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Theoretical Studies of the [*N*]Phenylenes

Jerome M. Schulman* and Raymond L. Disch

Contribution from the Department of Chemistry, The City University of New York, Queens College, Flushing, New York 11367

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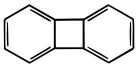
Abstract: This work explores the structures and energetics of linear and cyclic [*N*]phenylenes by ab initio calculation at the HF/6-31G* and BLYP/6-31G* density functional levels. Heats of formation were obtained from these energies by a group-equivalents method. In the acyclic case with $N = 3-5$, angular phenylenes are more stable than linear phenylenes. For the cyclic [6]phenylene (antikekulene), which is found to be planar, no appreciable destabilization is found relative to a linear [6]phenylene reference structure. The cyclic [4]- and [5]phenylenes adopt tub conformations. There is a simple relationship between the $\Delta H_f°$ of an [*N*]phenylene and that of the corresponding condensed benzenoid. It provides, for example, an estimate of $\Delta H_f°$ of C_{120}, archimedene, from that of C_{60}.

The [*N*]phenylenes are comprised of alternating benzene and cyclobutadiene rings.[1] Phenylenes larger than the parent biphenylene (**1**)[2] have interior benzene rings that can be substituted in a linear or angular manner, as in the [3]phenylenes **2**[3] and **3**,[4] or a branched manner, as in [4]phenylene **4a**.[5] This gives rise to a rapidly increasing number of isomers, e.g. five [4]phenylenes (Chart 1), twelve [5]phenylenes, thirty-seven [6]-phenylenes, etc.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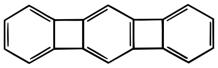
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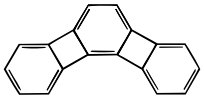
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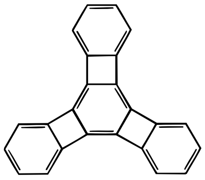
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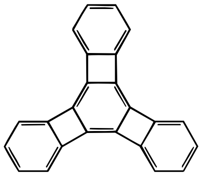
Phenylenes can also form or contain cyclic structures such as the *cyc*[6]phenylene **6** (antikekulene),[4b] *cyc*[5]phenylene **7**, and (much) larger systems.

We report here the results of an ab initio study of acyclic and cyclic [*N*]phenylenes. These are the first such calculations on cyclic phenylenes, while for the acyclic case the work extends prior ab initio studies.[6] It provides estimates of the heats of formation of [*N*]phenylenes which reveal energetic patterns that are applicable to larger systems. In the absence of experimental thermochemical data, the calculations also provide a basis for testing empirical (Hückel and graph-theoretic) and semiempirical treatments.[7]

Chart 1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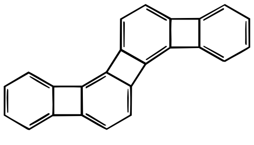
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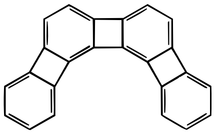
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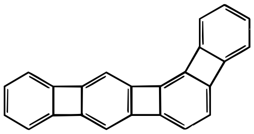
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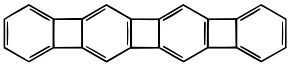
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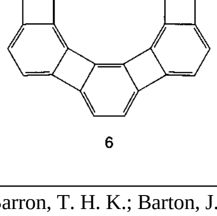
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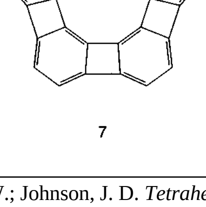
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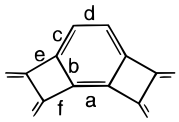


Figure 1. Bond lengths of angular phenylenes referred to in the text and in Table 1.

Methods

Calculations were performed with programs developed by us and optimized for IBM vector processors, and with GAUSSIAN 94[8] on Digital Alpha AXP 2100 servers and IRIS indigo workstations. Optimized geometries and energies were obtained in the 6-31G* basis[9] at the HF level and with the density functional BLYP, which uses the non-local exchange functional of Becke[10] and the correlation functional of Lee, Yang, and Parr.[11] Calculations were also performed with the BPW91 functional to test the efficacy of the gradient-corrected Perdew−Wang correlation functional.[12] The results are in qualitative agreement with those obtained with BLYP. Vibrational frequencies were calculated at lower levels of theory, such as HF/3-21G and AM1.[13]

