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Properties of Phenylene-Based Hydrocarbon Bowls and Archimedene

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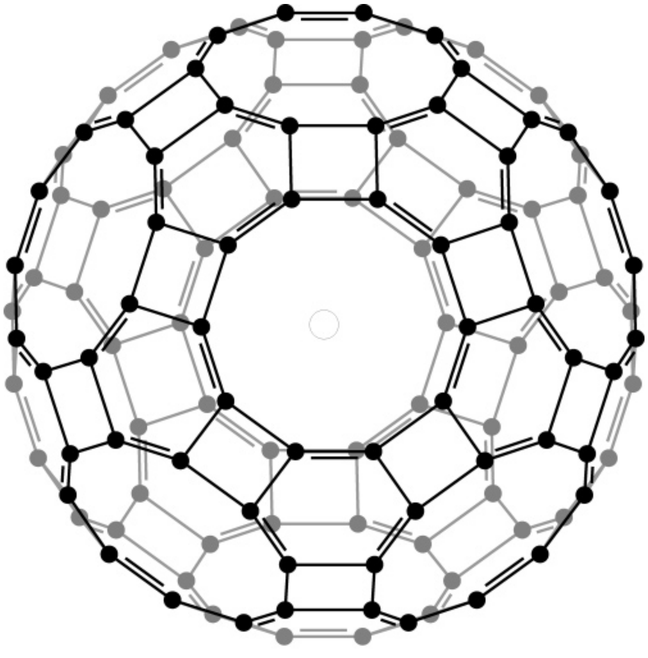
Geometries, energies and magnetic shieldings are reported at the ab initio B3LYP/6-31G* level for the phenylene cluster C_{120} (archimedene) and eight phenylene-based hydrocarbon bowls consisting of four-, six-, and ten-membered rings. The six-membered rings are branched, angular, or terminal. The latter are the most aromatic, based upon NICS criteria and lack of substantial bond alternation. At the other extreme are branched rings, having less negative NICS values. Four-membered rings, except those on a rim, are nearly square. Regularities are found in the ab initio energies, heats of formation (ΔH_f°), and strain energies relative to those of hypothetical planar acyclic analogues. The bowls appear to have little aromatic character, and their interiors are but slightly shielded. Archimedene, with $\Delta H_f^\circ = 2191$ kcal/mol, has energetic and structural properties akin to those of phenylene-based bowls.

The past two decades have seen syntheses and studies of convex polyhedral clusters of carbon atoms based upon networks of fused five- and six-membered unsaturated rings: fullerenes and their bowl-shaped hydrocarbon fragments. An analogous class of bowls could be based upon phenylene units: alternately fused unsaturated four- and six-membered rings. C_{120}, the polyhedral phenylene known as archimedene,[1] with 20 six-membered, 30 four-membered, and 12 ten-membered rings corresponds to fullerene C_{60}, having 20 six-membered and 12 five-membered rings; both are of I_h symmetry. Archimedene and its fragment hydrocarbons, primarily bowls, are the subject of this study. The bowls are of interest in their own right, and as synthetic intermediates in rational syntheses of archimedene. Phenylene-based bowls are also potential nanomaterials such as nanotips and semiconductors.

Synthetic realization and characterization of many acyclic phenylenes have come largely from the efforts of Vollhardt and collaborators,[2] in a variety of motifs, most recently helical phenylenes.[2f,g] The experimental work to date has been accompanied and to some extent encouraged by theoretical work.[3]

In this work ab initio theory is used to obtain energies, geometries, and magnetic shieldings of archimedene (**1**) and eight bowl-shaped phenylene hydrocarbons (**2**−**9**, Charts 1 and 2).[4] The selected bowls have hexagons, decagons, or rectangles of carbon atoms as their bases, giving rise to molecules of C_{3v}, C_{5v}, and C_{2v} symmetry, respectively (Table 1). The rings are nearly planar, exactly so when required by symmetry, as in the case of a base ring or any ring in archimedene. We denote each symmetrically equivalent set of six-membered rings 6A, 6B, ..., in order of increasing "distance" from the base. Similarly, 4A, 4B, ... and 10A, 10B, ... are sets of four-membered and ten-membered rings.

