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Are Antiaromatic Rings Stacked Face-to-Face Aromatic?†

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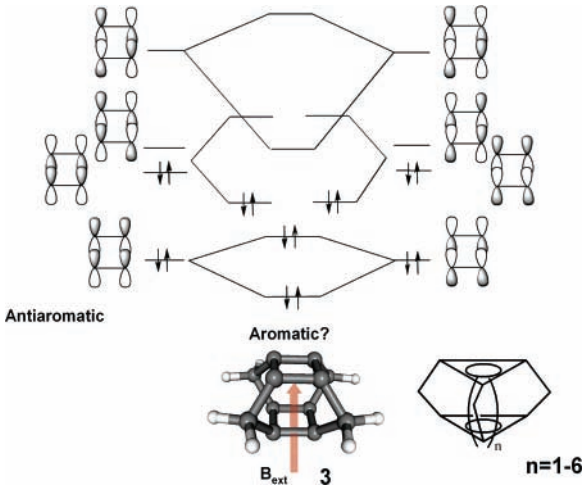
ABSTRACT



The stacking of 4*n* π electron hydrocarbon rings into superphane structures can eliminate their antiaromaticity and result in through-space three-dimensional aromatic character. This is demonstrated by the bond length equalized geometries and diatropic NICS values of the methano-bridged superphane series with interacting three- to nine-membered 4*n* π electron rings. Along with triplet and Möbius strategies, stacking is the third way to achieve aromatic ring systems with 4*n* π electrons.

Stacked hydrocarbon rings can exhibit three-dimensional electron delocalization (3D aromaticity) circulating through space. We now describe intriguing chemical and magnetic properties of phanes comprised of two nominally anti-aromatic rings. Classical examples of 3D delocalized systems (e.g., closoboranes,[1,2] Zintl ions,[3] and classical hydrocarbon cages[4−7]) profit from spherical (isotropic) circulation of electrons generally through interacting bonds. Similarly, nanotubes[8] and belt-shaped structures,[9] such as cyclacenes[10] and transannulenes,[11] are characterized by cylindrical through-bond delocalization. In contrast to such structural cages or tubes, systems with interacting chromophore subunits, such

† Dedicated to Professor Ken Houk on the occasion of his 65th birthday.
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as cyclophanes,[12] superphanes[13] (i.e., multibridged cyclophanes), and related compounds benefit from through-space delocalization giving rise to the transannular effects discussed in the pioneering work of Cram.[14] The relative size, distance, and orientation between individual chromophore subunits is known to affect the bulk properties of these systems.[14a,b,15] Understanding and ultimately controlling the through-space electron delocalization between organic subunits is a fundamental challenge for the creation of molecular electronic devices.[16]

Many superphanes comprised of benzenoid arenes and bridging chains, varying from two to four CH_2 or heteroatom units, have been prepared[13,17] and computed[18] during the last two decades. However, investigations of similar systems with non-benzenoid $4n+2$ π electron or $4n$ π electron rings are sparse. Despite the successful synthesis of metal-capped cyclobutadieno-superphanes by Gleiter et al.,[19] those phanes do not have interacting antiaromatic rings.[20] We now show that phanes comprised of two formally antiaromatic rings actually can exhibit aromatic behavior.

Qualitative frontier orbital analysis suggests that a parallel "face-to-face" orientation of two *aromatic* rings should result in their repulsive interaction.[21] Conversely, the analogous interaction of two stacked *antiaromatic* rings should lead to stabilization. As shown in the TOC figure, the unfavorable individual HOMOs of the monomeric units relate to the favorable doubly degenerate HOMOs of the dimer. Not only ground states but also transition states are stabilized, as suggested by the experimental syn dimerizations of both cyclobutadiene[22] and pentalene.[23] Such stabilizing interactions have often been anticipated for cyclophane-type structures, but Böhm's MINDO study[24] suggested that they should not be significant at inter-ring distances greater than about 2.4 Å. This is the smallest distance realized experimentally to date. Li and Houk's study of cyclobutadiene dimerization[25] found a D_{4h} syn stationary point with two stacked cyclobutadienes separated by 2.45 Å (Figure 1).

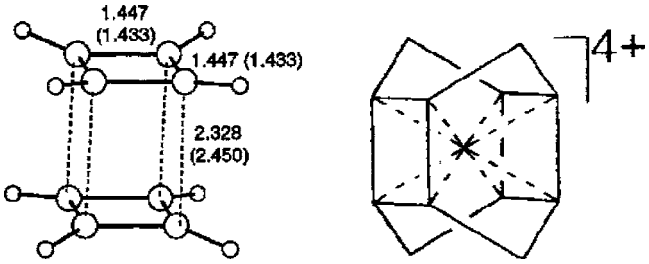

Figure 1. Left: second-order saddle point optimized by Houk and Li[25] at the CASSCF/3-21G (CASSCF/6-31G*) level; bond lengths are in Å. Right: cage structure with interacting cyclobutadienes investigated by Wang et al. in ref 27.

