

## A Theoretical Study of Large Planar [N]Phenylenes

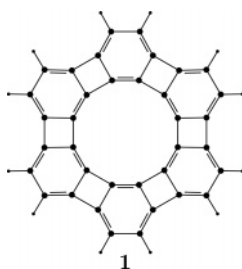
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Ab initio studies of 14 [N]phenylenes containing 12-membered rings furnish geometries, energies, standard heats of formation, NICS(1) values, and proton chemical shifts. The extent of double-bond localization,  $\Delta R$  (in Å), for each type of the 58 unique six-membered rings—angular, branched, and terminal—varies linearly with both their NICS(1) values and proton resonances. Values of these parameters depend upon the number and type of neighboring rings.  $\Delta R_{\text{tot}}$ , the molecular sum of the bond localizations, correlates linearly with the ab initio energy and heat of formation. Reactions that conserve the numbers of angular, branched, terminal, and 12-membered rings are thermoneutral, and their net  $\Delta R_{\text{tot}}$  and  $\Delta \text{NICS}(1)$  are also nearly zero.

[N]Phenylenes are polycyclic hydrocarbons in which the *N* benzene rings are separated by cyclobutadienes. Already synthesized in zigzag, linear, and helical forms, and combinations thereof,<sup>1</sup> phenylenes are potential fullerenes, bowls, cycles, and sheets.<sup>2</sup> Some could serve as a basis for nanostructural and/or electronic materials, given their unusual nature. This work considers 14 polycondensed planar phenylenes containing one or more 12-membered rings (Charts 1 and 2), the parent of which is cyclic [6]phenylene (**1**), antikekulene.<sup>3</sup> “Antikekulenes” **1–8** are planar sheets, converging in principle to a phenylene carbon monolayer; **9–14** have one or more terminal benzene rings through angular benzocyclobutadiene annelation.



Ab initio calculations provide energies, geometries, standard enthalpies of formation, and chemical shieldings of these antikekulenes. The energetics are well described by use of ring-conserving (“homocyclic”) reactions and by an increment scheme. The extents of bond alternation, nucleus-independent chemical shielding, and proton shifts are used to assess the degree of aromatic or antiaromatic character of the angular (A), branched (B), and terminal (T) six-membered rings, and 12-membered rings.

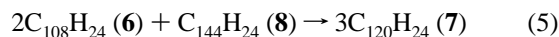
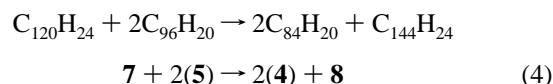
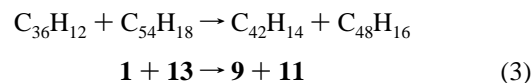
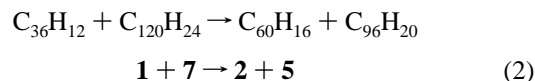
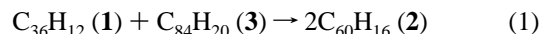
### Methods

Geometries and energies were obtained from ab initio calculations in the 6-31G\* basis<sup>4</sup> at the B3LYP density-functional<sup>5</sup> level using Gaussian 03.<sup>6</sup> The energies, supplemented by zero-point and thermal energy corrections, were used to estimate standard enthalpies of formation. Proton chemical shifts relative to TMS were calculated at the HF/6-31G\* level

and B3LYP/6-31G\* geometries by the GIAO method.<sup>7</sup> NICS(1) values<sup>8</sup> are calculated at points 1.0 Å from the ring centroids. Vibrational frequencies were calculated at the B3LYP/6-31G\* level. All the molecules are planar and have real vibrational frequencies, the smallest ranging from 10 to 42 cm<sup>-1</sup> (*a<sub>2u</sub>* modes of 8 and 1, respectively).

### Energetics

The B3LYP/6-31G\* ab initio energies (in hartrees) of **1–14** are given in Table 1. They show that homocyclic reactions **1–5**, which conserve the numbers of A, B, T, and 12-membered rings,



are remarkably thermoneutral, with  $\Delta E$  (kcal/mol) of  $-0.13$ ,  $-1.53$ ,  $+0.24$ ,  $+0.70$ , and  $-0.96$ , respectively. The corresponding  $\Delta H_{298}^{\circ}$  values for these reactions are quite similar: zero-point contributions for hydrocarbon reactions of net zero molecularity are small,<sup>9</sup> and the present calculations show a similar near cancellation of the thermal contributions.