Nucleus-independent chemical shifts (NICS) introduced by Schleyer and co-workers[5] are used to assess the extent of aromatic or antiaromatic character by computation of the magnetic shielding at points 1 Å from the centroids of the rings, both inside and outside the bowl.



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Methods. Ab initio calculations were performed with Gaussian 98[6] on servers of the Digital Alpha architecture. Geometries were obtained from calculations in the 6-31G* basis[7] at the B3LYP density-functional[8] level. Such calculations give bond lengths in good agreement with experimental X-ray values, where available; for example, the average deviation between experiment and theory for [8]heliphene is 0.004 Å.[2g] Proton and ^{13}C chemical shifts relative to TMS and NICS values were calculated at the B3LYP/6-31G* geometries using the GIAO method[9] at the HF/6-31G* level. Vibrational frequencies were calculated at the B3LYP/6-31G* level, except for $C_{108}H_8$, $C_{114}H_6$, and C_{120}, where the B3LYP/6-31G level was used. All of the frequencies were found to be real, ranging from 20 to 40 cm^{-1} for the lowest of each bowl. The lowest frequency of C_{120} is 124 cm^{-1} (t_{2u}). The ab initio energies are listed in Table 1.

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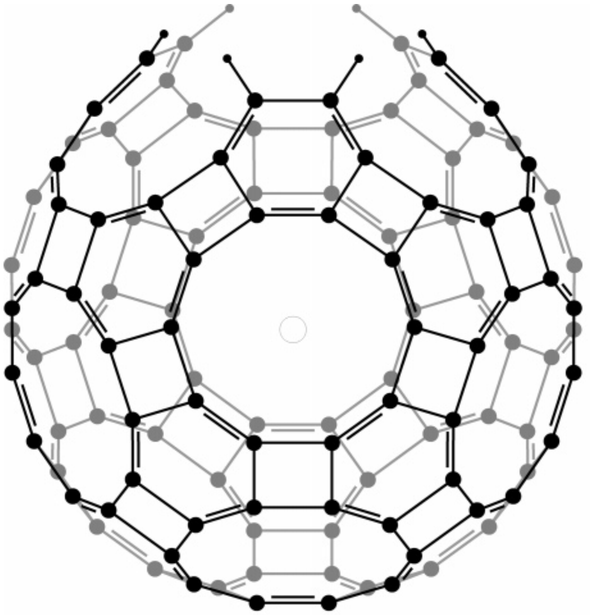
CHART 1



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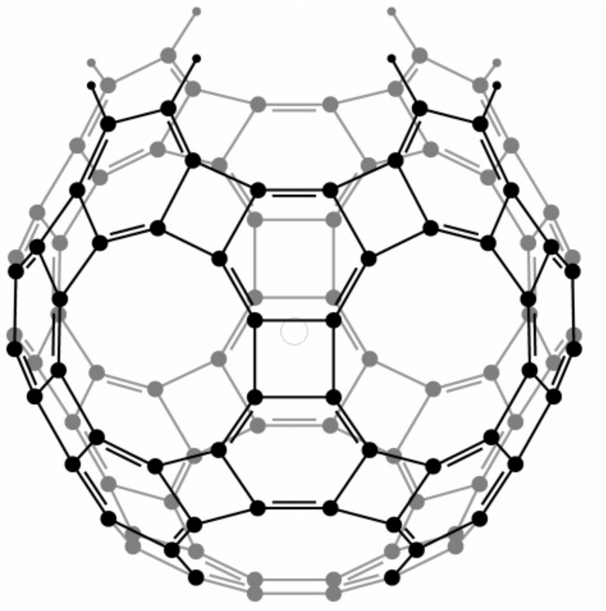

