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Aromatic Character of [*n*]Helicenes and [*n*]Phenacenes

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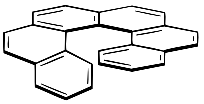
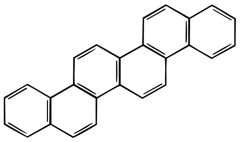
Ab initio calculations have been made on [*n*]helicenes and their planar, zigzag isomers, the [*n*]phenacenes, at the HF/6-31G* and B3LYP/6-31G* levels for $n = 6-10$ and 16 and at B3LYP/6-311G** for $n = 6-10$. The energies and magnetic susceptibilities of the helicenes and phenacenes are found to vary linearly with *n* in both series; comparison of them indicates only slight loss of aromatic character in the helicenes despite their large departures from planarity. Proton chemical shifts of [7]helicene and [7]phenacene are in good agreement with experiment. For [16]phenacene, the eight inner rings have nearly identical bond lengths and chemical shifts, showing their convergence to the zigzag infinite-polymer limit. While geometrical convergence is also evident in [16]helicene, the magnetic shielding, subject to effects of nonadjacent rings, requires a larger value of *n* for convergence.

Helicenes have been of interest since the synthesis and chiral resolution of [6]helicene by Newman and Lednicer in 1956.[1] Subsequent synthetic and spectral studies have been undertaken, including investigation of the large optical rotation of these C_2-symmetric helical polycyclic benzenoids.[2] Both experimental[3] and theoretical[4] investigations have been made of the barriers and mechanisms of racemization, which causes loss of optical activity. A question not heretofore addressed is the extent of aromatic character in the helicenes compared with that in their planar, zigzag isomers, the [*n*]phenacenes,[5] e.g., [6]helicene, **1a**, vs [6]phenacene, **1b**. The present study employs ab initio energies, magnetic susceptibilities, and chemical shifts. These methods have recently been applied to helical [*N*]phenylenes.[6]



1a



1b

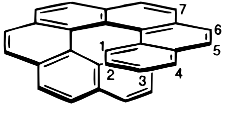
Computational Methods

Calculations were performed with GAUSSIAN 98[7] on Digital Alpha AXP servers. Optimized geometries and energies were obtained in the 6-31G* basis[8] at the HF and B3LYP density functional[9] levels for $n = 6-10$ and 16 ([16]helicene and [16]-phenacene) and at B3LYP/6-311G** for $n = 6-10$. Magnetic susceptibilities were computed by means of the continuous set of gauge transformations (CSGT).[10] NMR chemical shifts were calculated by the GIAO method[11,12] at B3LYP/6-31G*. The absence of imaginary frequencies was verified at the HF/3-21G level through $n = 10$.

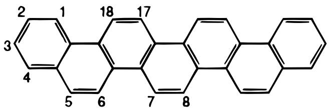
Energetics

Energies of the [*n*]helicenes (Table 1) increase nearly linearly with *n*, the increments being −152.640, −153.634, and −153.666 ± 0.001 h at HF/6-31G*, B3LYP/6-31G*, and B3LYP/6-311G**, respectively. Similarly, energies of the phenacenes increase by nearly constant increments of −152.65213, −153.64402, and −153.6765 ± 0.0002 hartree at these levels. These latter results are consistent with earlier theoretical findings on the zigzag series to $n = 5$.[13]

A phenacene is more stable than its isomeric helicene. For example, [7]phenacene, **2b**, is more stable than heptahelicene, **2a**, by 27.2 (HF/6-31G*), 23.2 (B3LYP/6-31G*), and 22.8 kcal/mol (B3LYP/6-311G**). The energy difference in favor of the phenacene (ΔE_n, the extra strain energy attending helical distortion) increases with *n* by ca. 6.3 kcal/mol per ring at the density-functional levels. These changes reflect only a small distortion of each ring. The enthalpy change of homodesmic reaction 1 is $\Delta E_7 - \Delta E_6$, 6.2 kcal/mol at B3LYP/6-31G*.



2a

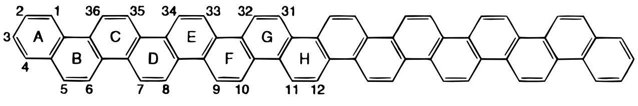


2b

$$\mathbf{1a} + \mathbf{2b} \rightarrow \mathbf{2a} + \mathbf{1b} \qquad (1)$$

$$\mathbf{1a} + \mathbf{3b} \rightarrow \mathbf{3a} + \mathbf{1b} \qquad (2)$$

Similarly, for reaction 2, involving [16]helicene **3a** (displayed in Figures 1 and 4) and [16]phenacene **3b**, $\Delta H = \Delta E_{16} - \Delta E_6 = 66.4$ kcal/mol, consistent with the fact that this reaction is a 10-fold scaling of reaction 1.