Geometries

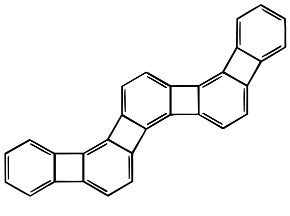
The ab initio geometries of angular [*N*]phenylenes exhibit cyclohexatriene-type bond alternation in their interior benzene rings. With reference to Figure 1 and Table 1, the HF/6-31G* lengths of the formal double bonds (*a* and *c*) in **3**, **4b**, and **5a** range from 1.335 to 1.354 Å, and the single bonds (*b* and *d*) from 1.436 to 1.451 Å. The calculated bond lengths of **3** are in good agreement with the X-ray structure.[4b] For the branched [4]phenylene **4a**, calculated with the assumption of D_{3h} symmetry, $a = 1.328$ Å, $b = 1.481$ Å, and $f = 1.493$ Å, showing even more pronounced bond alternation. The distances are in good agreement with the X-ray values[5] of the hexa(trimethylsilyl) derivative of **4a**: $a = 1.333-1.338$ Å, $b = 1.486-1.502$ Å, and $f = 1.497-1.508$ Å. These X-ray data indicate some deviation from D_{3h} symmetry and planarity. Indeed, we find a weak out-of-plane A''_2 vibrational mode (48 cm^{-1} in 3-21G) for the parent, **4a**.

The BLYP/6-31G* (PDW91/6-31G*) CC distances for **4a** are $a = 1.361$ (1.359) Å, $b = 1.502$ (1.494) Å, and $f = 1.495$ (1.488) Å. Thus, with these functionals the length of the double bond in its central ring is in somewhat poorer agreement with experiment than the HF/6-31G* value, 1.328 Å. This effect is seen in other [*N*]phenylenes (Table 1).

The cyclic [*N*]phenylenes present the possibility of substantial deviations from planarity for small *N*. In D_{nh} symmetry the cyclic phenylenes with $N = 4$, 5, and 6 are strained due to their longer *e*-type bonds (Figure 1) and to their interior rings of 8, 10, and 12 carbons, with CCC angles of 135°, 144°, and 150°, respectively.

Since the acyclic phenylenes have $C-C=C$ angles at their interior carbons of ca. 150°, *cyc*[6]phenylene **6** is likely to be the least strained. Indeed, we find **6** to have D_{6h} symmetry. At the HF/3-21G level, its lowest vibrational frequencies (cm^{-1}) are 40 (A_{2u}, out of plane) and 64 (E_{2u}). The AM1 values are similar: 42 and 64 cm^{-1}. Thus, **6** is planar but flexible.

All computational methods find bowl conformations for *cyc*[5]phenylene **7** (C_{5v}, Figure 2) and *cyc*[4]phenylene **8** (C_{4v}, Figure 3). Their dipole moments are 3.7 and 4.4 D (HF/6-31G*), respectively, with the negative end toward the ten-carbon or eight-carbon basal plane. Excluding the planar structure **7a**, which is a transition state, cyclic [*N*]phenylenes have formal double bonds (*a* and *c*) which range in length from 1.334 to 1.365 Å, and single bonds (*b* and *d*) from 1.426 to 1.454 Å. The single bonds of the cyclobutadiene ring (*e* and *f*) range from 1.459 to 1.552 Å. These bond lengths are similar to those in the angular acyclic [*N*]phenylenes. In contrast, the D_{5h} transition state **7a** shows a distorted trapezoidal structure with bond lengths $e = 1.606$ Å and $f = 1.427$ Å. Clearly, a planar form of *cyc*[4]phenylene would have even greater distortions of its four-membered rings.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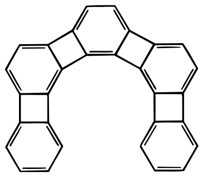
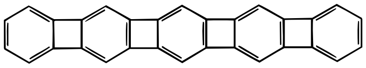

5b


5c

The lowest HF/3-21G frequencies of **7** are 89 (E_2) and 101 (A_1) cm^{-1}, while the higher-energy planar form **7a** is a transition state, having one imaginary frequency, 79*i* (A''_2), and real frequencies of 102 (E''_2) and 141 (E''_1) cm^{-1}. The unstable A''_2 mode connects the bowl forms **7**, as in the analogous bowl-to-bowl interconversion of corannulene. We previously reported the HF/6-31G* frequencies of corannulene in both bowl and planar (transition state) forms.[14] The frequencies of bowl structure are 143 (A_1) and 164 (E_2) cm^{-1}; those of the planar form are 90*i* (A''_2) and 165 (E''_2) cm^{-1}. Thus, corannulene is slightly more rigid than *cyc*[5]phenylene.

