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Chemical Shifts of the [*N*]Phenylenes and Related Compounds

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Proton chemical shifts and nucleus-independent chemical shifts (NICS) have been computed for [*N*]phenylenes and related compounds using the GIAO/HF method. Proton chemical shifts calculated in the 6-31G* basis agree with measured values, where available, within ∼0.3 ppm. NICS values were calculated at the HF/3-21G level using B3LYP/6-31G* geometries. Both proton chemical shifts and NICS values show attenuation of aromatic and antiaromatic character in the six- and four-membered rings, respectively, in a manner dependent upon the positions of these rings in the molecule. These effects are greater in angular than in linear phenylenes. The central ring of a branched phenylene is found to be only slightly aromatic. The protons of the cyclic phenylenes resonate at slightly higher field than their angular counterparts. Both NICS and proton shifts of antikekulene suggest only slight additional antiaromatic character.

The [*N*]phenylenes contain alternating fused benzene and cyclobutadiene rings linked in an angular, linear, or branched manner.[1] The number of possible isomers increases rapidly with *N* including, in principle, cyclic, helical, and fullerenic structures or substructures. The geometry and thermochemistry of phenylenes have been surveyed recently by ab initio methods.[2] We now consider the aromatic character of the phenylenes. There is a large literature dealing with the relationship between proton chemical shifts and aromatic or antiaromatic character.[3] More recently, nucleus-independent chemical shifts (NICS),[4] based upon magnetic shieldings computed at selected locations such as the centers of rings, have helped to establish relationships between structure and aromatic character. For a large set of five-membered rings, NICS values have been shown to be directly related to energetic, geometric, and other magnetic criteria of aromatic character.[4a,d] Although these relationships in polycyclic heteroatomic systems can be more complicated when other factors predominate,[4f,g] increasing experience with NICS suggests that hydrocarbon species behave more regularly.[4] Calculations of both proton chemical shifts and NICS are applied to phenylenes in this study, in anticipation of the preparation of many of these systems.

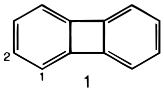
Computational Methods

Calculations were performed with GAUSSIAN 94[5] on Digital Alpha AXP 2100 servers and IRIS indigo workstations. Optimized geometries and energies were obtained in the 6-31G* basis[6] at the HF and B3LYP density functional levels.[7] NMR chemical shifts were calculated according to the GIAO method[8] at the HF/6-31G* level. Calculations of the proton chemical shifts of the phenylenes at this level generally reproduce experimental values to within 0.3 ppm, with the theoretical values at higher δ. Given that the experimental proton shifts have a small solvent dependence, the agreement is satisfactory. Where experimental values are not yet available, the computed shifts may serve as aids to assignment of spectra.

NICS(X) values were obtained with the GIAO method at the HF/3-21G level for B3LYP/6-31G* optimized geometries at points *X* Å above the ring centroids. Several verifications were made of the adequacy of the HF/3-21G level for computation of magnetic shieldings by comparison with results for representative phenylenes at higher levels. For purposes of discussion, the NICS values for both four- and six-membered rings (4-rings and 6-rings) are NICS(1.0). The 6-rings have their most negative NICS values very close to this point. The 4-ring values are positive, attaining a maximum at the ring centroid; such values are large, due in part to proximity to the test point of the four carbon nuclei and the CC and CH sigma bonds, which contribute locally.[4d] (This has been demonstrated by IGLO calculations,[9] which distinguish local sigma and pi contributions.) The NICS(1.0) values should be more indicative of π-electron effects and should provide better comparisons with the values found for 6-rings.

Biphenylene and Angular Phenylenes

The GIAO proton shifts of biphenylene **1** are H_1, δ 6.83 (6.60), and H_2, 6.90 (6.70) (experimental values[10] in parentheses). The NICS values are −8.0 (6-ring) and +7.0 (4-ring).



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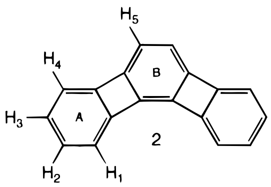

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Both the aromatic character of the 6-ring and the antiaromatic character of the 4-ring are attenuated[4a,j] with respect to benzene and cyclobutadiene, for which the respective calculated proton shifts are δ 7.59 (7.25) and 5.56; their NICS(1.0) values are −12.5 and +15.1 ppm.

