5596 J. Phys. Chem. A 1997, 101, 5596−5599

Energetics of the [*N*]Phenylenes with Application to Helical Conformers

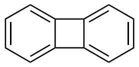
Jerome M. Schulman* and Raymond L. Disch

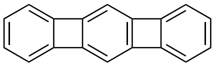
Department of Chemistry, The City University of New York, Queens College, Flushing, New York 11367

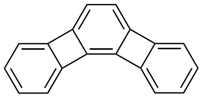
Received: March 13, 1997; In Final Form: May 13, 1997⊗

Ab initio HF/6-31G* and BLYP/6-31G* density functional calculations of [*N*]phenylenes are reported for all twelve [5]phenylenes and for helical [*N*]phenylenes with $N = 6-8$. The energetics of the [*N*]phenylenes are put on a systematic basis by means of a simple fragment-based additivity scheme, allowing both ab initio energies and heats of formation of larger phenylenes to be estimated without resort to extensive calculation. Helical [6]phenylene racemizes through a planar transition state with a barrier of 4−5 kcal/mol. A nonplanar [5]phenylene derivative is obtained by substitution of methyl for an interior hydrogen.

The [*N*]phenylenes are organic π systems having *N* benzene rings with interposed cyclobutadiene rings.[1a] In addition to biphenylene **1** and the linear and angular [3]phenylenes **2**, and **3**, some [4]phenylenes and larger systems have been prepared.[1]


1


2


3

There have been several theoretical studies,[2] including recent ab initio SCF and density functional calculations. These predict, in addition to the smaller, planar phenylenes, larger nonplanar phenylenes, such as the bowl-shaped cyclic [5]phenylene[2a] and the [20]phenylene carbon cluster of I_h symmetry, archimedene.[2b] They are analogues of corannulene and C_{60}, respectively.

The present work describes [*N*]phenylenes that adopt helical structures. It also places the energetics of the phenylenes on a systematic basis by means of a simple fragment-based additivity scheme in which the ab initio energies of 20 [*N*]phenylenes, including all 12 [5]phenylenes, are used to obtain energy increments for phenylene fragments. This allows estimation of ab initio energies and heats of formation of larger phenylenes without the need for extensive calculation. It also provides hypothetical phenylene reference energies for nonplanar [*N*]-phenylenes.

Methods

Ab initio SCF and BLYP[3] density functional calculations, with geometry optimization, were performed in the 6-31G* basis set[4] with GAUSSIAN 94[5] on Digital Alpha AXP 2100 and IRIS indigo workstations. Some frequency calculations were performed with smaller basis sets and with AM1.[6] The ab initio energies were used to obtain energy increments corresponding to C_6H_4, C_6H_2, and C_6 fragments ("nodes"), as described in the following section. In conjunction with the group equivalents (GEs) for $=C_b<$ and $=C_bH-$ moieties previously obtained for computation of heats of formation of benzenoid aromatics from their ab initio energies,[2a] they allow direct calculation of ΔH_f^o of [*N*]phenylenes from knowledge of their structures.

Energetics

The structure of any [*N*]phenylene can be represented as a combination of at most four distinct benzene fragments (nodes): terminal (t; C_6H_4), linear and angular (l, a; C_6H_2), and branched (b, C_6), as shown in Figure 1. The five [4]phenylenes and their corresponding nodal diagrams are displayed in Figure 2. By means of a scheme analogous to that introduced by Cioslowski[7] for benzenoid aromatics, the energy of an [*N*]-phenylene is approximated as the sum of energies of its nodes, denoted by E_t, E_l, E_a, and E_b. The energy of D_{3h} [4]phenylene (**4a**), for example, is given by $E_b + 3E_t$.

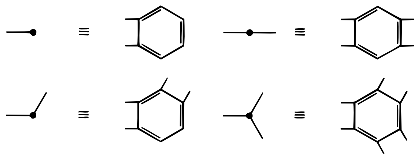
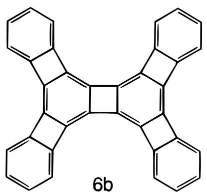


Figure 1. The four phenylene fragments and their nodes.