The inversion barrier of **7** is 17.5 kcal/mol in HF/6-31G* and 17.1 kcal/mol in BLYP/6-31G*. These values are considerably larger than the 8.8 kcal/mol energy difference between the C_{5v} and D_{5h} forms of corannulene found in HF/6-31G* and $\Delta G^{\ddagger} = 10.2$[15a] and 10.5[15b] kcal/mol found experimentally for the inversion of the dimethylcarbinol and bis(bromomethyl) derivatives of corannulene.

Energies and Heats of Formation

Biphenylene is the only phenylene for which thermochemical data are available. Its $\Delta H_f°$, 99.88 kcal/mol,[16] is well reproduced at the MP2/6-31G* level,[6c] which gives 99.8. For the larger [*N*]phenylenes we need a computationally less demanding method of estimating heats of formation. We therefore devised a two-parameter group-equivalent method, similar to that applied

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Table 1. HF/6-31G* and BLYP/6-31G* Bond Lengths (Å) of Phenylenes[a]

molecule	*a*	*b*	*c*	*d*	*e*	*f*
			Acyclic Phenylenes			
[3]phenylene, **3**[b]	1.335 (1.345)	1.449 (1.449)	1.345 (1.348)	1.451 (1.446)	1.502 (1.505)	1.498 (1.503)
[3]phenylene, **3** (BLYP)	1.366 (1.345)	1.470 (1.449)	1.377 (1.348)	1.455 (1.446)	1.505 (1.505)	1.504 (1.503)
[4]phenylene, **4b**[c]	1.339	1.442, 1.445	1.349, 1.349	1.444	1.495, 1.504	1.495, 1.499
[5]phenylene, **5a**[d]	1.344	1.438	1.354	1.436	1.496	1.496
			Cyclic Phenylenes			
[6]phenylene, **6**	1.335	1.435	1.356	1.446	1.521	1.476
[6]phenylene, **6** (BLYP)	1.364	1.458	1.387	1.455	1.525	1.481
[5]phenylene, **7**	1.334	1.432	1.359	1.454	1.542	1.459
[5]phenylene, **7** (BLYP)	1.366	1.457	1.390	1.461	1.543	1.469
[5]phenylene, **7a**	1.321	1.418	1.366	1.474	1.606	1.427
[4]phenylene, **8**	1.338	1.426	1.365	1.447	1.552	1.474

[a] The values are HF/6-31G* unless specified as BLYP. [b] Experimental X-ray values, ref 4b, are in parentheses. [c] The interior benzene rings are in an asymmetric environment, giving rise to two values of *b*, *c*, *e*, and *f*. [d] Parameters are those of the central benzene ring.

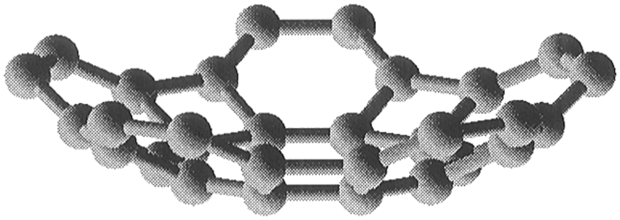

Figure 2. A ball-and-stick model of *cyc*[5]phenylene **7**.

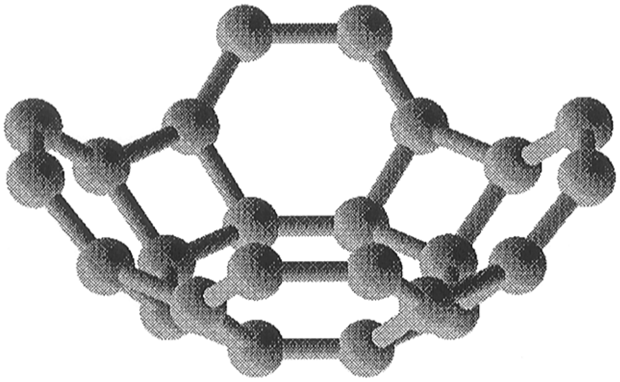

Figure 3. A ball-and-stick model of *cyc*[4]phenylene **8**.

previously to benzenoid aromatics,[17] to convert the [*N*]phenylene HF/6-31G* and BLYP/6-31G* energies to heats of formation.[18] The results, given in Table 2, show very similar values of the two heats of formation.