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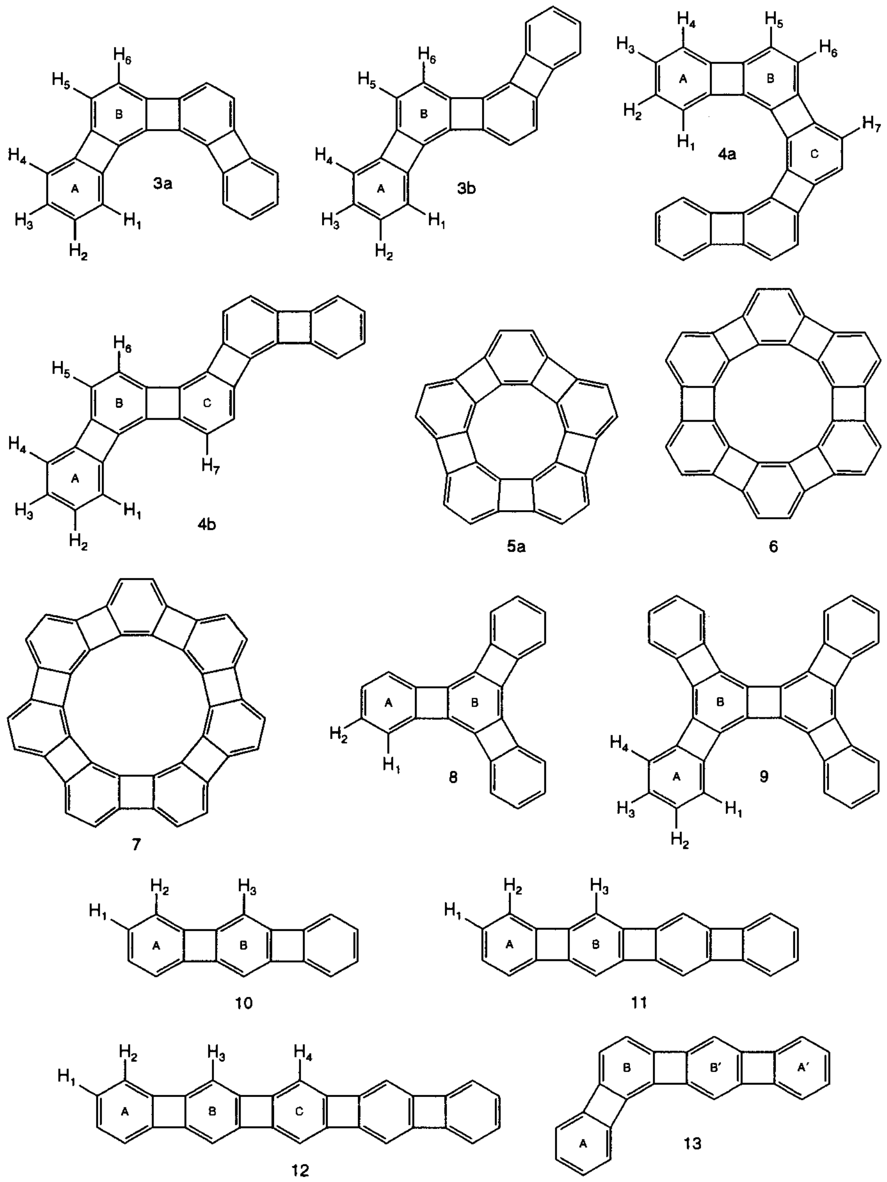
CHART 1



Computed proton chemical shifts of the angular [*N*]phenylenes for $N = 3$, 4, and 5 (structures **2**−**4**, of which **3** and **4** are in Chart 1) are given in Table 1, together with available experimental values. NICS values are in Table 2. Computed shifts for the protons on the A rings (H_1-H_4) range from 7.04 to 7.30 ppm, slightly downfield from the protons of **1**. (In the following, a terminal 6-ring of an angular phenylene is identified by the letter A; the adjoining interior ring is B, etc.) The NICS values for the A rings are in the narrow range −9.1 to −9.5, indicating a slightly greater aromatic character in **2**−**4** relative to that of **1**.

For the B ring of angular [3]phenylene **2**, the NICS value is −3.3 and the chemical shift of H_5 is δ 6.14. These results imply significantly diminished aromatic character in the central ring. There are similar chemical shifts (and nearly identical NICS values) in the two angular [4]phenylenes **3a** (C_{2v}) and **3b** (C_{2h}). The NICS value, −4.7 ppm, indicates that the B rings of both are somewhat more aromatic than the central ring of **2**. The chemical shifts of the interior protons (H_5 and H_6) of **3a** and **3b** are downfield from H_5 of **2**.