The energy increments for the nodes were obtained by minimizing

$$\sum_{i=1}^{M} w_i[E_i - (n_{t,i}E_t + n_{l,i}E_l + n_{a,i}E_a + n_{b,i}E_b)]^2$$

where phenylene *i* has N_i benzene rings, $n_{t,i}$ terminal fragments, etc., and the weighting factor w_i is equal to N_i^{-2}. Ab initio energies of $M = 20$ acyclic [*N*]phenylenes, including all [3]-, [4]-, and [5]phenylenes (Chart 1) and the doubly branched [6]-phenylene **6b**, are given in Table 1.


6b

The fitting has a root mean square error of 0.0020 au at the SCF level and 0.0018 au at the BLYP level, producing the *E* values given in Table 2. The poorest agreement is 0.0033 (HF) and 0.0039 au (BLYP). Thus, the ab initio energies of larger phenylenes can be simply estimated as the sum of the component nodal increments. This is useful, since the rapidly increasing number and size of the phenylenes preclude ab initio calculation on almost all of them. (The phenylenes are in approximately one-to-one correspondence with the catacondensed benzenoid aromatics, the number of which grows rapidly[8] with increasing *N*.)

⊗ Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)00940-7 CCC: $14.00

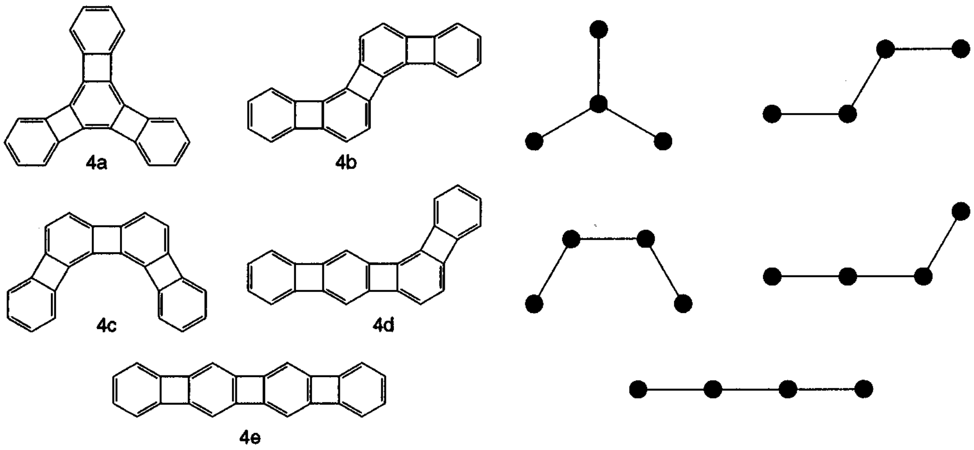


Figure 2. The five [4]phenylenes and their nodal diagrams.

TABLE 1: SCF and Density Functional Energies (hartrees) of [*N*]Phenylenes[a]