Although the square symmetry of the four-membered rings (4MRs) clearly indicates a stabilizing diminution of their antiaromaticity, the stationary point has two imaginary frequencies corresponding to the degenerate synchronous cycloaddition modes. Similarly, the C_{2h} [3$_4$](1,2,3,4) superphane structure with rectangular 4MRs, reported by Mireles et al.,[18a] is a second-order saddle point at the B3LYP/6-31G* level.[26] Further optimization led to a syn Diels−Alder dimer structure. Wang et al. described carbon atom inclusion compounds having a cage structure containing two 4MRs held face-to-face in D_{4h} symmetry[27] (Figure 1). However, the aromatic properties of such cages were not discussed (we consider this issue here).

We now analyze a series of methano-bridged superphane singlets resulting from the interaction of three- to nine-membered annulene rings, aromatic as well as antiaromatic [see the TOC Figure as well as Figure 2 (enlarged in the Supporting Information)]. Such small bridges maximize both

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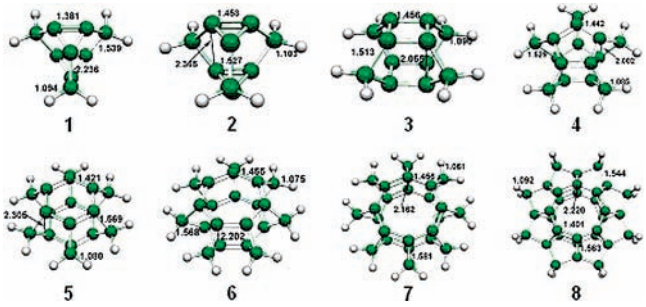

Figure 2. Illustrative bond lengths and structures of **1**−**8** optimized at the B3LYP/6-311+G** level; see Supporting Information Figure 1S for **9**. A larger version of Figure 2 is also given in the Supporting Information.

the transannular and, to some extent, the through-bridge orbital interactions by forcing the rings to lie close together.

The geometries of the $[1_n](1,....,n)$ superphane series ($n = 3-9$) were optimized at the B3LYP/6-311+G** level; vibrational frequencies verified that all structures are minima.[28] Nucleus-independent chemical shift indexes[29,30] were computed at the GIAO-PW91/IGLO-III level.

General Structural Trends. The smallest arene-based superphane is built by connecting two cyclic C_3^+ units with CH_2 bridges to give the 4π $[1_3](1,2,3)$cyclophane dication (**1**); its inter-ring distance is 2.236 Å. Similar bridging of two 4π antiaromatic $C_3H_3^-$ units gives the analogous dianionic cyclophane (**2**). The two C_3^- rings are spaced further apart (2.365 Å) due to the Coulomb repulsion experienced by the 4 π electrons in the individual 3MRs. In contrast, the neutral cyclobutadiene-based 8π $[1_4](1,2,3,4)$ cyclophane (**3**) (see TOC Figure) has a much shorter inter-ring distance (2.055 Å). The $C_{ring}-C_{ring}$ bond length (1.456 Å) is about the same as in the Houk and Li stationary point (Figure 1). The local D_{4h} symmetry of the 4MRs is consistent with decreased antiaromaticity.

The shorter inter-ring distance (2.002 Å) and smaller $C_{ring}-C_{bridge}-C_{ring}$ bond angle (81.8°) (see Table 1) in the 8 π electron D_{5h} $[1_5](1,2,3,4,5)$ cyclophane (**4**) are somewhat surprising, given its dipositive charge. Reducing this CCC angle evidently helps relieve the tangential H···H repulsion (H_{tang}) by moving the bridging carbons further apart. The longer $C_{bridge}-C_{ring}$ bonds in $[1_6](1,2,3,4,5,6)$ cyclophane (**5**) (1.569 Å) also reflect the greater repulsion between the tangential H atoms with increasing ring size. The larger inter-ring distance in **5** (2.306 Å), as compared to **3** and **4**, demonstrates that stronger $\pi-\pi$ repulsion occurs between the two benzenoid rings. This interpretation is reinforced by the geometrical properties of the smallest 16 π electron phane, C_{2v} $C_{21}H_{14}^{2-}$ (**6**). Although **6** has $C_{bridge}-C_{ring}$ bond lengths similar to **5**, the 7MR separation (2.202 Å) in **6** is 0.1 Å smaller than that between the two benzenoid rings in **5**, *despite the doubly negative charge* in **6**. Larger superphanes with 16 π electrons were constructed by bridging eight- (**7**) and nine-membered annulenes. However, these structures are increasingly perturbed by the proximity of the tangential H's. As a result, D_{9h} $C_{27}H_{18}$ is not a minimum. Although D_{8h} $C_{24}H_{16}$ (**7**) is a minimum, consequences of its steric constraints are evident; **7** has very short C−H bond lengths (1.061 Å) and elongated $C_{bridge}-C_{ring}$ bond distances (1.581 Å). Both the inter-ring separation (2.162 Å) and the delocalized D_{8h} symmetry of the rings suggest large transannular molecular orbital interactions.