[5]phenylene **4a** and its zigzag counterpart **4b**, which have nearly identical NICS values, are analogues of **3a** and **3b**. Their B rings have a NICS value of −4.3 ppm. The nearly identical chemical shifts of the protons of the B ring of **4a** (H_5 and H_6), δ 6.3, are essentially the same as those of **3a**. However, the NICS value of the central (C) ring of **4a**, −6.2, is more negative than that of the B ring. By the NICS criterion, then, the central 6-rings of these [5]phenylenes are somewhat more aromatic than the B rings. The resonances of the two equivalent protons of the central ring of **4a** (H_7), δ 6.57, are substantially upfield from benzene and even from the proton resonances of all terminal phenylene rings but are downfield from the proton shifts of the B rings of **2**, **3a**, and **3b**.

The suggestion of a damped alternation of aromatic character in the 6-rings of **4a** and **4b** led us to investigate the zigzag angular [7]phenylene, a C_{2v} structure analogous to **4b**. The NICS values (Table 2) show that the B ring (−4.4) has the least aromatic character, which rises significantly at the C ring (−5.9) and diminishes somewhat in the central ring (−5.3). A corresponding alternation is seen in the NICS values of the 4-rings and the proton shifts.

Angular phenylenes may in principle assume helical form for $N \geq 6$.[2a] For helical [6]phenylene, the proton shifts of H_1-H_4 (Table 1), δ 7.20, 6.99, 7.16, and 7.08, respectively, are

TABLE 1: Proton Chemical Shifts (δ) of Phenylenes

molecule	H_1	H_2	H_3	H_4	H_5	H_6	H_7-H_{10}
biphenylene, **1**, D_{2h}	6.83 (6.60)[a]	6.90 (6.70)					
			Angular and Helical Phenylenes				
[3]phenylene, **2**, C_{2v}	7.18 (6.959)[b]	7.16 (6.976)	7.18 (6.991)	7.09 (6.889)	6.14 (6.176)		
[4]phenylene, **3a**, C_{2v}	7.16 (6.888)[b]	7.11 (6.939)	7.14 (6.927)	7.04 (6.825)	6.35 (6.312)	6.32 (6.312)	
[4]phenylene, **3b**, C_{2h}	7.09	7.10	7.12	7.04	6.33	6.41	
[5]phenylene, **4a**, C_{2v}	7.30 (6.934)[b]	7.19 (7.011)	7.20 (6.993)	7.08 (6.871)	6.32 (6.294)	6.30 (6.294)	6.57 (6.511)
[6]phenylene, C_2	7.20	6.99	7.16	7.08	6.35	6.33	6.54, 6.54
[8]phenylene, C_2	7.26	6.94	6.98	6.85	6.08	6.17	6.53−6.58
			Branched Phenylenes				
[4]phenylene, **8**, D_{3h}	7.43 (7.31)[c]	7.40 (7.24)					
[6]phenylene, **9**, D_{2h}	7.39	7.34	7.33	7.35			
			Linear Phenylenes				
[3]phenylene, **10**, D_{2h}	6.53 (6.19)[d]	6.73 (6.44)	6.56 (5.91)				
[4]phenylene, **11**, D_{2h}	6.40 (6.81)[e]	6.65	6.38 (5.89)				
[5]phenylene, **12**, D_{2h}	6.35	6.61 (6.81)[f]	6.30 (5.90)	6.25 (5.56)			

[a] Reference 10. [b] Values in CD_2Cl_2, ref 1. [c] Values in acetone-d_6, ref 11. [d] Values in C_6D_6, ref 16. [e] Value for the tetrakis(trimethylsilyl) derivative in C_6D_6, ref 1. [f] Value for the tetrakis(trimethylsilyl) derivative in C_6D_6, ref 17.