molecule	HF/6-31G*	BLYP/6-31G*
[3]phenylene, **2**, D_{2h}	−687.325 85 (1.8)	−691.525 68 (2.4)
[3]phenylene, **3**, C_{2v}	−687.331 32 (0.0)	−691.529 58 (0.0)
[4]phenylene, **4a**, D_{3h}	−915.653 49 (0.0)	−921.236 31 (0.0)
[4]phenylene, **4b**, C_{2h}	−915.646 59 (4.3)	−921.229 63 (4.2)
[4]phenylene, **4c**, C_{2v}	−915.646 36 (4.5)	−921.229 43 (4.3)
[4]phenylene, **4d**, C_s	−915.644 10 (5.9)	−921.228 56 (4.9)
[4]phenylene, **4e**, D_{2h}	−915.636 00 (11.0)	−921.222 68 (8.6)
[5]phenylene, **5a**, C_{2v}	−1143.962 24 (3.3)	−1150.929 95 (4.2)
[5]phenylene, **5b**, C_{2v}	−1143.961 23 (3.9)	−1150.929 40 (4.5)
[5]phenylene, **5c**, D_{2h}	−1143.945 76 (13.7)	−1150.919 60 (10.7)
[5]phenylene, **5d**, C_s	−1143.945 74 (8.0)	−1150.925 99 (6.7)
[5]phenylene, **5e**, C_{2v}	−1143.961 76 (3.6)	−1150.930 89 (3.6)
[5]phenylene, **5f**, C_{2h}	−1143.961 75 (3.6)	−1150.930 84 (3.6)
[5]phenylene, **5g**, C_s	−1143.958 79 (5.5)	−1150.928 05 (5.4)
[5]phenylene, **5h**, C_s	−1143.959 02 (5.3)	−1150.928 27 (5.2)
[5]phenylene, **5i**, C_s	−1143.962 02 (3.5)	−1150.929 77 (4.3)
[5]phenylene, **5j**, C_s	−1143.967 34 (0.1)	−1150.935 03 (1.0)
[5]phenylene, **5k**, C_{2v}	−1143.967 52 (0.0)	−1150.936 62 (0.0)
[5]phenylene, **5l**, C_{2v}	−1143.957 23 (6.5)	−1150.928 10 (5.3)
[6]phenylene, **6a**, C_2	−1372.273 30	−1380.626 93
[6]phenylene, **6a**‡, C_{2v}	−1372.264 65	−1380.621 14
[6]phenylene, **6b**, D_{2h}	−1372.286 95	−1380.639 26
[7]phenylene, **7**, C_2	−1600.586 69	−1610.324 40
[7]phenylene, **8**, C_2	−1828.898 67	−1840.022 73

[a] Relative energies of isomers (kcal/mol) are in parentheses.

The E values can be used in conjunction with the group equivalents GE(=C_b<) and GE(=C_bH−) to give a set of enthalpic increments, H, which provides estimates of the heats of formation of the [*N*]phenylenes:

$$H_t \equiv E_t - [4\mathrm{GE}({=}\mathrm{C_bH}{-}) + 2\mathrm{GE}({=}\mathrm{C_b}{<})]$$

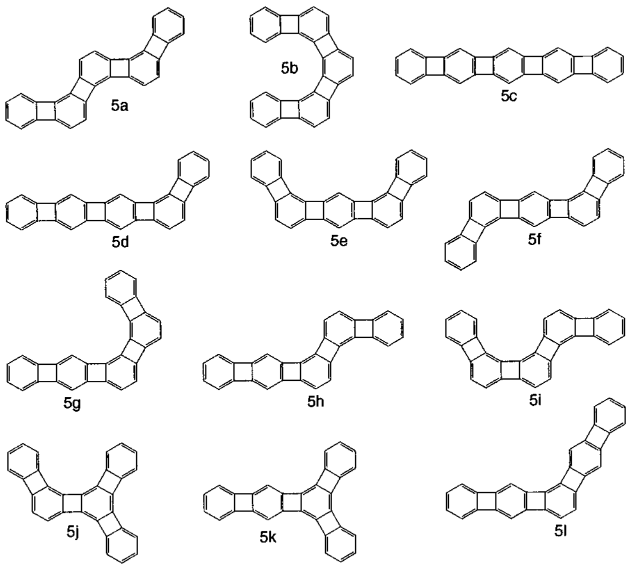
$$H_l \equiv E_l - [2\mathrm{GE}({=}\mathrm{C_bH}{-}) + 4\mathrm{GE}({=}\mathrm{C_b}{<})]$$

$$H_a \equiv E_a - [2\mathrm{GE}({=}\mathrm{C_bH}{-}) + 4\mathrm{GE}({=}\mathrm{C_b}{<})]$$

$$H_b \equiv E_b - 6\mathrm{GE}({=}\mathrm{C_b}{<})$$

These estimates are in good agreement with the values for **2**−**5** published previously.[2a] Comparison of E_a and H_a with E_l and H_l shows that angular and zigzag phenylenes are thermodynamically more stable than their linear counterparts, except where significant steric interactions occur, as in the helical phenylenes discussed below. Similarly, since $H_t + H_b < 2H_a$, phenylenes containing branches are more stable than their unbranched counterparts, probably because of the larger number of less strained terminal benzenes. Of the [5]phenylenes, **5j** and **5k** have the lowest energies and ΔH_f^o, while **6b**, having two branches, is probably the most stable [6]phenylene.

