0.0634	0.0563	0.0221	0.0193	

The aromaticity of the *ipso*-ring can be tuned by adding extra 6-MRs to it, following a linear topology. As it was commented before, for [*n*]acenes with migrating π-sextet, the aromaticity of all rings decreases while increasing the size of the chain. Keeping this idea in mind, results show that the aromaticity of the *ipso*-ring, which has from the very beginning a low aromaticity because it resembles to the central ring of triphenylene, decreases with the increase in the number of 6-MRs attached to the *ipso*-ring. Because of that, the C=C bond in the ring junction between the *ipso*-ring and the *quasi*-ring becomes more localized for larger systems. The increase in the double character of this bond strengthens the RAHB, which becomes very short for **KM-L5** (going from 1.689 Å in **KM-1** to 1.575 Å in **KM-L5**).

As the *quasi*-ring has more available its π-electron pair for larger systems, its aromaticity increases going from, for instance, 0.0149 e for ring **A'** of **KM-1** to 0.0221 e for **KM-L5**. Indeed, for **KM-L5**, the *quasi*-ring is more aromatic than the *ipso*-ring with a PDI of 0.0181 e. Another important issue different from the previous linear and kinked systems studied is that convergence is not fully achieved for n=5, neither on the RAHB distance nor on the aromaticity of the RAHB *quasi*-ring.

As it was pointed out before, substituent effect are not changing while enlarging the chain for each series, so we can analyze the relation between aromaticities of the *ipso*-ring and the *quasi*-ring and the HB distances. The linear representation for the different parameters can be found in the SI for each *quasi*-ring. There are four different *quasi*-rings to take into account; one for **KP-Lna**, system with one 2HRI, one for **KP-Lnb**, species with two 2HRI, and two for **KM-Ln**, with one 2HRI and one weak HB, all of them with different HB distances. Figure S1 in SI shows a very good linear relationship between the aromaticity of the *quasi*-ring and the *ipso*-ring for the four series of different RAHB (average R^2 of 0.999); when the aromaticity of the *ipso*-ring decreases, that of the *quasi*-ring increases. Previous works[33,34] reported that an increase of the PDI in the *quasi*-ring reinforces the RAHB, and the HB distance is shortened. With this idea in mind, we expect to find four linear relationships between both parameters, the aromaticity of the *ipso*-ring and the HB length. This correlation is fulfilled for **A'** and **B'** *quasi*-rings of **KP-1a** and quasi-ring **B'** of **KM-1**. For the other two *quasi*-rings the expected correlation in not followed (Fig S2 in SI). In this case, the calculated HB distances in **A'** and **B'** *quasi*-rings of **KP-1b** and *quasi*-ring **A'** of **KM-1** are much longer that expected from the correlation of the series. Comparing these two compounds with the rest of the series, it can be observed that when a second 6-MR is added to **KP-1b** and **KM-1** an extra 2HRI between the H atom of the HCO group of the *quasi*-ring and one of the H atoms of the added benzene-ring that decreasing the hydrogen bond length. This repulsion is the same in the rest of the series, and therefore, the linear correlation between aromaticity of the *quasi*-ring, the *ipso*-ring and the RAHB

distances is kept, except for the **KP-1b** and **KM-1** that are not affected by any 2HRI.

The different behavior of **KP-1a** and **KM-1** (ring **B'**) can also be assessed analyzing the relative energy between conformers of the same size (Table 4). These two conformers present a very different stability through (10.86 kcal mol^{-1} for **KP-1a** and 9.09 kcal mol^{-1} for **KP-1b** both with respect to **KM-1**) when compared to the rest of the series. These relative energies keep constant (approx. 5 and 12 kcal mol^{-1} respectively) through the series **KP-Lna**, **KP-Lnb** and **KM-Ln** when there are more than one acene-like ring, as the number of 2HRI remains the same. The relative stability of the three series (**KM-Ln** being the most stable, followed by **KP-Lna** and **KP-Lnb**) is ruled by the 2HRI between *quasi*-ring and the added benzene ring in **KP-Lnb** and between both *quasi*-rings and the added benzene ring in **KP-Lna**.

In the series of triphenylene-like compounds studied, the substituent effect remains the same. For this reason, in these systems we could assess the importance of π-delocalization within the *ipso* and *quasi* ring (aromaticity). This delocalization assists the HB, shortening it, so reinforcing the concept of resonance-assisted hydrogen bond.

