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Limiting Properties of Large [*N*]Phenylenes

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Geometries, energies, and magnetic properties are reported at the ab initio B3LYP/6-31G* level for three classes of [*N*]phenylene: helical ([*N*]heliphenes) ($N = 14$, 19, and 24); zigzag, and linear ($N = 14$ and 19). Bond lengths, proton chemical shifts, and nucleus-independent chemical shift (NICS) values are converged for all three forms. Limiting values for the proton shifts are δ 6.50, 5.92−5.97, and 5.87 for the zigzag, helical, and linear classes, respectively. NICS values have converged for zigzag and linear [19]phenylenes and for [24]heliphene. The inner four-membered rings of [19]heliphene and [24]heliphene are sandwiched between six-membered rings (and vice versa). NICS values for the heliphenes are small and positive along the helical axis. The length of [24]heliphene is ca. 14.6 Å, and its internal diameter is ca. 5.3. For $N = 14$ and 19, the zigzag isomer is lowest in energy, the linear is the highest; the differences are, at most, 2 kcal/mol per ring. A similar ordering is found for isotropic magnetic susceptibilities.

Introduction

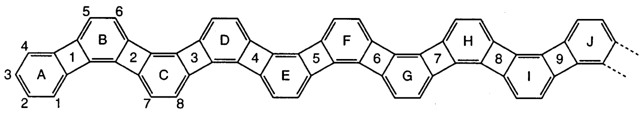
[*N*]Phenylenes comprise *N* benzene rings capping and alternating with $N - 1$ interior cyclobutadiene rings; the simplest, biphenylene ($N = 2$), was first synthesized in 1941. The higher homologues can exhibit a variety of topologies, including angular, linear, branched, and cyclic, and possess both planar and nonplanar geometries. Synthetic realization and characterization of many new phenylenes have come largely from the efforts of Vollhardt and collaborators,[1] beginning in the 1980s and leading recently to helical [9]phenylene,[1c] styled "[9]-heliphene" by analogy to the all-benzenoid helicenes. This work has been accompanied and, to some extent, encouraged by theoretical work of several groups.[2] It seems appropriate now to bring theory to bear on some significantly larger phenylenes, to determine their limiting properties. Here, we report calculations on zigzag and linear [14]phenylenes and [19]phenylenes, and helical phenylenes for $N = 14$, 19, and 24. In addition to obtaining optimized geometries, energies, proton chemical shifts, and magnetic susceptibilities, we utilize the nucleus-independent chemical shifts (NICS) introduced and exploited by Schleyer and co-workers[3] to assess the extent of aromatic and antiaromatic character. We compute the magnetic shielding at or near ring centroids and along helical axes.

Methods

Ab initio calculations were performed with Gaussian 98[4] on servers of the Digital Alpha architecture. Geometries were obtained from calculations in the 6-31G* basis[5] at the B3LYP density-functional[6] and SCF levels. The former level has been found to give bond lengths in good agreement with experimental X-ray values, where available; e.g., the average deviation between experiment and theory for [8]heliphene is 0.0037 Å.[1c] Proton chemical shifts relative to TMS were calculated at the B3LYP/6-31G* geometries, using the GIAO method[7] at the HF/6-31G* level. Calculations of the proton shifts of the phenylenes at this level generally reproduce experimental values (which include solvation effects) to within 0.3 ppm. NICS(0) and NICS(1) were similarly calculated for the zigzag and linear forms. For the nonplanar rings of the heliphenes, the shielding was computed only at the ring centroids (NICS(0)) to avoid ambiguity in the selection of other points. Magnetic susceptibilities were calculated by means of the continuous set of gauge transformations (CSGT).[8] Vibrational frequencies were calculated at the B3LYP/3-21G level for zigzag, helical, and linear [14]phenylenes.