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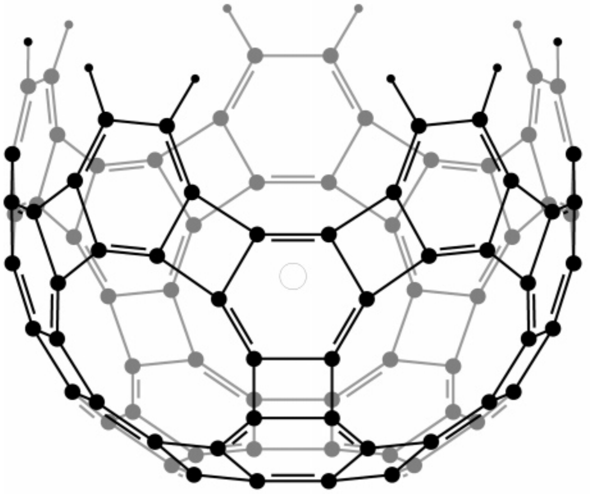

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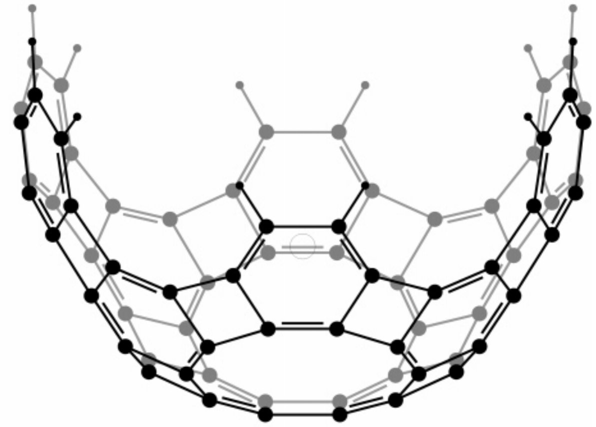

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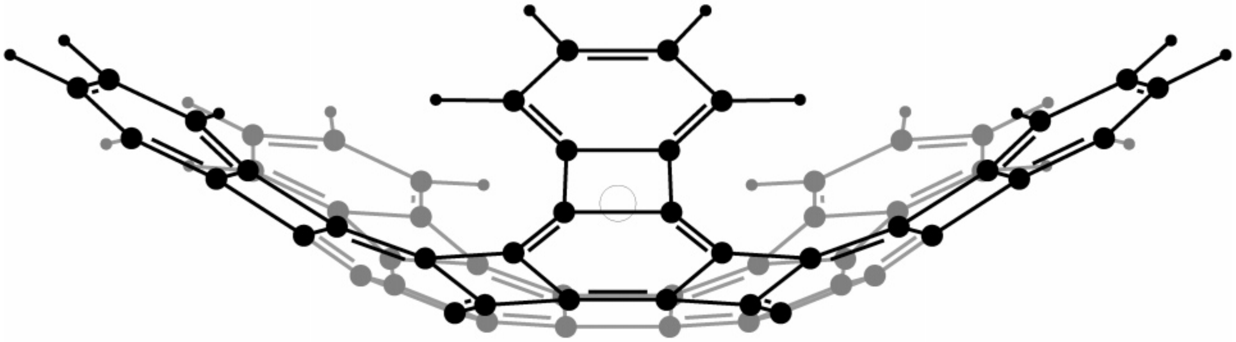

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Supplemented by zero-point and thermal corrections, they are used to calculate standard enthalpies of formation.

Geometries. The six-membered rings in phenylene bowls are branched, angular, or terminal, having, respectively, three, two, and one fused four-membered rings ("cyclobutadienes") and, equivalently, zero, two, and four hydrogen atoms. The six-membered rings of archimedene are branched. Angular six-membered rings are found on the bowl rims, except for $C_{60}H_{20}$ (**6**); derived from $C_{30}H_{10}$ (**9**, cyclic [5]phenylene,[3b,d] shown below viewed along its C_5 axis, it is one of several possible bowls having terminal but no angular rings.