Superior structural alternatives for the larger superphanes involve substituting tangential pairs of H atoms by additional CH_2 bridges (e.g., **8** and **9**). Both $C_{32}H_{16}$ D_{8h} (**8**; Figure 2) and $C_{36}H_{18}^{2+}$ D_{9h} (**9**; Supporting Information, Figure 1S) have short $C_{ring}-C_{ring}$ and inter-ring distances (2.220 Å and 2.198 Å, respectively).

Overall, the geometrical parameters of the $[1_n](1,....,n)$ superphane series depend on the H_{tang} repulsive interactions, the extent of transannular stabilizing interactions, and the molecular charge. Note that stacked antiaromatic rings (**3**, **4**, and **6**−**9**) have shorter inter-ring separations than the benzenoid superphane (**5**).

General NICS Trends. The isotropic NICS[29,30] values at the superphane centers of symmetry ($NICS_{cage}$ in Table 1) demonstrate that stacked ring systems with total $4n$ π electron counts do not exhibit paratropicity (antiaromaticity). The same is true at the centers of each of the rings comprising the phanes, where $NICS_{ring}$ is always locally diatropic (aromatic), irrespective of the number of π electrons in the parent $(CH)_n^q$ rings ($4n+2$ or $4n$ π). However, the stacking of the *aromatic* parent rings in **1** and **5** results in only weakly negative (diatropic) $NICS_{cage}$ values (−4.1 and −8.1, respectively), whereas the phanes with interacting parent *antiaromatic* rings exhibit large negative $NICS_{cage}$ values (−29.8 to −56.4). The latter behavior documents the transannular electron interactions illustrated in the TOC Figure.

Moreover, the $NICS_{ring}$ values in the phanes range from −11.5 for **5** to −47.2 for **2** and *do not* correlate either with increasing ring size or with the number of π electrons. On the basis of isotropic NICS, we conclude that both stacked aromatic and antiaromatic rings result in diatropic superphanes, with the latter having larger through-space electron delocalization. Likewise, the isotropic $NICS(1)_{ring}$ values for the aromatic ring based **1** and **5** at points 1 Å above the ring centers[29b,c,30] on the outside of the cages are more positive (paratropic) than those of the other phanes. The 3MR systems exhibit contrasting magnetic properties, before and after stacking. Although $NICS(1)_{ring}$ of D_{3h} $C_3H_3^+$ is −14.7

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Table 1. Inter-Ring Distances (D), $C_{ring}-C_{bridge}$ and $C_{ring}-C_{ring}$ Bond Lengths (Å), and $C_{ring}-C_{bridge}-C_{ring}$ Bond Angles at the B3LYP/6-311+G** Level for the Methano-Bridged Superphane Series[a]

	D	$C_{ring}-C_{bridge}$	$C_{ring}-C_{ring}$	$C_{ring}-C_{bridge}-C_{ring}$	HOMO−LUMO gap	$NICS_{cage}$	$NICS_{ring}$	$NICS(1)_{ring}$	$NICS_{zzcage}$	$NICS_{zzring}$	$NICS(1)_{zzring}$
$C_9H_6^{2+}$ D_{3h} **1**	2.236	1.539	1.381	93.2	3.39	−4.1	−26.5	+3.1	−23.7	−34.0	+17.1
$C_9H_6^{2-}$ D_{3h} **2**	2.365	1.527	1.453	101.5	1.69	−47.9	−47.2	−6.7	−44.0	−43.0	−15.3
$C_{12}H_{18}$ D_{4h} **3**	2.055	1.513	1.456	85.6	2.63	−41.6	−13.8	−7.6	−20.5	+22.0	−7.6
$C_{15}H_{10}^{2+}$ D_{5h} **4**	2.002	1.529	1.442	81.8	3.38	−46.7	−12.1	−4.8	−43.7	−7.1	−9.2
$C_{18}H_{12}$ D_{6h} **5**	2.305	1.569	1.421	94.5	1.89	−8.1	−11.5	−2.8	−42.9	−20.0	−7.4
$C_{21}H_{14}^{2-}$ C_{2v} **6**	2.202	1.568	1.455	89.2	1.95	−29.8	−17.5	−9.4	−29.0	−10.4	−17.0
$C_{24}H_{16}$ D_{8h} **7**	2.162	1.581	1.456	86.3	2.73	−35.5	−22.0	−9.6	−51.4	−33.5	−21.8
$C_{32}H_{16}$ D_{8h} **8**	2.220	1.563	1.401	90.4	2.14	−40.0	−21.7	−8.4	−49.0	−28.2	−19.4
$C_{36}H_{18}^{2+}$ D_{9h} **9**	2.198	1.586	1.412	87.6	2.30	−56.4	−40.7	−8.2	−49.2	−33.5	−19.7
$C_3H_3^+$ D_{3h}[b,c]	/	/	/	/	7.10	/	−21.1	−14.7	/	−31.4	−28.4
$C_3H_3^-$ C_s[b,c]	/	/	/	/	1.39	/	−9.3	+9.1	/	+15.6	+19.0
C_4H_4 D_{2h}[b]	/	/	/	/	1.93	/	+27.4	+17.9	/	+111.0	+56.3
$C_5H_5^+$ C_{2v}[b,d]	/	/	/	/	0.44	/	*+100*	+78	/	*+300*	*+237*
C_6H_6 D_{6h}[b]	/	/	/	/	4.21	/	−9.2	−7.6	/	−23.1	−15.0