Zigzag Phenylenes

Zigzag [19]phenylene (**Z19**), of C_{2v} symmetry, has 10 unique six-membered rings, A, B, C, ..., J, and nine unique four-membered rings, counted from the terminus inward. The B3LYP/6-31G* bond lengths (Figure 1) of the (symmetrical) innermost six-membered ring, J, are identical to those of six-membered rings F−I, within 0.0001 Å. Similarly, lengths e and f of four-membered rings 5−8 agree with those of ring 9 within the same small amount. Thus, an effective convergence of bond lengths is found in the innermost nine six-membered rings. In fact, within 0.001 Å, corresponding bond lengths in all rings, excluding only rings A, B, 1, and 2 (and their symmetrical equivalents), are the same.



Data on chemical shifts (Table 1) reveal the same pattern: proton shifts on rings D−J are each δ 6.50 ppm, implying very similar ring currents. The negative NICS(1) values for the six-membered rings (Table 2), which indicate aromatic character, include A, −9.16; B, −3.95; C, −5.57; F, −5.08; and G−J, −5.18 ppm. There is nearly identical aromatic character in the nine innermost rings of **Z19**. Of the six-membered rings, A is the most aromatic, B the least—a pattern confirmed by the chemical shifts and observed previously in the smaller angular

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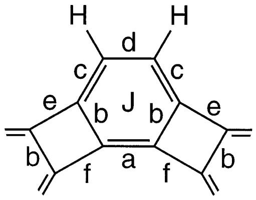

bond	zigzag	helical
a	1.361	1.362
b	1.452	1.453
c	1.371	1.371
d	1.438	1.435
e	1.492	1.489
f	1.491	1.496

Figure 1. Bond lengths (given in angstroms) at the centers of **Z19** and **H19**. Either four-membered ring may be taken as number 9.

TABLE 1: Proton Chemical Shifts

	chemical shift, δ (ppm)					
proton[a]	H24	Z19	H19	L19	H14	Z14
Ring A						
H_1	7.03	7.08	7.07	6.33	7.12	7.08
H_2	6.67	7.09	6.69	6.59	6.73	7.09
H_3	6.73	7.11	6.69	6.59	6.79	7.11
H_4	6.67	7.02	6.71	6.33	6.72	7.02
Ring B						
H_5	5.95	6.26	5.99	6.12	6.01	6.26
H_6	5.95	6.32	5.98	6.12	6.03	6.32
Ring C						
H_7	6.15	6.47	6.19	5.97	6.26	6.54
H_8	6.16	6.48	6.20	5.97	6.28	6.53
Ring D						
H_9	6.08	6.50	6.12	5.91	6.21	6.47
H_{10}	6.11	6.50	6.15	5.91	6.24	6.48
Ring E						
H_{11}	6.11	6.50	6.16	5.88	6.24	6.50
H_{12}	6.16	6.50	6.19	5.88	6.29	6.50
Ring F						
H_{13}	6.14	6.50	6.16	5.87	6.23	6.49
H_{14}	6.16	6.50	6.17	5.87	6.28	6.49
Ring G						
H_{15}	5.98	6.50	6.01	5.87	6.11	6.50
H_{16}	5.81	6.50	5.87	5.87	6.17	6.50
Ring H						
H_{17}	5.90	6.50	5.98	5.87		
H_{18}	5.97	6.50	6.05	5.87		
Ring I						
H_{19}	5.96	6.50	6.05	5.87		
H_{20}	5.92	6.50	6.00	5.87		
Ring J						
H_{21}	6.16	6.50	6.04	5.87		
H_{22}	5.93	6.50	6.04	5.87		
Ring K						
H_{23}	5.92					
H_{24}	5.92					
Ring L						
H_{25}	5.93					
H_{26}	5.97					

[a] Atom numberings in the helical case follow those of refs 1b and 1c.

phenylenes.[2a] The four-membered rings are all antiaromatic (NICS(1) > 0), the innermost 10 being almost equally so, with a NICS(1) of +3.30 ± 0.01. The damped oscillations that characterize NICS values in the smaller phenylenes[2a] become imperceptible after six-membered ring G and four-membered ring 7 of **Z19**.