Conclusions

Double-headed compounds having two intramolecular resonance-assisted hydrogen bonds (RAHB) have been designed with the aim of studying the relation between the RAHB length and the aromaticity of the different *ipso*-rings. For these purpose, we have built [*n*]acenes (linear) and [*n*]phenancenes (kinked) like compounds with different number of benzene rings. Two different effects are controlling the HB distances, namely, the connectivity between substituents of the *ipso*-ring and the topology of the benzene chains (being linear or kinked). The first effect has been decreased by adding up to five benzene rings between *quasi*-rings in [*n*]acenes and [*n*]phenancenes, so being the topology of the chain the

responsible of ruling the different HB strength. The HB lengths observed can be explained in most cases using an extended Clar's aromatic π-sextet model that incorporates the *quasi*-rings as if they were rings in benzenoids. In general, shorter HBs are found for the more aromatic *quasi*-rings. The existence of H···H bond repulsions in some kinked systems explain the exceptions found to this extended Clar's aromatic π-sextet model.

Finally, in order to assess the relation between aromaticity (based on PDI values) and HB length, triphenylene-like compounds have been studied. In these systems, where the connectivity between substituent is the same, we found good linear correlation between aromaticity of the *ipso*- and *quasi*-ring and the RAHB distances, thus reinforcing the Gilli's concept of resonance assisting the hydrogen bond formations in the *quasi*-ring.

Computational methods

All molecules considered in this study were calculated using the long-range corrected hybrid CAM-B3LYP level of theory[43] including the D3 version of Grimme's dispersion with Becke-Johnson damping[44] to provide a correct description of the distance-dependence of the hydrogen bonding interactions[45] as well as the inter-ring electron delocalization effects in the condensed benzenoid systems[38,46,47,38] The standard 6-311++G(d,p) basis set was used for all atoms. Vibrational analyses of optimized structures showed that the structures are minima in the potential energy surface. All calculations were carried out with the Gaussian 09 package.[48] To avoid the numerical-integration accuracy issues[49] and the basis-set dependence problems,[50] in this study the delocalization indices (DIs)[51] have been calculated within the representation of natural atomic orbitals (NAO)[52] available within the NBO6[53] and JaNPA[54] program interfaces.

DIs are among the most popular bonding indicators. They are closely related to the covalent bond-order indices[55] and provide a quantitative information on the

electron density shared between two atoms/fragments A and B. Within the NAO-based partitioning scheme the delocalization index for one-determinant closed-shell systems is congeneric with the quadratic bond-order originally proposed by Wiberg[56]

$$\delta(\mathrm{A},\mathrm{B}) = 2\sum_{\mu\in\mathrm{A}}\sum_{\nu\in\mathrm{B}}\left|P_{\mu\nu}\right|^2 \quad (1)$$

where $P_{\mu\nu}$ are the elements of the reduced density matrix in the NAO basis.[52]

Based on the finding of Fulton[55] and Bader[57] who showed that benzene has larger DIs in *para*-related atoms than in *meta*-related ones, the PDI[58] index uses the DIs of *para*-related atoms as a measure of aromaticity for six-membered rings (6-MRs):

$$PDI = \frac{\delta(A_1,A_4)+\delta(A_2,A_5)+\delta(A_3,A_6)}{3} \quad (2)$$

For PDI, the larger the index, the greater the aromaticity of the ring. Obviously, this index can only be applied to 6-MRs. We use it to discuss the aromaticity of both the benzene rings (PDI) and the *quasi*-ring (PDI_Q), also known as *quasi*-aromaticity.[59] It was demonstrated[60] for simple derivatives of benzene that PDI gives qualitatively the same results as other electronic indices as well as indices like the HOMA[61] structural index or the NICS magnetic index.[49] For this reason, in our studies we are using exclusively the PDI index.

Supporting Information

Linear correlation between PDI for the *ipso* and *quasi*-rings (Figure S1) and linear correlation between aromaticity of the *ipso*-ring and RAHB bond length (Figure S1) for the triphenylene-like compound. Optimized Cartesian coordinates for all compounds considered at the CAM-B3LYP/6-311+G(d,p)+GD3B level of theory are given in a separated file.

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