CHART 1



An interesting application of H_b is to the phenylene-based carbon monolayer, consisting of 4-, 6-, and 12-membered rings, shown in Figure 3. The ΔH_f^o/C of the monolayer, H_b/6, is 16.6 and 16.8 kcal/mol at the HF/6-31G* and BLYP/6-31G* levels, respectively. These values are smaller than that of 19.6 kcal/mol obtained by Baughman et al.,[9] based upon the experimental ΔH_f^o values of benzene and biphenylene.

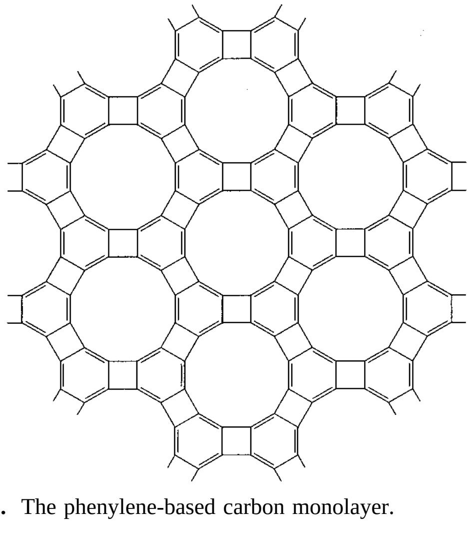


Figure 3. The phenylene-based carbon monolayer.

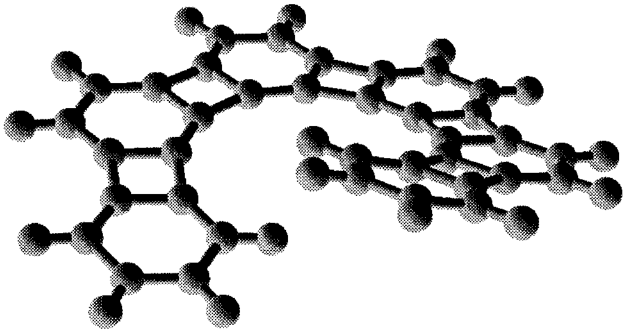


Figure 4. Helical [6]phenylene **6a**.

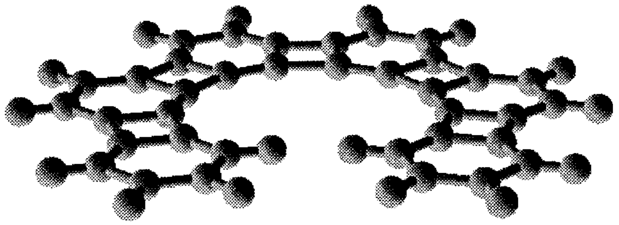
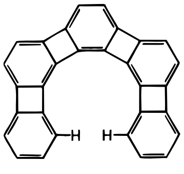


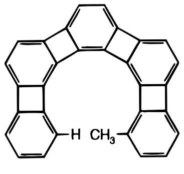
Figure 5. The transition state **6a**‡.

Helical [*N*]Phenylenes

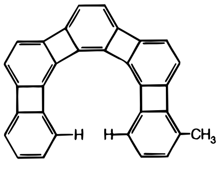
The H···H contact distance between opposing interior hydrogens of [5]phenylene **5b** is 2.05 Å. Since it has several low vibrational frequencies, the smallest being 27 cm^{-1} (3-21G), replacement of these hydrogens with larger groups should lead to nonplanarity. A nonplanar derivative of **5b** is calculated to result from replacement of an *endo* hydrogen of the terminal benzene with methyl, whereas the *exo* isomer retains planarity, being the more stable form by 2 kcal/mol.