^{13}C chemical shifts in these same rings reveal only three types of carbon atoms (to within 0.1 ppm): δ 119.8, 145.2, and 135.5 for the outer (H-bearing), middle, and inner carbons.

Bond lengths, proton shifts, and NICS values of all rings of (C_{2h}) zigzag [10]phenylene (**Z10**) and [14]phenylene (**Z14**) are virtually identical to their counterparts in **Z19**.

Helical [*N*]Phenylenes (Heliphenes)

The helical [*N*]phenylenes have C_2 symmetry. To obtain converged geometries and magnetic properties, it is necessary to have several consecutive six-membered rings sandwiched between upper and lower turns of the helix, and the latter not to include rings A and B, because they are themselves unique in their distortion. The [24]heliphene (**H24**) seems to be a reasonable compromise between what one might expect in convergence of properties and availability of computing power. Side and top views of **H24** are shown in Figures 2 and 3.

Analysis requires that a "helical axis" be defined. We take this to be that axis within the helical cavity and perpendicular to the C_2 symmetry axis that is farthest from any carbon atom. (The center of mass cannot lie at the intersection of the helical axis and the symmetry axis.) We define the internal radius of the helix as this maximum distance. Only H_1 of each terminal ring lies within the radius.

H24 consists of ~3.75 helical turns. Its length, given by the distance between the centroids of the two (terminal) A rings projected onto the helical axis, is 14.55 Å; the internal diameter is ca. 5.3 Å. In the interior of the molecule, six-membered rings and four-membered rings stack alternately. For example, four-membered ring 12 is sandwiched between six-membered rings F and S; the distance between the centroid of ring 12 and that of ring F or S is ca. 4.1 Å. Viewed down the helical axis, bonds a of rings F and S are approximately superimposed upon bond f of ring 12. The hydrogen atoms of rings F and S are ca. 4.6 Å from the nearest carbon atoms of four-membered ring 12.

The bond lengths of the innermost (central) four-membered ring and its flanking six-membered rings L and M in **H24** are identical, within 0.001 Å, to those of **H19** (Figure 1). These same bond lengths are found for all rings except A, B, C, 1, and 2. Moreover, they are almost identical to those of **Z19**, the largest differences being 0.003 and 0.004 for e and f, respectively. Thus, strain in the heliphenes is largely torsional.

Table 3 contains the dihedral angles about the twelve bonds e (angle c−e−c) and f (angle a−f−a) of the outer and inner peripheries of **H24**. They are denoted as e_{12}, f_{12} for four-membered ring 12, etc. For rings 8−12, these angles are in the range 5.9°−6.2° for e and 12.1°−13.1° for f. These small differences are probably due to slightly different environments along the helix. The helical phenylenes, however long, are in a certain sense aperiodic structures; their rings have progressively changing vertical phase relationships that prevent precise repetition. Note the slight variance of chemical shifts (Table 1) and NICS(0) values (Table 2). Proton shifts in rings K and L range from δ 5.92 to 5.97.

NICS(0) values (Table 2) for rings H−L of **H24** are −4.54 ± 0.02. This value is slightly more negative than that of **Z19**. Values for the innermost four-membered rings of **H24**, on average, are 11.51 ± 0.05; the comparable average for the innermost four-membered rings in **Z19** is 12.04. NICS values were also calculated at points on the helical axis at intervals of 1 Å. The interior values are ca. 1.0 (deshielding).