Each standard heat of formation given in Table 1 is computed from an ab initio B3LYP/6-31G\* heat of reaction and experimental  $\Delta H_f^{\circ}$  values. For example,  $\Delta H_f^{\circ} = 526.1$  kcal/mol for **9** is obtained from the calculated  $\Delta H = 7.7$  kcal/mol of reaction **6** combined with the experimental  $\Delta H_f^{\circ}$  of biphenylene ( $\text{C}_{12}\text{H}_8$ ),

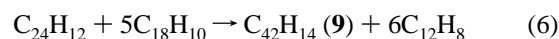
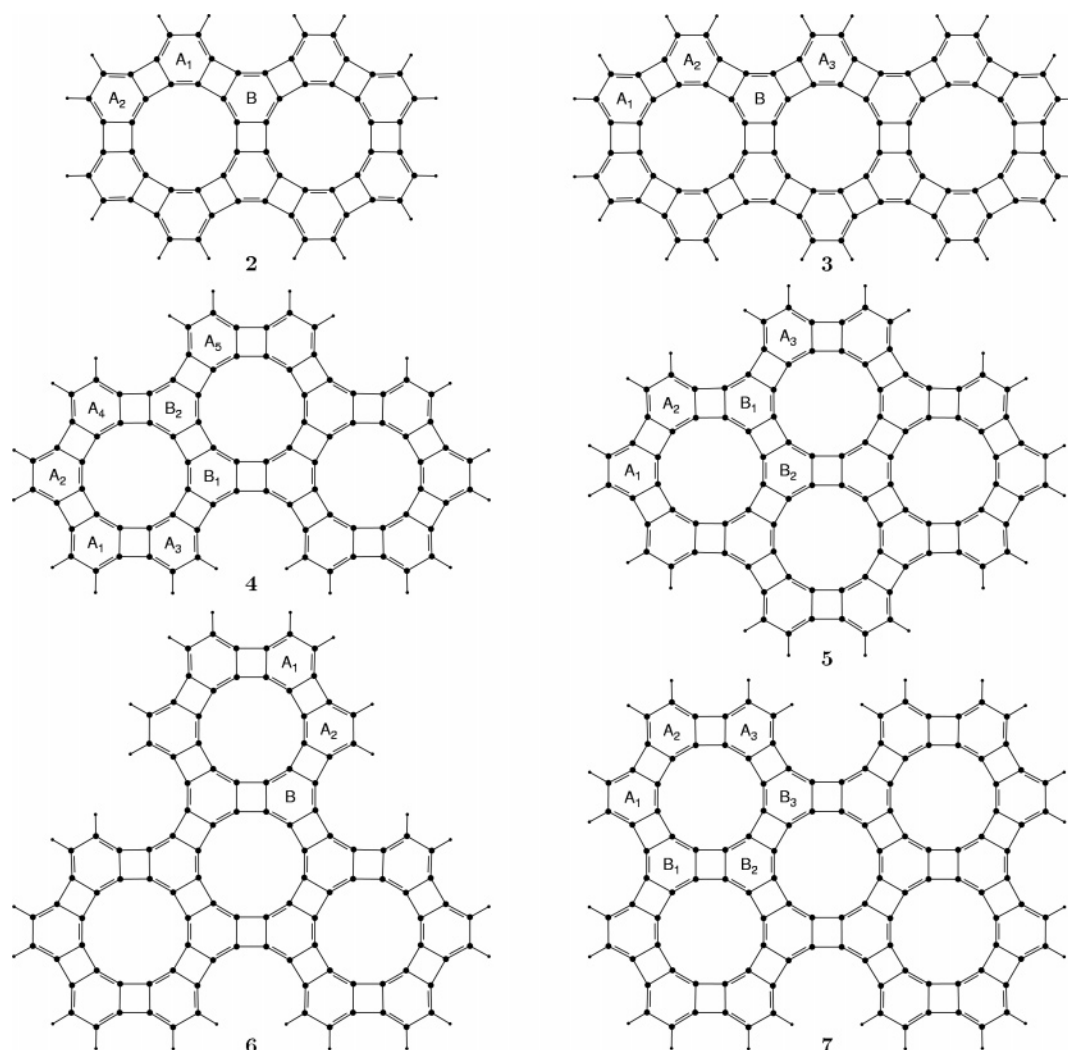