5b



endo-methyl-**5b**



exo-methyl-**5b**

Homologues of **5b** with $N = 6$, 7, and 8 have helical structures of C_2 symmetry, such as that shown for [6]phenylene **6a**, Figure 4. There are low-frequency modes in **6a**, the smallest being 29 and 27 cm^{-1} in HF/STO-3G and AM1, respectively. The helical distortions in **6a** increase the H···H contact distance to 2.54 Å (HF/6-31G*) from 1.85 Å in the planar form, **6a**‡. The latter, shown in Figure 5, has one imaginary frequency ($\nu = 87i$ cm^{-1}, AM1; $58i$, STO-3G) and is the transition state for racemization.

The inversion barrier for **6a** is 5.4 and 3.6 kcal/mol in HF/6-31G* and BLYP/6-31G*, respectively. Phenylene **6a** is the analogue of [4] helicene (3,4-benzophenanthrene), the racemization of which has been calculated to occur through a nearly planar transition state, with a barrier of ca 4 kcal/mol.[10]

Discussion

The C_2 axis of the helical structures passes through the central four-membered ring for even N and through the central benzene ring when N is odd. If the inner CC bond of the central four- and six-membered rings for N even and odd are denoted by f_1 and s_1, respectively, and numbered outward from the center, the dihedral angles (degrees, HF/6-31G*) about the inner CC bonds of [6]phenylene **6a** are $f_1 = 10.9$, $f_2 = 8.0$, $f_3 = 1.9$, $s_1 = 3.0$, $s_2 = 0.9$. Thus, the termini of **6a** are much less distorted than its center. A greater disparity is seen in helical [8]phenylene **8**, where the dihedrals are $f_1 = 16.3$, $f_2 = 12.0$, $f_3 = 4.0$, $f_4 = 0.2$, $s_1 = 3.5$, $s_2 = 1.0$ and $s_3 = 2.7$. The largest distortions in **6a**, **7**, and **8** are in the central cyclobutadiene rings.

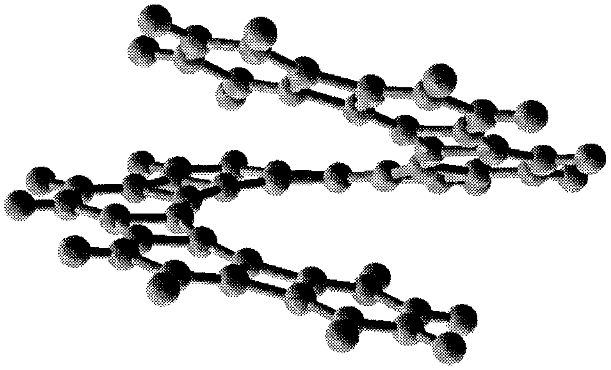


Figure 6. Helical [8]phenylene **8**.

TABLE 2: Nodal Increments *E* (hartrees) and *H* (kcal/mol) obtained from HF/6-31G* and Density Functional BLYP/6-31G* Energies

increment	HF/6-31G*[a]	BLYP/6-31G*[b]
E_t	−229.505 738	−230.914 091
E_l	−228.311 617	−229.698 160
E_a	−228.316 202	−229.700 952
E_b	−227.130 204	−228.492 891
H_t	49.89	49.99
H_l	80.06	78.74
H_a	77.18	76.99
H_b	101.23	100.80

[a] HF *H* values were obtained from GE(=C$_b$H−) = −38.455 76 and GE(=C$_b$<) = −37.881 92. [b] BLYP *H* values were obtained from GE(=C$_b$H−) = −38.693 98 and GE(=C$_b$<) = −38.108 92.