The energies of the acyclic [*N*]phenylenes of the same *N* are quite similar, with slightly lower values for the more angular structures. For $N = 3$, there is a difference of 3.5 (2.4) kcal/mol between **2** and **3**. ($\Delta H_f°$(BLYP) energies are in parentheses.) The energies of the five [4]phenylenes span a range of 11.0 (8.5) kcal/mol. If the lowest-energy branched isomer, **4a**, is excluded, this difference diminishes to 6.7 (4.4) kcal/mol (4.1 at the BPW91/6-31G* level). The angular and zigzag [4]phenylenes **4b** and **4c** have energies which differ by only 0.1 kcal/mol. Similarly, the energies of **5a** and **5b** are within 1 kcal/mol. The angular phenylenes are all more stable than their linear counterparts, the energy differences being smaller with the DFT methods than with HF. This is consistent with the interesting report of Maksić et al. that at the RMP2/6-31G* level the angular and linear [4]phenylenes **4b** and **4e** differ by only 1.9 kcal/mol.[6d] It is noteworthy that despite the relative thermal stability of **4a**, its central benzene ring is reactive, undergoing

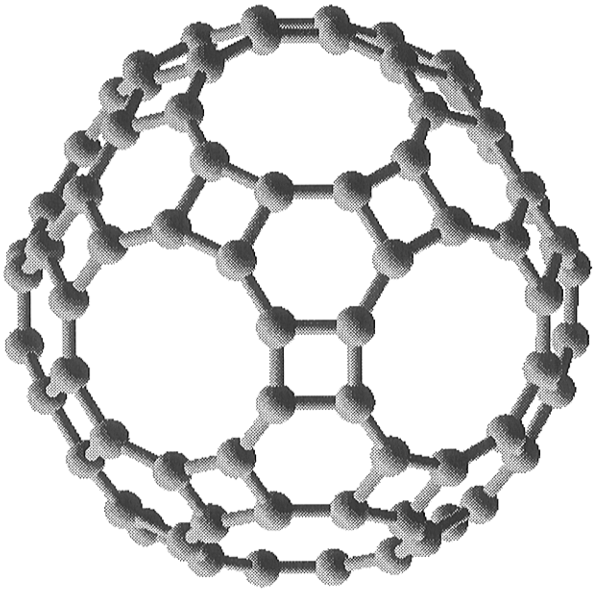

Figure 4. Archimedene **9**, C_{120}, shown with hidden atoms omitted for clarity. In I_h symmetry, all atoms are equivalent and lie on no element of symmetry.

Table 2. $\Delta H_f°$ of the [*N*]Phenylenes (kcal/mol)

molecule	$\Delta H_f°$ from HF/6-31G*	$\Delta H_f°$ from BLYP/6-31G*
	Acyclic Phenylenes	
biphenylene, **1**, D_{2h}	99.9	99.9
[3]phenylene, **2**, D_{2h}	180.2	179.1
[3]phenylene, **3**, C_{2v}	176.7	176.7
[4]phenylene, **4a**, D_{3h}	250.2	250.1
[4]phenylene, **4b**, C_{2h}	254.5	254.2
[4]phenylene, **4c**, C_{2v}	254.6	254.4
[4]phenylene, **4d**, C_s	256.1	254.9
[4]phenylene, **4e**, D_{2h}	261.2	258.6
[5]phenylene, **5a**, C_{2h}	332.0	331.6
[5]phenylene, **5b**, C_{2v}	332.7	332.0
[5]phenylene, **5c**, D_{2h}	342.4	338.1
	Cyclic Phenylenes	
[6]phenylene, **6**, D_{6h}	471.0	470.6
[5]phenylene, **7**, C_{5v}	434.3	425.1
[5]phenylene, **7a**, D_{5h}	451.8	442.2
[4]phenylene, **8**, C_{4v}	418.5	395.5

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(18) The [*N*]phenylene group equivalents for the HF case are as follows (hartrees): $GE(=C_bH-) = -38.45576$, taken from the benzenoid studies, and $GE(=C_b<) = -37.88192$, obtained by fitting the HF/6-31G* energy of biphenylene to its $\Delta H_f°$. The corresponding GE's for the BLYP/6-31G* case are $GE(=C_bH-) = -38.69398$ and $GE(=C_b<) = -38.10892$. Group equivalents obtained for the BPW91/6-31G* energies lead to $\Delta H_f°$ values nearly identical to the $\Delta H_f°$(BLYP) value.