TABLE 2: B3LYP Energies (Hartrees) and NICS(1) Values of Phenylenes and Model Compounds

molecule	energy	A ring	B ring	4-ring (outer)	4-ring (inner)
benzene	−232.24870	−12.5			
cyclobutadiene	−154.67547			+15.1	
biphenylene, **1**	−462.03202	−8.0		+7.0	
		Angular Phenylenes			
[3]phenylene, **2**	−691.82039	−9.5	−3.3	+3.1	
[4]phenylene, **3a**	−921.60746	−9.1	−4.7	+4.2	+0.8
[4]phenylene, **3b**	−921.60766	−9.1	−4.7	+4.3	+0.8
[5]phenylene, **4a**	−1151.39454	−9.2	−4.3 (−6.2)[a]	+4.0	+1.5
[5]phenylene, **4b**	−1151.39518	−9.2	−4.3 (−6.2)[a]	+3.9	+1.5
[7]phenylene	−1610.97012	−9.2	−4.4 (−5.9)[a,b]	+4.0	+1.4[b]
		Branched Phenylenes			
[4]phenylene, **8**	−921.61445	−10.7	−1.1	−0.4	
[6]phenylene, **9**	−1381.19193	−10.1	−2.4	+1.3	−2.4
		Linear Phenylenes			
[3]phenylene, **10**	−691.81635	−7.5	−5.4	+7.3	
[4]phenylene, **11**	−921.60021	−7.3	−5.2	+7.6	+7.5
[5]phenylene, **12**	−1151.38394	−7.3	−5.1 (−5.1)[a]	+7.6	+7.7
[4]phenylene, **13**	−921.60619	−9.8	−2.9	+2.3	+2.6
		−7.5[c]	−6.4[c]	+7.5[d]	
		Model Compounds			
14	−308.36036	−6.0		+10.4	
15	−385.80222	−11.8		−3.7	
16	−384.48969	−1.1		−0.7	
17	−539.35564	−11.3		−2.5	
18	−460.63043	−2.6		−4.2	
19	−692.09030	−10.5		−3.5	
20	−232.14504			−4.5	

[a] The value in parentheses is that of the C ring. [b] The value at the central 6-ring is −5.3 and that of the innermost 4-ring is +2.1 ppm. [c] Values for rings A′ and B′. [d] Value for the 4-ring between rings A′ and B′.

typical of terminal rings. The corresponding values in helical [8]phenylene are 7.26, 6.94, 6.98, and 6.85. Proton shifts for H_5 and H_6 (B ring) are 6.35 and 6.33 for [6]phenylene and 6.08 and 6.17 for [8]phenylene. The remaining interior hydrogens in both helical molecules resonate from δ 6.53 to 6.58.

Cyclic Phenylenes

The proton chemical shifts and NICS values of the as yet unknown cyclic [*N*]phenylenes, $N = 5$, 6, and 7, are given in Table 3. Cyclic [5]phenylene **5** (C_{5v}, the phenylene analogue of corannulene) is bowl-shaped, whereas the planar transition state for bowl interconversion (**5a**) has D_{5h} symmetry.[2b] Both *cyc*[6]phenylene ("antikekulene") **6** and *cyc*[7]phenylene **7** are planar.[2b] The proton chemical shifts of the cyclic [*N*]phenylenes are δ 6.45, 6.65, 6.30, and 6.45 for **5**, **5a**, **6**, and **7**, respectively. They are upfield from similar internal protons of the larger angular phenylenes, for example, δ 6.57 for H_7 in **4**.

TABLE 3: B3LYP Energies (Hartrees), Proton Shifts, and NICS(X)[a] for Cyclic [*N*]Phenylenes

molecule	energy	^1H	6-ring	4-ring	center
cyc[5]phenylene, **5**, C_{5v}	−1148.87385				
inside bowl		6.45	−10.2	−2.2	−1.4, −2.2
outside bowl		6.45	−7.5	−0.7	−1.4, −0.5
cyc[5]phenylene, **5a**, D_{5h}	−1148.84584	6.65	−6.2	+3.2	−2.0
cyc[6]phenylene, **6**, D_{6h}	−1378.71543	6.30	−5.2	+2.1	+2.5
cyc[7]phenylene, **7**, D_{7h}	−1608.14973	6.45	−5.2	+2.6	+0.2

[a] Values at $X = 1.0$ Å from the ring centroid. For the central ring of **5**, these are preceded by the NICS(0) value.

NICS values for the 6-rings of the planar cyclic phenylenes are −5.2 for **6** and **7** and −6.2 for **5a**. The latter value is that found for the C ring of angular [5]phenylene **4**. NICS(0) values at the centers of planar cyclic phenylenes (**5a**, **6**, and **7**) suggest slightly aromatic character for $N = 5$ (**5a**) and slightly antiaromatic character for antikekulene (**6**), perhaps associated with the inner 12-membered ring. This inference is supported by the proton resonance of antikekulene (**6**), δ 6.30, which is at somewhat higher field than in either **5a** or **7**.