The six-membered rings of archimedene have (formal) single and double bonds of lengths (B3LYP/6-31G*) 1.479 and 1.364 Å. Nearly identical lengths are found in the larger bowls. For branched rings 6A, 6B, and 6C of $C_{108}H_8$ (**3**) and $C_{114}H_6$ (**2**) the longest and shortest bond lengths are 1.479 ± 0.001 and

CHART 2

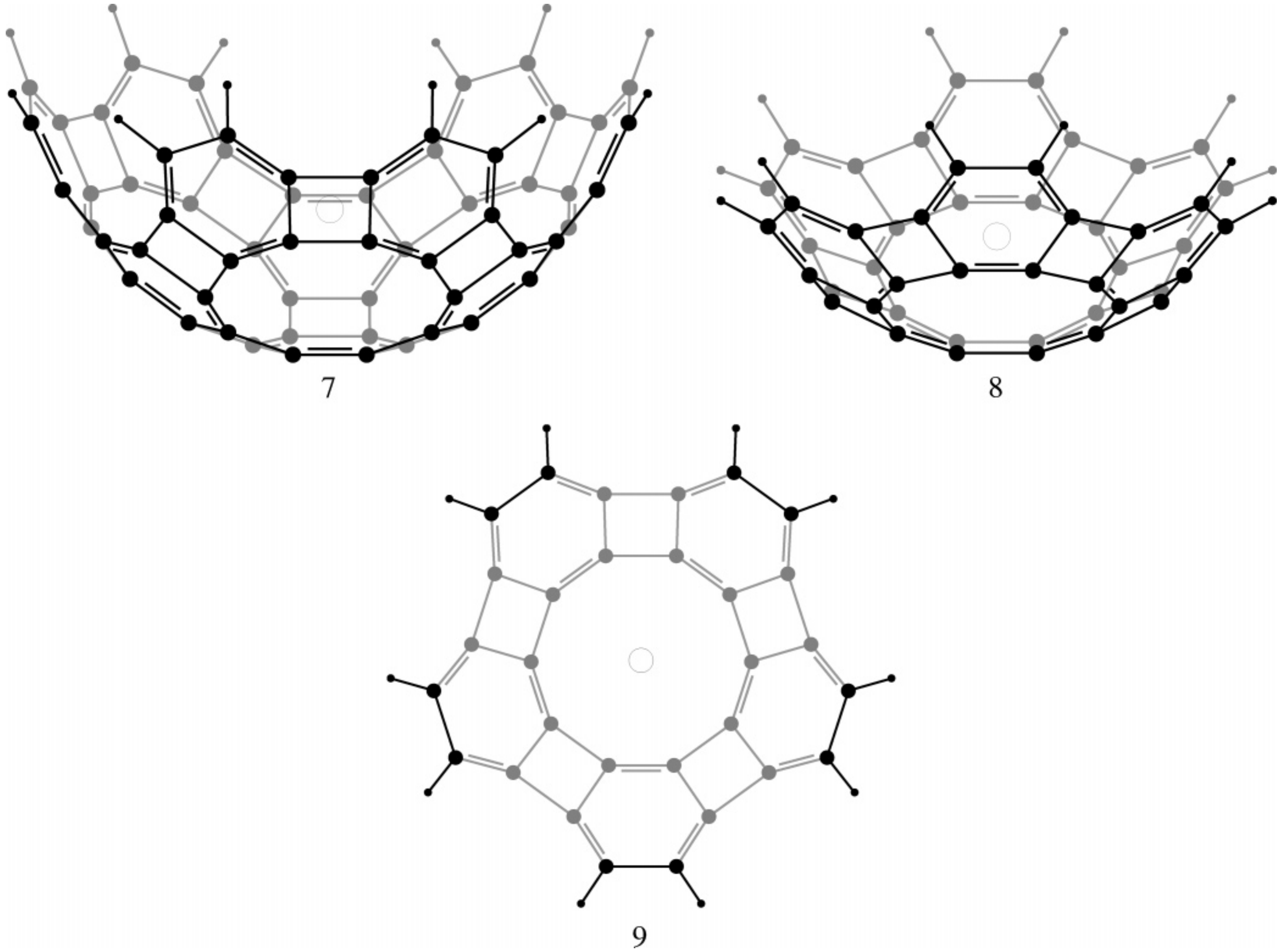


TABLE 1: Symmetries, Energies and Dipole Moments of Phenylene Bowls and Archimedene