Linear Phenylenes

The length of the four equivalent CC bonds of the (symmetrical) innermost six-membered ring, J, of linear [19]phenylene (**L19**, D_{2h}) is 1.395 Å; that of the two bonds shared by J and its flanking (equivalent) four-membered rings 9 and

TABLE 2: NICS(0) and NICS(1)[a] Values of [*N*]Phenylenes

ring	**H24**	**H19**	**H14**	**Z19**	**Z14**	**L19**	**L14**
Six-Membered Rings							
A	−8.38	−8.34	−8.31	−7.97 (−9.16)	−7.98 (−9.17)	−5.47 (−6.90)	−5.47 (−6.90)
B	−3.13	−3.08	−3.04	−2.85 (−3.95)	−2.86 (−3.95)	−3.13 (−4.58)	−3.14 (−4.59)
C	−4.98	−4.92	−4.82	−4.69 (−5.57)	−4.69 (−5.58)	−3.03 (−4.47)	−3.04 (−4.48)
D	−4.36	−4.31	−4.19	−4.23 (−5.08)	−4.13 (−5.09)	−2.93 (−4.37)	−2.94 (−4.38)
E	−4.48	−4.42	−4.31	−4.24 (−5.21)	−4.28 (−5.22)	−2.93 (−4.36)	−2.93 (−4.37)
F	−4.21	−4.18	−4.10	−4.24 (−5.17)	−4.24 (−5.18)	−2.92 (−4.35)	−2.93 (−4.36)
G	−4.84	−4.75	−4.70	−4.24 (−5.18)	−4.25 (−5.19)	−2.92 (−4.35)	−2.93 (−4.36)
H	−4.53	−4.42		−4.24 (−5.18)		−2.92 (−4.35)	
I	−4.56	−4.45		−4.24 (−5.18)		−2.92 (−4.35)	
J	−4.53	−4.41		−4.24 (−5.18)		−2.92 (−4.35)	
K	−4.54						
L	−4.52						
Four-Membered Rings							
1	14.19	14.23	14.26	14.54 (5.37)	14.54 (5.38)	18.50 (9.27)	18.48 (9.27)
2	10.79	10.84	10.92	11.20 (2.59)	11.20 (2.60)	18.25 (9.43)	18.25 (9.42)
3	11.77	11.83	11.90	12.24 (3.48)	12.24 (3.48)	18.64 (9.80)	18.64 (9.80)
4	11.46	11.52	11.62	11.97 (3.24)	11.96 (3.24)	18.67 (9.85)	18.67 (9.84)
5	11.51	11.54	11.70	12.05 (3.31)	12.06 (3.32)	18.70 (9.88)	18.69 (9.87)
6	11.41	11.45	11.60	12.03 (3.29)		18.70 (9.88)	18.69 (9.88)
7	11.35	11.46	11.34	12.04 (3.30)		18.70 (9.89)	18.69 (9.88)
8	11.54	11.59		12.04 (3.30)		18.70 (9.89)	
9	11.53	11.63		12.04 (3.30)		18.70 (9.89)	
10	11.49						
11	11.46						
12	11.51						

[a] NICS(0) and NICS(1) values are given in ppm. NICS(1) values for planar rings are given in parentheses. They are isotropic shieldings 1 Å from the ring centroid in a direction perpendicular to the ring. For benzene, NICS(0) = −11.54 and NICS(1) = −12.81; for cyclobutadiene, NICS(0) = 25.9 and NICS(1) = 17.5.

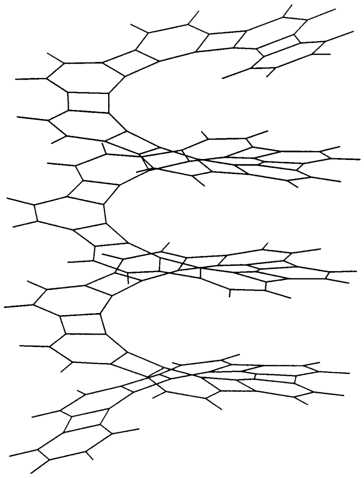

Figure 2. Side view of **H24** with the helical axis aligned vertically.