3b

Standard heats of formation of helicenes and phenacenes can be computed from the HF/6-31G* energies and group equivalents previously determined[13b] for benzenoid aromatics: −38.45576 for $=C_bH-$ and −37.88263 for $=C_b<$. For hexa-

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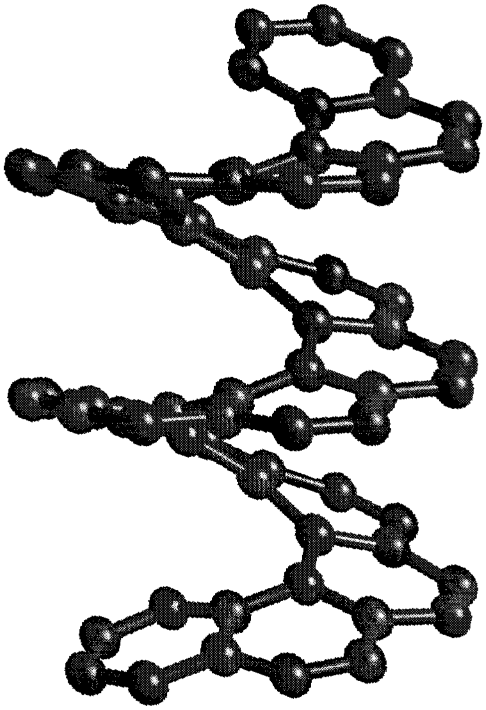
TABLE 1: Ab Initio Energies (hartree) of the Helicenes and Phenacenes

	HF/6-31G*			B3LYP/6-31G*			B3LYP/6-311G**		
n	phenacene	helicene	ΔE_n[a]	phenacene	helicene	ΔE_n[a]	phenacene	helicene	ΔE_n[a]
6	−993.965 32	−993.933 50	20.0	−1000.470 14	−1000.442 99	17.0	−1000.691 93	−1000.665 88	16.3
7	−1146.617 49	−1146.574 11	27.2	−1154.114 18	−1154.077 26	23.2	−1154.368 58	−1154.332 91	22.8
8	−1299.269 61	−1299.214 63	34.5	−1307.758 20	−1307.711 19	29.5	−1308.045 05	−1307.999 45	28.6
9	−1451.921 75	−1451.855 44	41.6	−1461.402 22	−1461.345 48	35.6	−1461.721 52	−1461.666 27	34.7
10	−1604.573 88	−1604.495 08	49.4	−1615.046 23	−1614.978 96	42.2	−1615.397 95	−1615.332 15	41.3
16	−2520.486 65	−2520.329 70	98.5	−2536.910 35	−2536.777 47	83.4			

[a] Energy difference in kcal/mol.



3a

Figure 1. Carbon-atom framework of [16]helicene at its B3LYP/6-31G* geometry.

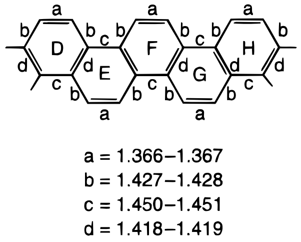


Figure 2. The carbon−carbon bond lengths of [16]phenacene at its B3LYP/6-31G* geometry.

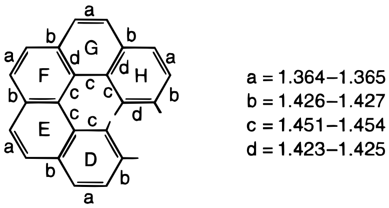


Figure 3. The carbon−carbon bond lengths of [16]helicene at its B3LYP/6-31G* geometry.

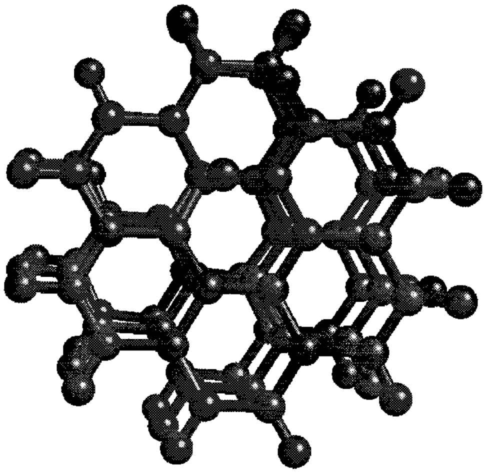


Figure 4. [16]Helicene (**3a**, B3LYP/6-31G*) viewed approximately along the helical axis.

helicene (**1a**), $C_{26}H_{16}$, we obtain $\Delta H_f^\circ = 116.1$ kcal/mol; for heptahelicene (**2a**), $C_{30}H_{18}$, $\Delta H_f^\circ = 138.8$ kcal/mol.