The conclusion that there is little additional antiaromatic character in **6**[2b] is confirmed by the small endothermic heat of homodesmic reaction 1, for which $\Delta E = 6.0$ kcal/mol at

$$2(\mathbf{4a}) \rightarrow \mathbf{6} + 2(\mathbf{1}) \tag{1}$$

$$6(\mathbf{4b}) \rightarrow \mathbf{6} + 6(\mathbf{3b}) \tag{2}$$

B3LYP/6-31G*. This is in good agreement with $\Delta H = 6.0$ and 6.2 kcal/mol at HF and BLYP/6-31G* levels, respectively, obtained for reaction 2 by means of an enthalpy increment for a hypothetical angular C_6H_2 reference moiety.[2b]

NICS values for the 4-rings of these planar cyclic phenylenes range from 2.1 to 3.2 ppm, slightly larger than those found in the inner 4-rings of the angular [5]phenylenes (Table 2).

We computed NICS(1.0) values for both the concave and convex sides of the bowl of the C_{5v} cyclic pentamer (**5**). The 6-ring NICS values are −10.2 (in the bowl) and −7.5 (out of the bowl). The former is comparable to those of terminal 6-rings of nonlinear acyclic phenylenes; its large magnitude can tentatively be ascribed to additive contributions from proximal 6-rings. The 4-rings of **5** have NICS(1.0) values of −2.2 (inside) and −0.7 (outside). Finally, the 10-membered ring has small NICS(0.0) = −1.4 and NICS(1.0) = +2.2 (inside) and −0.5 (outside).

Branched Phenylenes

Two branched [*N*]phenylenes have been considered: [4]-phenylene **8** (D_{3h}) and [6]phenylene **9** (D_{2h}). Their outer 6-ring NICS values are −10.7 and −10.1 (slightly more negative than the A rings of the angular phenylenes), and their protons resonate from δ 7.33 to 7.43. Thus, the outer 6-rings in **8** and **9** are almost as aromatic as benzene, whereas all other rings are essentially nonaromatic. The inner 6-ring NICS values in **8** and **9** are only −1.1 and −2.4, respectively. The inner 6-ring of **8** has highly alternating bond lengths: 1.348 and 1.490 Å at B3LYP/6-31G*; the X-ray lengths for its hexakis(trimethylsilyl) derivative range from 1.333 to 1.502 Å.[11] Significant bond alternation is also found in **9**.

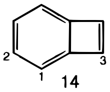
The NICS value of the 4-rings of **8** is −0.4; the outer and inner 4-rings of **9** have NICS values of 1.3 and −2.4.

Linear Phenylenes

The range of NICS(1.0) values in the 6-rings of the linear compounds is rather small: −7.5 to −5.1 ppm. An even smaller range is found for the 4-ring NICS values: +7.3 to +7.7. Proton chemical shifts of the linear phenylenes for $N = 3-5$ (**10**−**12**) are given in Table 1. Resonances for protons on the outer two benzene rings decrease slightly with *N*: $H_1 = \delta$ 6.53, 6.40, 6.35; $H_2 =$ 6.73, 6.65, 6.61; $H_3 =$ 6.56, 6.38, 6.30. These proton shifts are considerably smaller than those of the terminal rings of the angular phenylenes (which *increase* with *N*). The protons on the central benzene ring of linear [5]phenylene have δ 6.25. In general, linear [*N*]phenylenes have smaller NICS values in their outer 6-rings (A) than do the corresponding angular compounds. Thus, for $N = 3$, 4, and 5 (**10**−**12**) the A-ring NICS values are −7.5, −7.3, and −7.3, respectively. This effect is also seen in the "mixed" linear-angular [4]-phenylene **13** of C_s symmetry, in which the NICS values of the A rings at the angular and linear termini are −9.8 and −7.5, respectively. The penultimate (B) rings of **10**−**12** have NICS values of −5.4, −5.2, and −5.1, respectively. The central (C) ring of linear [5]phenylene **12** has NICS = −5.1.

Discussion

The interaction between fused benzene and cyclobutadiene rings can be probed further by examining several compounds related to the phenylenes (Table 2). Benzocyclobutadiene **14**, a reactive compound that readily dimerizes,[12] has NICS values of −6.0 and +10.4 ppm for its 6- and 4-rings,[4a] respectively. These rings are less aromatic and antiaromatic[4j] than benzene (−12.5) and cyclobutadiene (+15.1). The bond alternation in the HF/6-31G* and B3LYP/6-31G* geometries of benzocyclobutadiene is that shown in structure **14**. Quinoid structure **14a** has been proposed for benzocyclobutadiene because its observed proton shifts resemble those of *o*-xylylene.[13] However, hypothetical structure **14a** would be ~50 kcal/mol higher in energy than **14**.[14] Moreover, the calculated proton shifts of **14** are in excellent agreement with experiment: $H_1 = 5.76$ (5.78), $H_2 = 6.27$ (6.26), and $H_3 = 6.43$ (6.36). Thus, there is no need to invoke the quinoid form **14a**.