TABLE 1: Ab Initio Energies (H) of Antikekulenes

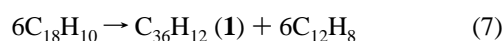
			rings <sup>a</sup>	B3LYP/6-3G*	increment method <sup>b</sup>	$\Delta H_f^c$
1	C <sub>36</sub> H <sub>12</sub>	D <sub>6h</sub>	(6, 0, 0), 1	-1378.71544	-1378.71610(-0.4)	450.6
2	C <sub>60</sub> H <sub>16</sub>	D <sub>2h</sub>	(8, 2, 0), 2	-2295.41125	-2295.41066(+0.4)	803.2
3	C <sub>84</sub> H <sub>20</sub>	D <sub>2h</sub>	(10, 4, 0), 3	-3212.10685	-3212.10521(+1.0)	1156.0
4	C <sub>84</sub> H <sub>20</sub>	C <sub>2v</sub>	(10, 4, 0), 3	-3212.10587	-3212.10521(+0.4)	1156.5
5	C <sub>96</sub> H <sub>20</sub>	D <sub>2h</sub>	(10, 6, 0), 4	-3669.22825	-3669.22774(+0.3)	1359.0
6	C <sub>108</sub> H <sub>24</sub>	D <sub>3h</sub>	(12, 6, 0), 4	-4128.79903	-4128.79977(-0.5)	1510.5
7	C <sub>120</sub> H <sub>24</sub>	D <sub>2h</sub>	(12, 8, 0), 5	-4585.92162	-4585.92229(-0.4)	1712.7
8	C <sub>144</sub> H <sub>24</sub>	D <sub>6h</sub>	(12, 12, 0), 7	-5500.16527	-5500.16734(-1.3)	2118.3
9	C <sub>42</sub> H <sub>14</sub>	C <sub>2v</sub>	(5, 1, 1), 1	-1608.50958	-1608.50949(+0.1)	526.1
10	C <sub>48</sub> H <sub>16</sub>	D <sub>2h</sub>	(4, 2, 2), 1	-1838.30352	-1838.30288(+0.4)	601.7
11	C <sub>48</sub> H <sub>16</sub>	C <sub>2v</sub>	(4, 2, 2), 1	-1838.30385	-1838.30288(+0.6)	601.5
12	C <sub>48</sub> H <sub>16</sub>	C <sub>2v</sub>	(4, 2, 2), 1	-1838.30157	-1838.30288(-0.8)	602.8
13	C <sub>54</sub> H <sub>18</sub>	D <sub>3h</sub>	(3, 3, 3), 1	-2068.09838	-2068.09626(+1.3)	676.7
14	C <sub>54</sub> H <sub>18</sub>	C <sub>2v</sub>	(3, 3, 3), 1	-2068.09383	-2068.09626(-1.5)	679.3

<sup>a</sup> The numbers of six-membered rings are in parentheses in the order angular, branched, and terminal, followed by the number of 12-membered rings. <sup>b</sup> Ab initio increments are  $E_A = -229.786017$ ,  $E_B = -228.561261$ , and  $E_T = -231.018143$ , as discussed in the text; deviations (kcal/mol) are in parentheses. <sup>c</sup> In kcal/mol.

CHART 1



100.5;<sup>10a</sup> C<sub>2v</sub> [3]phenylene (C<sub>18</sub>H<sub>10</sub>), 174.3;<sup>10b</sup> and D<sub>3h</sub> [4]phenylene (C<sub>24</sub>H<sub>12</sub>), 249.9.<sup>10b</sup> The  $\Delta H_f^c$  of antikekulene (1), 450.6 kcal/mol, is obtained from  $\Delta H = 7.8$  kcal/mol for reaction 7.