TABLE 3: Total Energies (hartrees) and Strain Energies Δ*H* (kcal/mol) of Helical [*N*]Phenylenes

N	total energy[a]	reference energy[b]	strain energy
		HF/6-31G*	
6	−1372.273 30	−1372.27628	1.9
7	−1600.586 69	−1600.59249	3.6
8	−1828.898 67	−1828.90869	6.3
		BLYP/6-31G*	
6	−1380.626 93	−1380.63199	3.2
7	−1610.324 40	−1610.33294	5.4
8	−1840.022 71	−1840.03389	7.0

[a] From Table 1. [b] From the increments of Table 2.

The HF/6-31G* and BLYP/6-31G* energies of the helical [6]phenylene, given in Table 1, are −1372.273 30 and −1380.626 93 hartrees, respectively. Using the increments in Table 2, the energies of the hypothetical planar [6]phenylene, $2E_t + 4E_a$, are equal to −1372.276 28 and −1380.631 99. This indicates that despite its torsional deformations helical [6]phenylene has a small strain energy: 1.9 (HF) and 3.2 (BLYP) kcal/mol. Strain energies for [7]- and [8]phenylenes, given in Table 3, are also small. It seems likely that the relief of antiaromatic character in the cyclobutadiene rings partially offsets strain in and about the sigma bonds.

Acknowledgment. This work was supported in part by grants of the PSC-CUNY Research Award Program of the City University of New York (Grants 667322, 666313, and 668348). A grant of computing time from City University Computing and Information Services is gratefully acknowledged.

References and Notes

(1) (a) Berris, B. C.; Hovakmeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670. (b) Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153. (c) Boese, R.; Matzger, A. J.; Mohler, D. L.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1478. (d) Schmidt-Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1992**, *114*, 9713. (e) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 266. (f) Barton, J. W.; Walker, R. B. *Tetrahedron Lett.* **1978**, 1005. (g) Diercks, R.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *108*, 3150. (h) For **1**, see: Lothrop, W. C. *J. Am. Chem. Soc.* **1941**, *63*, 1187.

(2) (a) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 8470. (b) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1996**, *262*, 813. (c) Maksić, Z. B.; Kovaček, D.; Eckert-Maksić, M.; Böckmann, M.; Klessinger, M. *J. Phys. Chem.* **1995**, *99*, 6410. (d) Nambu, M.; Hardcastle, K.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 369. (e) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583. (f) Aihara, J. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 57. (g) Schulman, J. M.; Disch, R. L. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *259*, 173. (h) Trinajstić, N.; Schmalz, T. G.; Živković, T. P.; Nicolić, S.; Hite, G. E.; Klein, D. J.; Seitz, W. A. *New J. Chem.* **1991,** *15*, 27. (i) Randić, M. *Pure Appl. Chem.* **1980**, *52*, 1587. (j) Barton, J. W.; Rowe, D. J. *Tetrahedron* **1985**, *41*, 1323. (k) Randić, M. *Tetrahedron* **1977**, *33*, 1905. (l) Randić, M. *J. Am. Chem. Soc.* **1977**, *99*, 444. (m) Barron, T. H. K.; Barton, J. W.; Johnson, J. D. *Tetrahedron* **1966**, *22*, 2609.

(3) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Wang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *137*, 785.

(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Wong, M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. L.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision B.3, Gaussian, Inc.: Pittsburgh, PA, 1995.

(6) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 1902.

(7) Cioslowski, J.; O'Connor, P. B.; Fleishmann, E. D. *J. Am. Chem. Soc.* **1991**, *113*, 1086.

(8) (a) Harary, F.; Read, R. C. *Proc. Edinburgh Math. Soc., Ser. 2* **1970,** *17*, 1. (b) Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1989.

(9) Baughman, R. H.; Galvão, D. S.; Changxing, C.; Wang, Y.; Tománek, D. *Chem. Phys. Lett.* **1993**, *204*, 8.

(10) Grimme, S.; Peyerimhoff, D. D. *Chem. Phys.* **1996**, *204*, 411.