all-cis hexahydrogenation,[19a] as well as triscyclopropanation and trisoxacyclopropanation.[19b]

From the data available, there appears to be a nearly constant enthalpic increment for addition of links to the phenylene "chain". In the zigzag series **1** → **3** → **4b** → **5a** the increments are 76.8, 77.8, and 77.5 kcal/mol, and for the linear (D_{2h}) series **1** → **2** → **4e** → **5c** 80.3, 81.0, and 81.2 kcal/mol. Therefore, homodesmic reactions of the form

$$2[N-1]\text{phenylene} \rightarrow [N-2]\text{phenylene} + [N]\text{phenylene} \quad (1)$$

are nearly thermoneutral. For example, for $N = 5$, the HF $\Delta H = -0.3$ and 0.2 kcal/mol for the zigzag and linear cases, respectively.

In contrast, additivity fails in the case of cyclic [*N*]phenylenes. Division of the $\Delta H_f°$ of **6**, **7**, and **8** (Table 2) by 12, 10, and 8, respectively, yields 39.2, 43.4, and 52.3 kcal/mol, the stability decreasing markedly with decreasing *N*. Thus,

$$2[5]\text{phenylene } \mathbf{7} \rightarrow [4]\text{phenylene } \mathbf{8} + [6]\text{phenylene } \mathbf{6} \quad (2)$$

analogous to reaction 1, has $\Delta H = 20.9$ kcal/mol (15.9 in BLYP/6-31G*).

It is possible to address the question of extra destabilization of *cyc*[6]phenylene (antikekulene). The $\Delta H_f°$ of **6** can be compared with 6 times the C_6H_2 increment for **4b** → **5a**, which provides the enthalpy of a hypothetical reference acyclic $C_{36}H_{12}$ phenylene. At the HF level we obtain

$$\Delta H = 471.0 - 6 \times (332.0 - 254.5) = 6.0 \text{ kcal/mol}$$

The $\Delta H_f°$ (BLYP) value is 6.2 kcal/mol. Thus, there is at most only a slight antiaromatic character in **6** over and above any such local character. For *cyc*[5]phenylene, we find a marked instability relative to a reference structure containing 5 C_6H_2 units:

$$\Delta H = 434.3 + 5 \times (332.0 - 254.5) = 46.8 \text{ kcal/mol}$$

the major part of which is presumably strain energy.

Relationship of the [*N*]Phenylenes to the Benzenoids

The [*N*]phenylenes are "obtained" from the condensed benzenoids by changing fused benzene bonds into biphenylene moieties, formally an interpolation of C_2 fragments. We refer to this process as "phenylation", examples being naphthalene → **1**, phenanthrene → **3**, corannulene → *cyc*[5]phenylene **7**, and coronene → *cyc*[6]phenylene **6**.

The availability of approximate heats of formation makes the discussion of the energetics of these transformations straightforward. For the process in the zigzag series, for example:[20]

$$\text{naphthalene} \rightarrow \text{biphenylene } \mathbf{1} \qquad \Delta H = 64.0$$

$$\text{phenanthrene} \rightarrow [3]\text{phenylene } \mathbf{3} \qquad \Delta H = 127.1$$

$$\text{chrysene} \rightarrow [4]\text{phenylene } \mathbf{4b} \qquad \Delta H = 190.0$$

$$\text{corannulene} \rightarrow [5]\text{phenylene } \mathbf{7} \qquad \Delta H = 323.5$$

$$\text{coronene} \rightarrow [6]\text{phenylene } \mathbf{6} \qquad \Delta H = 402.0$$

It is observed that $\Delta H/n_{cb}$ of phenylation, where n_{cb} is the number of cyclobutadiene rings created, varies from 63.6 to 67.0, a small range.