	unique rings	total rings[a]	energy, h	dipole moment, D[b]
1 $C_{120}H_0$ (I_h)	1, 1, 1	30, 20, 12	−4570.96328	0.0
2 $C_{114}H_6$ (C_{3v})	6, 5, 3	27, 19, 9	−4346.09865	3.7
3 $C_{108}H_8$ (C_{2v})	8, 6, 3	25, 18, 8	−4118.78033	5.3
4 $C_{90}H_{10}$ (C_{5v})	3, 3, 2	20, 15, 6	−3434.36576	7.5
5 $C_{72}H_{12}$ (C_{2v})	5, 4, 2	15, 12, 4	−2749.94619	7.5
6 $C_{60}H_{20}$ (C_{5v})	2, 2, 1	10, 10, 1	−2297.85495	4.3
7 $C_{60}H_{12}$ (C_{3v})	3, 3, 1	12, 10, 3	−2292.84782	6.9
8 $C_{48}H_{12}$ (C_{2v})	3, 3, 1	9, 8, 2	−1835.75073	5.4
9 $C_{30}H_{10}$ (C_{5v})	1, 1, 1	5, 5, 1	−1148.87380	3.2
10 $C_{60}H_{20}$ (D_{5d})[c]	1, 1, 0	10, 10, 0	−2297.76139	0.0

[a] Number of four-membered, six-membered, and ten-membered rings, respectively. [b] The sense of the electric dipole is from the base toward the rim. [c] Not a bowl, but a circular band of angular six-membered rings.

1.364 ± 0.001. Branched six-membered rings along rims show somewhat more bond alternation. Thus, ring 6D of $C_{114}H_6$ (**2**) and rings 6D and 6E of $C_{108}H_8$ (**3**) have the longest and shortest lengths of 1.486 and 1.358 ± 0.001.

Angular six-membered rings show less bond alternation than the branched rings. For ring 6E of $C_{114}H_6$ (**2**), 6F of $C_{108}H_8$ (**3**), and 6B of $C_{90}H_{10}$ (**4**) the bond lengths are 1.444 ± 0.001 and 1.367 ± 0.001 Å. The five equivalent terminal six-membered rings of $C_{60}H_{20}$ (**6**) show the least bond alternation: 1.424 and 1.379. The fact that they are the most aromatic rings is confirmed by NICS(1) values.

The (planar) four-membered rings of archimedene are approximately square, with formal single CC bonds endocyclic and exocyclic to the six-membered rings of lengths 1.479 and 1.477 Å, respectively. Four-membered rings of the phenylene bowls, excluding those lining the hydrogenated rim, are also nearly square: the shorter, 1.474 ± 0.002, and the longer, 1.480 ± 0.001. Four-membered rings on a rim have bond lengths of up to 1.503 Å.

Energetics. Energies of phenylene bowls (Table 1) show regularities such as those found in the sequence $C_{72}H_{12}$ (**5**), $C_{48}H_{12}$ (**8**), and $C_{60}H_{12}$ (**7**). Thus, Δ*E* for reaction 1 is only 0.86 kcal/mol, arising from ab initio energy and zero-point contributions of 0.80 and 0.06 kcal/mol.

$$C_{72}H_{12}\,(\mathbf{5}) + C_{48}H_{12}\,(\mathbf{8}) \rightarrow 2C_{60}H_{12}\,(\mathbf{7}) \qquad (1)$$

Similarly, a small Δ*E*, 3.75 kcal/mol, is found for reaction 2, from ab initio energy and zero-point contributions of 4.15 and −0.40 kcal/mol.

$$2C_{90}H_{10} + 5C_{48}H_{12} \rightarrow 2C_{30}H_{10} + 5C_{72}H_{12}$$

$$2(\mathbf{4}) + 5(\mathbf{8}) \rightarrow 2(\mathbf{9}) + 5(\mathbf{5}) \qquad (2)$$

The small ab initio contributions depend upon equal numbers of six-membered rings *of each type* in products and reactants; for example, a total of 30 branched and 40 angular rings in reaction 2. Such ring-conserving reactions may be termed