Magnetic Susceptibilities

Magnetic susceptibilities of the helicenes and phenacenes were calculated by the CSGT method. Values of the isotropic component χ_{iso} (Table 2) show a nearly constant increase within each series. For the [n]phenacenes they change by ca. −32.1 and −35.6 ppm cgs at the B3LYP/6-31G* and B3LYP/6-311G** levels, respectively; χ_{iso} of the helicenes change by smaller amounts: −28.0 ± 0.4 and −31.9 ± 0.5.

The difference in magnetic susceptibility $\Delta\chi_{iso}$ between the [n]helicene and the [n]phenacene should be a useful indicator of the loss of aromatic character.[14] It is seen that each [n]phenacene has the more negative χ_{iso}: $\Delta\chi_{iso}$ is always positive, consistent with less aromatic character for the helicenes. The loss of aromatic character by this criterion is small: at the density-functional levels, $\Delta\chi_{iso}$ increases by 4.2 ± 0.3 or 3.75 ± 0.5 ppm cgs for each additional inner ring, while $|\chi_{iso}|$ of the [n]phenacene increases by 32.1 ± 0.1 or 35.6 ± 0.1. This implies a 13.1% or 10.5% loss of aromatic character for an interior helicene ring. The value at HF/6-31G* is 8.1%.

Magnetic susceptibilities computed at the B3LYP/6-311G** level give values for χ_{iso} in good agreement[15] with measured values.[16] For heptahelicene and [7]phenacene we obtain $\chi_{iso} = -257.5$ and -267.3 ppm cgs, respectively, giving $\Delta\chi_{iso} = 9.8$. Calculated χ_{iso} values for phenanthrene and chrysene are −124.4 and −160.7, which extrapolate to −269.6, close to the value of −267.3 found here. Thus, [7]phenacene has a magnetic susceptibility consistent with those of other planar aromatics, and χ_{iso} of heptahelicene is similar to that of [7]phenacene.

Chemical Shifts

The proton and ^{13}C chemical shifts of many of the larger helicenes have been determined and partially assigned by the late R. H. Martin, N. Defay, and others.[17] Our proton shifts, computed by GIAO at the B3LYP/6-31G* level, agree reasonably well with the experimental values. The calculated (experimental[17a]) proton shifts (δ) for the nine unique protons of heptahelicene (**2a**) are H_1, 7.3 (7.0); H_2, 6.5 (6.3); H_3, 6.9

TABLE 2: Ab Initio Magnetic Susceptibilities χ_{iso} (ppm cgs) of the Helicenes and Phenacenes

	HF/6-31G*			B3LYP/6-31G*			B3LYP/6-311G**		
n	phenacene	helicene	$\Delta\chi_{iso}$	phenacene	helicene	$\Delta\chi_{iso}$	phenacene	helicene	$\Delta\chi_{iso}$
6	−217.3	−211.4	5.9	−207.5	−200.6	6.9	−231.8	−225.2	6.6
7	−250.8	−242.2	8.6	−239.5	−228.7	10.8	−267.3	−257.5	9.8
8	−284.4	−272.9	11.5	−271.7	−256.4	15.2	−303.0	−288.9	14.1
9	−317.9	−303.9	14.0	−303.8	−284.7	19.1	−338.6	−320.6	18.0
10	−351.4	−334.4	17.0	−335.9	−312.4	23.5	−374.3	−352.0	22.3
16	−552.7	−515.5	37.2	−528.8	−483.0	45.8			

(6.8); H_4, 7.2 (7.1); H_5, 7.2 (7.4); H_6, 7.6 (7.6); H_7, 7.8 (7.8); H_8, 7.8 (8.0); H_9, 7.8 (7.9).

The calculated (experimental[5b]) proton shifts in [7]phenacene (**2b**) are H_1, 8.8 (9.01); H_2, 7.7 (7.92); H_3, 7.6 (7.83); H_4, 7.8 (8.17); H_5, 7.9 (8.20); H_6, 8.7 (9.00); H_7, 8.9 (9.16); H_{17}, 9.0 (9.23); H_{18}, 8.9 (9.12).

Discussion

We have shown that the [*n*]helicenes are closely related in their energies and magnetic susceptibilities to the [*n*]phenacenes. The two series have identical local connectivities, Kekulé counts, conjugated circuits, and other graph-theoretic properties.[18] The [*n*]helicenes are kinetically stable and have been prepared through $n = 14$,[19] the [*n*]phenacenes through $n = 11$ (for a derivative[5b]). Both series differ markedly from the polyacenes (anthracene, tetracene, etc.), which become rapidly more unstable or reactive with increasing *n*.