Another computational route to the phenylenes employs "joining" reactions, for example, the three formations of [5]phenylene **5a**, which have similar values of $\Delta H/n_{cb}$:

$$\text{biphenylene} + [3]\text{phenylene } \mathbf{3} \rightarrow [5]\text{phenylene } \mathbf{5a} \qquad \Delta H/n_{cb} = 55.4$$

$$2\text{benzene} + [3]\text{phenylene } \mathbf{3} \rightarrow [5]\text{phenylene } \mathbf{5a} \qquad \Delta H/n_{cb} = 57.9$$

$$\text{benzene} + [4]\text{phenylene } \mathbf{4b} \rightarrow [5]\text{phenylene } \mathbf{5a} \qquad \Delta H/n_{cb} = 57.7$$

The results for phenylation and joining processes suggest a means of estimating the heats of formation of larger and less obvious phenylenes. Consider, for example, archimedene **9**, C_{120}, a phenylene-based carbon cluster of probable I_h symmetry containing 30 four-membered rings, 20 six-membered rings, and 12 ten-membered rings.[22] This structure is known as a truncated icosidodecahedron.

Each benzene ring of archimedene has a local environment similar to that of the central ring in [4]phenylene **4a**. Since three C_2 fragments are interpolated in the phenylation reaction

$$\text{triphenylene} \rightarrow [4]\text{phenylene } \mathbf{4a} \qquad \Delta H = 184.6$$

whereas 30 C_2 fragments are required in the perphenylation of C_{60} to archimedene, ΔH of gaseous C_{120} exceeds that of gaseous C_{60} by 1846 kcal/mol. The four experimental values of $\Delta H_f°$ of solid buckminsterfullerene range from 543.3 to 578.9 kcal/mol.[23] Adjusted for its heat of sublimation, 54.7,[23b] the $\Delta H_f°$ of C_{60} is 598−634 kcal/mol. Thus, the estimated $\Delta H_f°$ of gaseous archimedene ranges from 2444 to 2480 kcal/mol or ca. 20.5 kcal/(mol·°C).

An independent approach to the $\Delta H_f°$ of archimedene employs the joining scheme: the molecule can be formed from four bowl-shaped *cyc*[5]phenylenes by joining the terminal benzenes of each to form ten additional four-membered rings. By this method, then, $\Delta H_f°$ of **9** is $4 \times \Delta H_f°_{\mathbf{7}} + 10 \times 56 = 2297$ kcal/mol or 19.1 kcal/(mol·°C). The estimated $\Delta H_f°$ per carbon of archimedene is much larger than the per-carbon value of C_{60}, ca. 10 kcal/mol, largely because each carbon participates in one phenylene-type cyclobutadiene ring.

Discussion

While the chemical reactivity of the [*N*]phenylenes is beyond dispute, their thermal stability is affected by retention of at least some (local) aromatic character in their strained interior benzene rings. This is clearly seen in antikekulene **6**, the $\Delta H_f°$ of which, relative to a model acyclic reference structure, shows only slight destabilization despite its having inner and outer $4n-\pi$-electron peripheries. This result is consistent with the graph-theoretic study of Aihara,[7g] who found only slight "superantiaromatic" character. However, the much smaller π-resonance energy of

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(19) (a) Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1151. (b) Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 563.

(20) Here we have used the experimental $\Delta H_f°$ values obtained from Pedley et al.,[16] $\Delta H_f° = 110.8$ kcal/mol for corannulene from ref 21, and a calculated $\Delta H_f° = 69$ kcal/mol for coronene, ref 17a.

(21) Kiyobashi, T.; Nagano, Y.; Sakiyama, M.; Yamamoto, K.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 3270.

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6, 0.095 eV, relative to that of zigzag [6]phenylene, 0.745 eV, found by the method of conjugate circuits,[7f] would not seem to be consistent with the present results. We concur with that method in finding that the HOMO-LUMO gap is smaller in the linear than in the corresponding zigzag phenylenes. For $N = 3-5$, the HF/6-31G* HOMO-LUMO gaps are (au) 0.31, 0.28, and 0.26 for the linear case and 0.35, 0.32, and 0.32 for the zigzag case, the latter showing the leveling off found by Trinajstić et al.[7f] The HOMO-LUMO gap for *cyc*[6]phenylene **6** is 0.29 au.

The [*N*]phenylenes studied here, aside from the transition state **7a**, have only real frequencies. They do, however, have one or more weak vibrational modes, an extreme case being the [5]phenylenes, where the lowest frequencies are ca. 20 cm^{-1} (3-21G). The [*N*]phenylenes are therefore highly flexible and will probably show deviations from planar symmetry, such as helicity, owing to substituent effects or, in condensed phases, to molecular interactions.

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Supporting Information Available: A table containing ab initio HF and BLYP energies in the 6-31G* basis (1 page). See any current masthead page for ordering and Internet access instructions.

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