TABLE 2: ΔH_f° and Extra Strain Energies, kcal/mol

	$\Delta H_f^{\circ a}$	ΔH_f°(planar)^b	ESE^c
1 $C_{120}H_0$ (I_h)	2191	1983	208
2 $C_{114}H_6$ (C_{3v})	1997	1808	189
3 $C_{108}H_8$ (C_{2v})	1858	1683	175
4 $C_{90}H_{10}$ (C_{5v})	1501	1361	140
5 $C_{72}H_{12}$ (C_{2v})	1145	1038	107
6 $C_{60}H_{20}$ (C_{5v})	781	747	34
7 $C_{60}H_{12}$ (C_{3v})	927	839	88
8 $C_{48}H_{12}$ (C_{2v})	708	641	67
9 $C_{30}H_{10}$ (C_{5v})	410	369	41
10 $C_{60}H_{20}$ (D_{5d})	812	738	74

[a] Calculated using homocyclic reactions with inclusion of zero-point energies and thermal effects. [b] (ΔH_f°) of a hypothetical planar acyclic phenylene having the same number of angular, branched, and terminal six-membered rings. Additive enthalpic increments H_a, H_b, and H_t are given in the text. [c] Extra strain energy attributable to nonplanarity.

"homocyclic." Small zero-point contributions are anticipated for any hydrocarbon reaction of zero molecularity, by an empirical formula.[10]

Enthalpies of formation (kcal/mol) of phenylene bowls (Table 2) were obtained from homocyclic reactions involving the bowl of interest, D_{2h} biphenylene ($C_{12}H_8$), C_{2v} [3]phenylene ($C_{18}H_{10}$), and branched D_{3h} [4]phenylene ($C_{24}H_{12}$). Experimental values of ΔH_f° for the latter three are 100.5,[11a] 174.3,[11b] and 249.9,[11b] respectively. Thus, for $C_{90}H_{10}$(**4**), use of reaction 3 and ab initio enthalpies corrected for zero-point energies and thermal effects leads to $\Delta H_f^\circ = 1501$.

$$5C_{18}H_{10} + 10C_{24}H_{12} \rightarrow C_{90}H_{10}\,(\mathbf{4}) + 20C_{12}H_8 \qquad (3)$$

Reactions 4 and 5 furnish $\Delta H_f^\circ = 781$ and 2191 for $C_{60}H_{20}$ (**6**) and C_{120} (**1**), respectively.

$$5C_{24}H_{12} \rightarrow 2C_{60}H_{20}\,(\mathbf{6}) + 5C_{12}H_8 \qquad (4)$$

$$20C_{24}H_{12} \rightarrow C_{120}\,(\mathbf{1}) + 30C_{12}H_8 \qquad (5)$$

Magnetic Shielding. Chemical shifts of protons, which generally increase with size of the bowl, range from δ 6.4 in $C_{48}H_{12}$ (**8**) to 7.2 in $C_{114}H_6$ (**2**); chemical shifts for the terminal-ring protons of $C_{60}H_{20}$ (C_{5v}) are δ 7.2 and 7.3. All of these values are slightly downfield from those calculated for large zigzag phenylenes: 6.5 for the angular and 7.0−7.2 for the terminal protons.[3a]

^{13}C chemical shifts of the basal carbons of $C_{90}H_{10}$ (**4**), $C_{108}H_8$ (**3**), and $C_{114}H_6$ (**2**) are in the narrow range δ 142−143 vs 141 for archimedene. Carbon atoms on the rims resonate from δ 138 to 153. The larger values of 150−153 are those of carbons in angular rings, adjacent to a CH moiety. Hydrogen-bearing carbon atoms have ^{13}C chemical shifts of 120−122, similar to δ 120 of planar zigzag phenylenes.[3a]

The aromatic character of individual rings can be assessed by calculations of NICS(1) and NICS(−1) values, at points 1 Å from the ring centroids, inside and outside the bowls, respectively (Table 3). NICS(1) values are all algebraically smaller than NICS(−1), indicating greater shielding within the bowl. Most aromatic are the five terminal rings of $C_{60}H_{20}$ (**6**), with NICS(1) and NICS(−1) values of −9.5 and −9.4 ppm. Other hydrogen-bearing rings have NICS(1) ranging from −5.1 to −8.7. NICS(1) values for the branched six-membered rings range from −1.3 to −5.6. The branched rings are less aromatic than the hydrogen-bearing rings, as is found for large zigzag phenylenes.[3a]

NICS(1) values for the four-membered rings are, with one exception, positive, as is usually the case in phenylenes.[3b] The few examples of small negative NICS(1) values in four-membered rings include those of the branched D_{3h} [4]phenylene.[3b] NICS values for the ten-membered rings are all small and negative, implying slight aromatic character, with the possible exception of $C_{60}H_{20}$ (**6**).