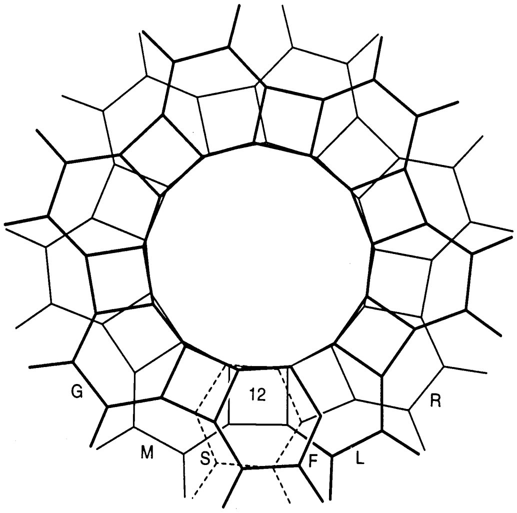

Figure 3. Top view of a cutaway of **H24**, showing the 14 six-membered rings F−S. The C_2 axis passes through four-membered ring 12, which has six-membered rings F (outlined by bold lines) and S (outlined by dashed lines) above and below it. For clarity, other stackings, such as 5 and 18 about six-membered ring L, are not entirely shown.

10 is 1.417. Ring J is approximately regular hexagonal, devoid of nominal single and double bonds. It is even more symmetrical than ring A, in contrast to the zigzag and helical phenylenes. Two CC bonds of length 1.511 Å, which join rings I and J, complete four-membered ring 9. All these bond lengths are identical to those of six-membered rings G−I and four-membered rings 7−8 within 0.0001 Å. Thus, an effective convergence of bond lengths is found in the innermost seven six-membered rings. Within 0.001 Å, corresponding bond lengths in all rings, excluding only A, B, C, 1, and 2, are the same.

Proton shifts on rings F−J are each δ 5.87, implying very similar ring currents. ^{13}C chemical shifts, which reveal only two types of carbon atoms (to within 0.1 ppm) in these same rings, are δ 108.2 (H-bearing carbon atoms) and 152.4.

The negative NICS(1) values for the six-membered rings (Table 2) include A, −6.90; B, −4.58; C, −4.47; and F−J, −4.35: there is nearly identical aromatic character in the nine innermost rings of **L19**. The aromatic character of the six-membered rings is largest for ring A, decreasing monotonically thereafter. This differs from the zigzag and helical cases, which show pronounced oscillation in NICS values for rings A, B, and C. The four-membered rings are all antiaromatic (NICS(1) > 0), the innermost 10 being almost equally so, with NICS(1) of +9.89 ± 0.01. All are considerably more antiaromatic than their counterparts in **Z19** and **H19**.

For linear [14]phenylene (**L14**), the bond lengths, proton and ^{13}C resonances, and NICS values are virtually identical to their counterparts in **L19**.

TABLE 3: Dihedral Angles[a] of H24 about the Four-Membered-Ring Single Bonds e and f

Single Bond e Data				Single Bond f Data			
e_{12}	6.0	e_6	6.7	f_{12}	12.5	f_6	10.7
e_{11}	5.9	e_5	5.7	f_{11}	13.1	f_5	12.7
e_{10}	6.2	e_4	4.9	f_{10}	12.7	f_4	13.1
e_9	5.9	e_3	3.8	f_9	12.1	f_3	10.8
e_8	6.0	e_2	2.8	f_8	12.6	f_2	4.6
e_7	5.5	e_1	2.1	f_7	13.7	f_1	−1.2

[a] Dihedral angles given in units of degrees.

TABLE 4: B3LYP/6-31G* Ab Initio Energies of the [*N*]Phenylenes

H9	−2070.53385	**Z19**	−4368.41981 (0.0)
Z10	−2300.33256	**H19**	−4368.37698 (26.9)
Z14	−3219.48253 (0.0)	**L19**	−4368.35539 (40.4)
H14	−3219.45550 (17.0)	**H24**	−5517.29803
L14	−3219.43705 (28.5)		

[a] Energies given in au.