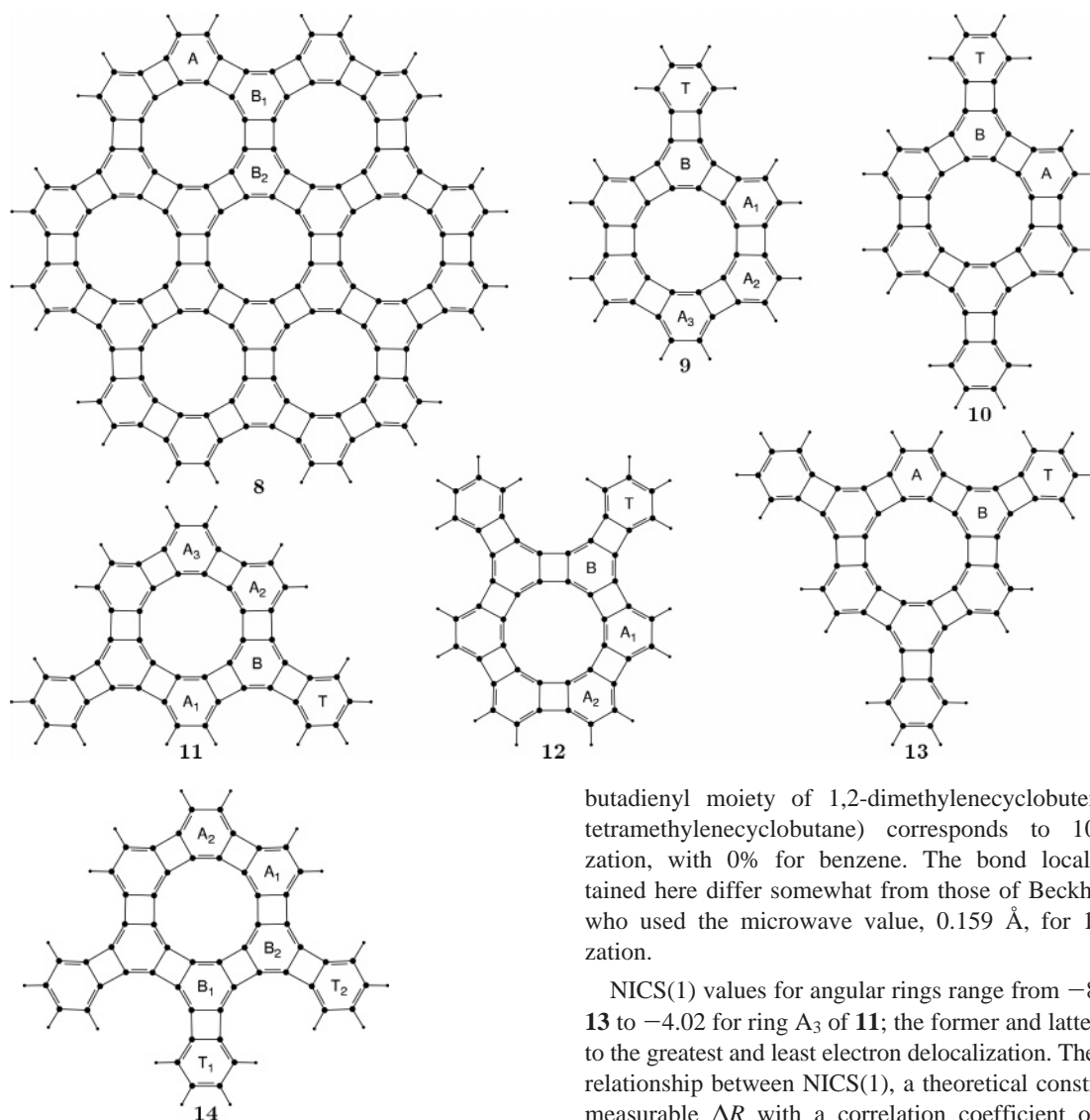


Reactions 6 and 7 balance the numbers of angular, branched, and terminal rings and create one 12-membered ring. In general,

$\Delta H$  of such reactions is 7–8 kcal/mol for each 12-membered ring created (e.g., five in 7); the amount by which  $\Delta H > 0$  can be viewed as a measure of the  $\sigma$  strain energy and antiaromatic  $\pi$  character of the antikekulene moieties,<sup>2c</sup> the inner and outer peripheries of which are  $4n$   $\pi$ -electron systems.