TABLE 3: NICS(1) and NICS(−1)^a Values (ppm) of Phenylene Bowls

	ring size		
	six	four	ten
1 C_{120}	A: −1.9(−1.3)	A: 3.2(4.2)	A: −0.2(−0.0)
2 $C_{114}H_6$	A: −2.4(−1.5)	A: 2.8(4.1)	A: −0.8(−0.1)
	B: −2.6(−1.2)	B: 2.3(4.3)	B: −1.8(−0.9)
	C: −3.2(−1.3)	C: 2.3(4.6)	C: −1.7(−0.5)
	D: −2.6(−1.2)	D: 1.6(4.0)	
	E: −7.0(−5.3)	E: 0.2(1.7)	
		F: 2.2(4.3)	
3 $C_{108}H_8$	A: −2.8(−1.3)	A: 2.5(4.2)	A: −1.0(−0.2)
	B: −3.2(−1.3)	B: 2.2(4.2)	B: −1.9(−1.0)
	C: −3.9(−1.7)	C: 2.2(4.6)	C: −2.0(−0.7)
	D: −2.8(−1.3)	D: 1.5(3.9)	
	E: −1.3(−0.0)	E: 0.7(3.6)	
	F: −7.8(−5.7)	F: 0.0(1.8)	
		G: 2.0(4.5)	
		H: 1.3(3.6)	
4 $C_{90}H_{10}$	A: −4.0(−1.6)	A: 1.9(4.7)	A: −1.4(−0.2)
	B: −1.6(−0.1)	B: 0.5(3.4)	B: −2.4(−0.9)
	C: −8.7(−6.2)	C: 0.9(3.7)	
5 $C_{72}H_{12}$	A: −4.9(−1.8)	A: 1.6(5.4)	A: −2.5(−0.9)
	B: −2.0(−0.3)	B: 0.5(3.9)	B: −2.6(−1.0)
	C: −8.4(−6.1)	C: 1.2(3.8)	
	D: −6.8(−4.7)	D: 0.6(3.2)	
		E: 3.9(6.7)	
6 $C_{60}H_{20}$	A: −3.8(−2.0)	A: −1.1(1.9)	A: −5.3(−3.5)
	B: −9.5(−9.4)	B: 4.0(5.0)	
7 $C_{60}H_{12}$	A: −5.6(−2.2)	A: 0.6(4.3)	A: −2.7(−1.0)
	B: −2.3(−0.4)	B: 0.8(3.3)	
	C: −6.8(−4.6)	C: 4.0(6.7)	
8 $C_{48}H_{12}$	A: −2.7(−0.7)	A: 0.1(3.6)	A: −2.7(−1.0)
	B: −7.2(−5.0)	B: 1.1(3.8)	
	C: −5.1(−3.2)	C: 3.2(5.9)	
9 $C_{30}H_{10}$	A: −5.6(−3.8)	A: 3.2(5.6)	A: −2.2(−0.6)
10 $C_{60}H_{20}$	A: −6.0(−4.0)	A: 1.6(4.2)	

[a] NICS(−1) values are in parentheses. NICS(1) and NICS(−1) are isotropic shieldings 1 Å from the ring centroid in a direction perpendicular to the mean plane of the ring and, respectively, inside and outside the bowl. For benzene, NICS(1) = −12.8; for cyclobutadiene, NICS(1) = 17.5.

Discussion

Electric dipole moments of phenylene bowls (Table 1) are oriented along the bowl axis with the positive end toward the rim. Similarly directed dipole moments are calculated for fullerene bowls, with magnitudes somewhat smaller than those of the analogous phenylene bowls (e.g., $C_{36}H_{12}$, 4.6 D[12] vs $C_{60}H_{12}$, **7**, 6.9 D) owing, in part, to the steepness of the latter.