An interesting question is how similar the inner benzene rings of [16]phenacene and [16]helicene are to those of the infinite one-dimensional polymers, where, for example, each benzene ring would be characterized by the four bond lengths a, b, c, and d shown in Figures 2 and 3. These parameters, calculated at the B3LYP/6-31G* level, have converged within ca. 0.001 Å to common values for the innermost eight rings of **3a** and **3b**. In fact, corresponding bond lengths in the two isomers are very similar. In [16]helicene (Figures 3 and 4), most of the torsional strain is about bonds c and d. The dihedral angles in the center of **3a**, defined by two bonded carbon atoms (this bond is specified second) and two adjacent atoms, are as follows: b−a−b, 10.2°; a−b−d, 0.7°; d−c−d, 16.5°; b−d−c, 17.3°. The sum of the angles about any carbon atom of **3a** is very close to 360°; there is some angular distortion at the inner carbons, where the angle between two C−C bonds (c) is 125.1°. Such distortions in hexahelicenes and related compounds have recently been discussed.[20]

An infinite zigzag polymer would have a single proton resonance and two ^{13}C resonances. For [16]phenacene, the proton shifts on the twelve inner rings (hydrogens 7−12 and 31−36) are nearly coincident, the range being δ 9.1−9.2. The bridgehead carbons (linking rings C−D, D−E, E−F, F−G, and G−H) resonate from δ 123.1 to 123.5, while the methine carbons in rings D−H are at δ 116.8−117.0.

An infinite helical polymer would have a single proton resonance and three ^{13}C resonances. For [16]helicene the proton shifts on the inner four rings (G−J) are in the range δ 6.4−6.6. The proton resonances of the innermost rings of [16]helicene are ca. 2.5 ppm upfield from those of [16]phenacene. The outer and inner bridgehead carbons (linking rings E−F, F−G, G−H, and H−I) resonate from δ 124.3 to 124.8 and δ 119.6 to 121.2, respectively, while the methine carbons in rings D−H are at δ 119.9−121.0.

The degree of aromatic character in each ring of [16]phenacene can also be assessed by the NICS method.[21] For the eight unique rings of **3b**, labeled A−H from the terminus, NICS values (ppm) at the B3LYP/6-31G* level at the ring centroids and 1.0 Å above the centroids (in parentheses) are −9.9 (−11.6), −7.2 (−9.6), −8.0 (−10.3), −7.6 (−9.9), −7.7 (−10.0), −7.6 (−10.0), −7.6 (−10.0), and −7.6 (−10.0). There is a damped alternation of the shielding similar to that found in larger zigzag [*N*]phenylenes,[6c] approaching a constant value toward the center. The nearly identical NICS values of rings E−H indicate equivalent aromatic character in the inner eight rings. (This convergence is essentially achieved in the E rings of [9]- and [10]phenacene.)

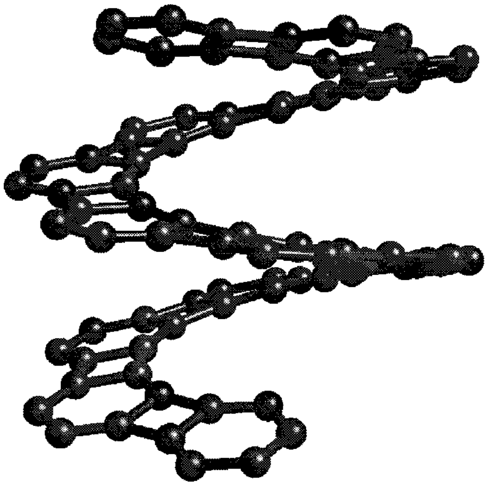


Figure 5. Carbon-atom framework of helical [14]phenylene.

For [16]helicene, NICS values at the centroids of (the nonplanar) rings A−H are −11.7, −8.7, −8.6, −7.7, −6.8, −7.3, −7.7, and −8.1. That they have not yet converged to a constant value probably reflects the fact that only the equivalent rings H and I have benzene rings directly above and below, since the two terminal rings, which “cover” rings G and J, are somewhat splayed outward. Comparison of the NICS-centroid values of **3a** and **3b** shows a relative enhancement of the shielding for nearly all rings of [16]helicene.

Finally, the helicenes can be compared with the recently discussed helical [*N*]phenylenes,[6a] consisting of alternating benzene and cyclobutadiene rings, e.g., Figure 5. Helical phenylenes are strikingly less strained relative to their planar zigzag models than are the helicenes, since much of the bending takes place in the (antiaromatic) cyclobutadiene rings. For example, helical [8]phenylene is more strained than its model zigzag [8]phenylene by only 6.6 kcal/mol (HF/6-31G*), whereas for [8]helicene $\Delta E = 34.5$ kcal/mol.

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