We note that small differences are found for the energies and  $\Delta H_f^c$  of isomers 3 and 4; 10, 11, and 12; and 13 and 14.

## CHART 2



Slightly higher energies in the latter cases are associated with adjacent terminal rings.

The *ab initio* energies are reasonably well approximated by summing the appropriate number of increments for each ring type:  $E_A = -229.786017$ ,  $E_B = -228.561261$ , and  $E_T = -231.018143$ . These have been obtained from a weighted least-squares fit<sup>2d</sup> to the 14 energies. The incremental sums (Table 1) are within 1.5 kcal/mol of the B3LYP/6-31G\* energies (rms = 0.00128 hartree).

### Chemical Shielding and Bond Alternation

The extent of bond alternation (cyclohexatrienic character) in the six-membered rings was assessed from  $\Delta R$  (in Å), the difference in average lengths between the (formal) CC single and double bonds. (Defining formal double bonds to have lengths  $\leq 1.41$  Å furnishes kekule structures for all rings studied here.) NICS(1) values<sup>8</sup> provide a measure of aromatic character as the negative of the isotropic magnetic shielding (given here in ppm) above the center of a ring.

**Angular Rings.** For the 32 unique angular rings (A) of **1–14**,  $\Delta R$  ranges from 0.06105 to 0.08222 Å (Table 2). These values correspond to 33.6–45.3% localization, based upon a scale in which the B3LYP/6-31G\* value,  $\Delta R = 0.1815$  Å, for the

butadienyl moiety of 1,2-dimethylenecyclobutene (and for tetramethylenecyclobutane) corresponds to 100% localization, with 0% for benzene. The bond localizations obtained here differ somewhat from those of Beckhaus et al.,<sup>10b</sup> who used the microwave value, 0.159 Å, for 100% localization.

NICS(1) values for angular rings range from  $-8.11$  ppm for **13** to  $-4.02$  for ring  $A_3$  of **11**; the former and latter correspond to the greatest and least electron delocalization. There is a linear relationship between NICS(1), a theoretical construct, and the measurable  $\Delta R$  with a correlation coefficient of 0.998, the maximum deviation in NICS(1) being 2.1%. Both metrics show that angular rings can be grouped roughly into those linked to zero, one, and two branched rings: NICS(1) values range from  $-4.0$  to  $-5.2$ ,  $-5.6$  to  $-6.7$ , and  $-6.9$  to  $-8.1$  ppm, respectively. The first group contains antikekulene itself ( $-4.89$ ) and the latter **11** and **13**, both having the sequence T–B–A–B–T.

Resonances of protons on the angular rings are nearly linearly related to the  $\Delta R$  values of those rings (Table 2) with a correlation coefficient of  $-0.972$ , and deviations from linearity are less than 0.1 ppm. The most deshielded protons,  $\delta$  6.87, are on ring A of **13** ( $\Delta R = 0.06105$  and NICS(1) =  $-8.11$ ). The most shielded protons have  $\delta$  ca. 6.2 on central rings of the sequence A–A–A, including antikekulene itself. In contrast, protons on terminal rings resonate from  $\delta$  7.20 to 7.34, the latter again for **13**.

**Branched, Terminal, and 12-Membered Rings.** For the 19 branched rings,  $\Delta R$  ranges from 0.1051 to 0.1334 Å (57.9–73.5% bond localization); NICS(1) values are from  $-4.12$  to  $-1.01$  ppm, again correlating linearly with  $\Delta R$ . Branched rings with the greatest electron delocalization (NICS(1) of ca.  $-4$  ppm) in **5**, **7**, and **8** are those linked to three other branched rings. Conversely, the most bond-localized