Discussion

Zigzag [19]phenylene (**Z19**), converged in its geometry, chemical shifts, and NICS values, provides a basis for interpreting B3LYP/6-31G* results on the other phenylenes. Thus, the bond lengths of the inner rings of **H19** and **H24** are quite similar to those of **Z19**. For the six-membered rings, the range of lengths is $\Delta R = 0.091$ Å. Referred to the calculated bond length of 1,2-dimethylene cyclobutene,[9] the rings of **H19** and **Z19** are 43% and 44% bond-fixed, respectively.

Comparison of the proton resonances of **Z19** and **H19** shows the protons of the heliphene to be more shielded by 0.46 ppm for ring J. A ring-by-ring comparison of the NICS(0) value of **Z19** with **H19** shows the six-membered rings to be more negative, the four-membered rings less positive, in the helical form. Both proton-shift and NICS effects arise from the combination of torsion and stacking. The protons of **L19** are slightly more shielded than those of **H19**.

Total energies of the [*N*]heliphenes, including that of **H9**, are given in Table 4. The energies decrease with increasing *N* in a linear manner. In the helical case, the three energy increments for $\Delta N = 5$ are -1148.92139 ± 0.0003 au.

For $N = 14$ and 19, the zigzag form is thermodynamically the most stable and the linear form is the least stable. The energies of **Z19** and **H19** differ by 26.9 kcal/mol, or only 1.4 kcal/mol per ring. For **Z14** and **H14**, the difference is 17.0, or 1.2 kcal/mol per ring. Most of the extra strain in the heliphenes arises from torsional distortions, because the framework CC lengths and CCC angles are almost identical to those of the zigzag forms. Isomer **L19** has an energy that is 40.4 kcal/mol greater than that of **Z19**. **L19** has a $^3B_{1u}$ triplet-state energy 7.4 kcal/mol above that of the ground-state singlet; its energy at the geometry of the singlet, corresponding to a vertical transition, is significantly higher (31.8 kcal/mol). The ^3B triplet state of [19]heliphene is 38.9 kcal/mol greater than that of the ground-state singlet; its energy at the geometry of the ground state is 46.9 kcal/mol. HOMO−LUMO gaps (au) for **Z19**, **H19**, and **L19** at the HF/6-31G* level are 0.301, 0.284, and 0.224, respectively. The gaps for linear phenylenes decrease slowly with (*N*): 0.308 (3), 0.252 (6), 0.237 (9), 0.228 (14), and 0.224 (19). At this level, **L14** and **L19** show no evidence of the Peierl's distortion from D_{2h} symmetry, as predicted by solid-state Hückel calculations for the infinite polymer.[2g]

The isotropic magnetic susceptibility of **Z19**, $\chi = -545.8$ cgs·ppm, is slightly more negative than that of **H19** (−523.8). This is consistent with **Z19** being slightly more aromatic *overall* than **H19**. Conversely, for **L19**, $\chi = -430.23$, implying that it is considerably less aromatic than the helical and zigzag forms.

Comparison can be made with the (all-benzenoid) helicenes, which also have less-negative susceptibilities than their zigzag analogues,[10] known as phenacenes[11] (phenanthrene, chrysene, etc.); for example, $\chi = -553$ for zigzag [16]phenacene, whereas that of [16]helicene is −516. Note that χ of **Z19** is almost equal to that of [16]phenacene, although it contains 48 more carbon atoms. This reflects the paramagnetic effect of the four-membered rings.

Vibrational frequencies have been calculated for the $N = 14$ phenylenes at the B3LYP/3-21G level. While they are all real, the lowest are quite small: 2.5 (a_u), 10.1 (a), and 3.0 (b_{3u}) cm^{-1} for **Z19**, **H19**, and **L19**, respectively. They presage extreme flexibility for these $C_{84}H_{32}$ systems, which is consistent with the nonplanarity of smaller phenylenes in the solid state due to crystal packing.[12]

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