[a] HOMO−LUMO gaps (eV) and NICS indexes (ppm) are at the PW91/IGLOIII level. [b] Geometrical parameters for the $(CH)_n$ monocycles ($n = 3-6$) are in the Supporting Information. [c] In addition to their opposite NICS values, the downfield proton chemical shift of $C_3H_3^+$ (∂ $^1H = 10$ ppm) contrasts sharply with the upfield shift of the unique proton pointing in C_s symmetry toward the shielding zone of $C_3H_3^-$ (∂ $^1H = 0$ ppm). [d] The abnormally large paratropic singlet C_{2v} cyclopentadienyl cation NICS values (in italics) are computational artifacts arising from its small HOMO−LUMO energy gap.

(aromatic), $NICS(1)_{ring}$ is +3.1 for its stacked counterpart, **1**. The nonplanar C_s $C_3H_3^-$ minimum $NICS(1)_{ring}$ is +9.1 (antiaromatic), whereas $NICS(1)_{ring}$ is −6.7 for stacked **2**. It is unlikely that electronic interactions with the CH_2 bridges are responsible for these differences.

The out-of-plane tensor component, $NICS_{zzcage}$ (z is the principal axis), provides a sounder analysis of ring current effects in the stacked systems than isotropic NICS.[30] However, the $NICS_{zzcage}$ and $NICS_{cage}$ results at the centers of symmetry are comparable, except for **1** and **5**. The $NICS_{zzcage}$ values for these two stacked aromatic ring systems are much more negative.

$NICS(1)_{zzring}$ is the best index for the analysis of individual rings. The behavior of the two 3MR systems differs dramatically. While $C_3H_3^+$ is aromatic (−28.4), its superphane (**1**) is antiaromatic (+17.1). Contrastingly, $C_3H_3^-$ is antiaromatic (+19), whereas **2** is aromatic (−15.3). The benzene $NICS(1)_{zzring}$ (−15.0) is reduced to only −7.4 in **5**, whereas $NICS(1)_{zzring}$ of the strongly antiaromatic cyclobutadiene (+56.3) is changed to −7.6 upon stacking into superphane **3**. The other superphanes, **4** and **6**−**9**, based on stacked singlet antiaromatic $C_nH_n^q$ $4n$ π electron rings, are also aromatic according to all the NICS indexes in Table 1.

These geometrical and NICS results demonstrate that stacking, along with triplet[32] and Möbius strategies,[31] is the third way to render $4n$ π electron systems aromatic. Note that the most stable $C_5H_5^+$ ring has D_{5h} symmetry and exhibits triplet aromaticity.[32] Its 8 π electron counterpart, the singlet [9]annulenyl cation, is a Möbius aromatic.[31b] The antiaromatic characteristics of individual rings with $4n$ π electrons disappear when two of them are stacked closely together, as in the methano-bridged superphanes described here. Even though the $4n$ π electron count is retained, these superphanes have delocalized structures and a high degree of diatropic (aromatic) character. They also exhibit larger transannular delocalization than the aromatic superphane analogues. Consequently, face-to-face stacked antiaromatic rings may offer better prospects than stacked aromatic rings for the creation of molecular electronic devices.

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Supporting Information Available: Figure S1 and enlarged Figure 2; geometries and energies of the structures given in Table 1; and complete ref 28. This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) The D_{5h} $C_5H_5^+$ triplet state has the lowest energy. See: Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.*, **1998**, *37*, 1945−1948. For a review of antiaromatic annulenes and triplet aromaticity, see: Wiberg, K. B. *Chem. Rev.* **2001**, *101*, 1317.