TABLE 2:  $\Delta R$  (Å) (% Localization), NICS(1) (ppm), and Proton Shifts of Six-Membered Rings

	angular rings			branched rings			proton shifts ( $\delta$ ) (angular rings)
	ring <sup>a</sup>	$\Delta R$ (% localized)	NICS(1)	ring	$\Delta R$ (% localized)	NICS(1)	
<b>1</b>	A	0.07787 (42.9)	-4.89				6.20
<b>2</b>	A <sub>1</sub>	0.07334 (40.4)	-5.91	B	0.11707 (64.5)	-2.76	6.38, 6.34
	A <sub>2</sub>	0.07877 (43.4)	-4.75				6.20
<b>3</b>	A <sub>1</sub>	0.07857 (43.3)	-4.76	B	0.11863 (65.4)	-2.69	6.20, 6.21
	A <sub>2</sub>	0.07252 (40.0)	-5.99				6.36, 6.41
	A <sub>3</sub>	0.06757 (37.2)	-6.93				6.52
<b>4</b>	A <sub>1</sub>	0.07826 (43.1)	-4.82	B <sub>1</sub>	0.11238 (61.9)	-3.62	6.21, 6.21
	A <sub>2</sub>	0.07877 (43.4)	-4.71	B <sub>2</sub>	0.11869 (65.4)	-2.72	6.19, 6.20
	A <sub>3</sub>	0.07403 (40.8)	-5.63				6.32, 6.36
	A <sub>4</sub>	0.07258 (40.0)	-5.97				6.35, 6.39
	A <sub>5</sub>	0.07351 (40.5)	-5.73				6.32, 6.35
<b>5</b>	A <sub>1</sub>	0.08038 (44.3)	-4.37	B <sub>1</sub>	0.12014 (66.2)	-2.67	6.15
	A <sub>2</sub>	0.07146 (39.4)	-6.19	B <sub>2</sub>	0.10664 (58.8)	-4.08	6.36, 6.40
	A <sub>3</sub>	0.07303 (40.2)	-5.79				6.32, 6.35
<b>6</b>	A <sub>1</sub>	0.07843 (43.2)	-4.77	B	0.11314 (62.3)	-3.53	6.20, 6.21
	A <sub>2</sub>	0.07395 (40.8)	-5.69				6.32, 6.36
<b>7</b>	A <sub>1</sub>	0.07165 (39.5)	-6.17	B <sub>1</sub>	0.12088 (66.6)	-2.53	6.37, 6.40
	A <sub>2</sub>	0.08016 (44.2)	-4.41	B <sub>2</sub>	0.10514 (57.9)	-4.12	6.16
	A <sub>3</sub>	0.07301 (40.2)	-5.90	B <sub>3</sub>	0.11468 (63.2)	-3.47	6.33, 6.37
<b>8</b>	A	0.07309 (40.3)	-5.80	B <sub>1</sub>	0.11873 (65.4)	-2.92	6.30, 6.34
				B <sub>2</sub>	0.10876 (59.9)	-3.96	
<b>9</b>	A <sub>1</sub>	0.06976 (38.4)	-6.44	B	0.13005 (71.7)	-1.36	6.47, 6.56
	A <sub>2</sub>	0.07978 (44.0)	-4.46				6.18, 6.19
	A <sub>3</sub>	0.07653 (42.2)	-5.21				6.26
<b>10</b>	A	0.07173 (39.5)	-5.98	B	0.12979 (71.5)	-1.59	6.43, 6.52
<b>11</b>	A <sub>1</sub>	0.06157 (33.9)	-7.96	B	0.13236 (72.9)	-1.18	6.84
	A <sub>2</sub>	0.06844 (37.7)	-6.70				6.51, 6.61
	A <sub>3</sub>	0.08222 (45.3)	-4.02				6.16
<b>12</b>	A <sub>1</sub>	0.07237 (39.9)	-6.05	B	0.12218 (67.3)	-2.34	6.42, 6.50
	A <sub>2</sub>	0.07910 (43.6)	-4.73				6.21, 6.22
<b>13</b>	A	0.06105 (33.6)	-8.11	B	0.13343 (73.5)	-1.01	6.87
<b>14</b>	A <sub>1</sub>	0.07153 (39.4)	-6.27	B <sub>1</sub>	0.11458 (63.1)	-3.49	6.43, 6.56
	A <sub>2</sub>	0.08124 (44.8)	-4.26	B <sub>2</sub>	0.12379 (68.2)	-2.15	

<sup>a</sup> NICS(1) values for the terminal rings: **9**, -10.51; **10**, -10.44; **11**, -10.59; **12**, -10.05; **13**, -10.65; **14**, -10.14(T<sub>2</sub>), -9.55(T<sub>1</sub>) ppm. The NICS(1) of benzene is -12.81.

branched rings are those linked to one terminal and two angular rings, as in **9–11** and **13**, with NICS(1) in the range -1.01 to -1.59 ppm.