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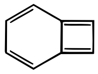
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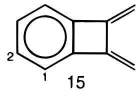

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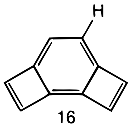
The proton resonances of benzocyclobutadiene are upfield from those calculated for bis(methylene)benzocyclobutane **15**, $H_1 = 7.56$ and $H_2 = 7.49$, which are typical of protons on benzene rings. Similarly, NICS values in the 6-ring and 4-ring of **15** are −11.8 and −3.7; the former is close to that of benzene. The B3LYP/6-31G* bond lengths of the 6-ring of **15** exhibit little alternation: 1.388, 1.404, 1.405, and 1.411 Å. Thus, **15** has a fully aromatic benzene ring. This implies that the attenuation of aromatic character in **14** arises from antiaromatic effects of its cyclobutadiene ring, not from hybridization or strain effects alone.

A similar comparison can be made for angular [3]phenylene **2**: angular benzodicyclobutadiene **16** and tetrakis(methylene)-benzodicyclobutane **17**. The benzene-like ring of **17** has little bond alternation (bond lengths = 1.373, 1.394, 1.411, and 1.420 Å). The chemical shift of the benzenoid protons at δ 7.48 is downfield from that of H_5 of **2**, δ 6.14, and the NICS values of the 6-ring and 4-ring are −11.3 and −2.5, respectively. Benzodicyclobutadiene (**16**), in contrast, has a cyclohexatriene-like 6-ring (bond lengths = 1.338, 1.350, 1.475, and 1.486 Å), the protons of which resonate at δ 4.97, higher even than those of its 4-rings at δ 6.77. NICS values of its 6-ring and 4-ring are −1.1 and −0.7, respectively. These magnetic criteria, together with its pronounced bond alternation, characterize the 6-ring of **16** as polyolefinic.



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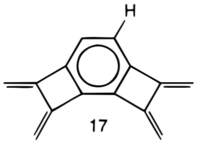

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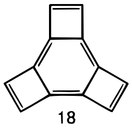
Unlike the branched [4]phenylene **8**, the analogous hexakis-(methylene) compound **19** has a NICS value of −10.5 and little bond alternation in its evidently quite normal benzene ring. In contrast, the central ring of **8** has a NICS value of −1.1. Benzotricyclobutadiene **18** has NICS values of −2.6 and −4.2, respectively, in its 6- and 4-rings. The negative NICS(1) value of its 4-rings and calculated proton shift, δ 6.86, are close to those of the known compound dimethylenecyclobutene **20**, the NICS value and ring-proton shift of which are −4.5 ppm and δ 6.94 (6.70, exptl[15]). The polyolefinic nature of **18** is extreme; the degree of bond alternation in its 6-ring, 1.338 and 1.515 Å in B3LYP/6-31G*, is the greatest of the compounds studied.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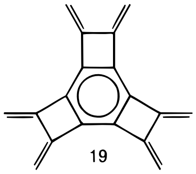
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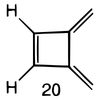

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Conclusion

The [*N*]phenylenes have attenuated benzenoid aromatic character, intermediate between fully aromatic exocyclic methylene analogues (e.g., **15**, **17**, and **19**) and model compounds having terminal cyclobutadienes (e.g., **14**, **16**, and **18**). Terminal 6-rings are the most aromatic, and B rings are usually the least so. Aromatic character in angular phenylenes may increase somewhat in more remote interior 6-rings, such as the central ring of [5]phenylene **4a**, and a damped alternation may be exhibited by larger angular systems such as [7]phenylene. Inner 4-rings of the phenylenes show much diminished antiaromatic character and in model compounds may even have negative NICS values. Examination of model compounds with exocyclic double bonds demonstrates that fused benzenoid and cyclobutadienoid moieties affect one another: the mutual diminution of aromatic and antiaromatic character[4j] is not ascribable to strain and hybridization.

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References and Notes

(1) For a recent review on phenylenes, see: Vollhardt, K. P. C.; Mohler, D. B. *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press: London, 1996; Vol. 5, p 121.

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