The seven terminal rings of **9–14** have  $\Delta R$  in the range 0.0298–0.0344 Å (16.4–19.1% localization), corresponding to a NICS(1) range of -10.65 to -9.55 ppm.

The 12-membered rings have positive NICS(1) in the narrow range 2.3–2.7 ppm and  $\Delta R$  from 0.1205 to 0.1240 Å (66.4–68.3% localization), consistent with bond alternation and weak antiaromatic character.

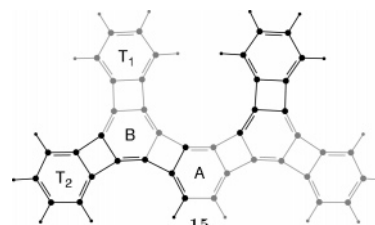
## Discussion

The  $\Delta R$  and their sum over all six-membered rings,  $\Delta R_{\text{tot}}$ , are useful in analyzing a phenylene structure. The latter ranges from 0.46722 Å in **1** to 2.24202 in **8** and replicates the ordering of the ab initio energies for isomers **3** and **4**; **10**, **11**, and **12**; and **13** and **14**. One can also define the net change in bond localization for a chemical reaction,  $\Delta R_r$ , as the weighted sum of the individual molecular localizations  $\Delta R_{\text{tot}}$ . For example,  $\Delta R_r$  for reaction 4 (**7** + 2(**5**)  $\rightarrow$  2(**4**) + **8**) employing  $\Delta R_{\text{tot}}$  as one would molecular energies gives  $2 \times 1.2164 + 2.2420 - 2 \times 1.4326 - 1.8100 = -0.0004$ , a small fraction of the value of each side. The small values also obtained for reactions 1–3 and 5 imply that thermoneutral homocyclic reactions have  $\Delta R_r$  close to zero and that phenylene energetics are directly related to bond localizations.

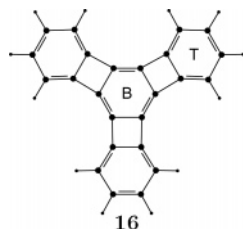
Moreover, because bond localizations are closely related to NICS(1), the total NICS(1) values can be used in reaction 4 to provide a  $\Delta \text{NICS}(1)$ , viz.  $93.1 + 2 \times 75.5 - 2 \times 66.4 - 110.9$

= +0.4, again very small. The nearly linear relationship of NICS(1) to  $\Delta R$  provides NICS(1) with a direct correspondence to a measurable property for the antikekulenes.

The pattern of alternation of NICS(1) and  $\Delta R$  in **11** and **13**, where angular rings embedded in the sequence T–B–A–B–T have their most negative NICS(1) values (-7.96 and -8.11 ppm), most deshielded protons ( $\delta$  6.84, 6.87), and smallest  $\Delta R$  values (Table 2), has a simple interpretation: with intervening nonaromatic (cyclohexatrienic) B rings – NICS(1) of -1.18 and -1.01 ppm – the adjacent T and A rings both become more aromatic and less bond-localized. Perhaps the limiting extent of aromatic character for an angular ring is found in **15**,



having the sequence T<sub>2</sub>B–A–BT<sub>2</sub>.<sup>11</sup> Its cyclohexatrienic B rings (NICS(1) = -0.65 ppm) support the enhanced aromatic character of the A ring (NICS(1) = -8.81 ppm,  $\delta_{\text{H}}$  = 7.13,  $\Delta R$  = 0.0608 Å (33.5%)) and the four T rings (NICS(1) = -10.59 and -10.70 ppm). Both A-ring and T-ring values are more negative than any of those of Table 2. **15** resembles D<sub>3h</sub> [4]phenylene (**16**), which has a cyclohexatrienic B ring with NICS(1) = -0.46 ppm and T rings with NICS(1) = -10.86 ppm<sup>12</sup> and  $\Delta R$  = 0.0282 Å (15.5%).



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## References and Notes

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- (12) NICS(1) values of  $-1.1$  and  $-10.7$  for **16** reported in ref 2c were obtained at the HF/3-21G//B3LYP/6-31G\* level.