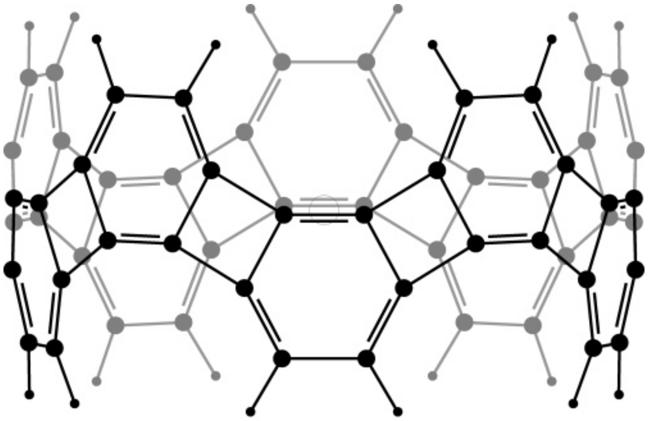
The large extent of bond alternation in their six-membered rings, and the near thermoneutrality of reactions 1 and 2 imply little aromatic character in phenylene bowls. This conclusion would seem to hold also for archimedene. Its cyclohexatrienic six-membered rings have NICS(1) and NICS(−1) of −1.9 and −1.3. From the ΔH_f° values of Table 2, ΔH° of reactions 6 and 7 are 9 and 6 kcal/mol, the smallness implying that in terms of energies archimedene is akin to bowl-shaped phenylenes.

$$2C_{90}H_{10}\,(\mathbf{4}) \rightarrow 2C_{30}H_{10}\,(\mathbf{9}) + C_{120}\,(\mathbf{1}) \qquad (6)$$

$$5C_{72}H_{12}\,(\mathbf{5}) \rightarrow 5C_{48}H_{12}\,(\mathbf{8}) + C_{120}\,(\mathbf{1}) \qquad (7)$$

We can estimate the extra strain energy (ESE) of a bowl or archimedene over and above that of a *hypothetical* planar acyclic phenylene with the same numbers of angular (a), branched (b), and terminal (t) rings. The ΔH_f° (planar) values of Table 2 are obtained from additive enthalpic increments (in kcal/mol): $H_a = 73.80$, $H_b = 99.15$ and $H_t = 50.25$. These are derived from the three experimental ΔH_f° values[11] of planar phenylenes; they are refinements of the values suggested previously.[3c] ESE values range from 34 for $C_{60}H_{20}$ (**6**) to 208 kcal/mol for C_{120} (**1**). They generally increase with molecular size, as do the values per carbon atom, all <2.0. This underscores, once again, the flexibility of phenylenes, whether planar, helical,[3a] or bowl-shaped.

As noted previously, $C_{60}H_{20}$ (**6**) is obtained by appending a terminal ring to each of the five angular rings of $C_{30}H_{10}$ (**9**), a change adding little extra strain energy. Thus, the two compounds have similar ESE values: 34 versus 41 kcal/mol, despite the fact that there are twice as many rings in **6** as in **9**. Conversely, archimedene fragment **10**, a D_{5d} isomer of $C_{60}H_{20}$ (**6**) in the form of a circular band of 10 zigzag-arranged angular rings, has a higher ESE, 74 kcal/mol.



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An independent means of confirming the ESE values is available. B3LYP/6-31G* energies of planar, zigzag [19]- and [14]phenylene differ by −1148.93728 h, which is attributable to five angular six-membered rings. This value can serve as a reference energy for $C_{30}H_{10}$ (**9**) (−1148.87380 h, Table 1), which itself is formed from five angular rings. The calculated strain energy, 40 kcal/mol, compares favorably with ESE = 41 of Table 2.

Similarly, D_{5d} $C_{60}H_{20}$ (**10**), composed of 10 angular six-membered rings, is found to have a strain energy of 71 kcal/mol from its ab initio energy (Table 1) plus 2 × 1148.93728. This is close to the ESE of 74 in Table 2. The strain energies calculated from "raw" ab initio values (Table 1) are not expected to be exactly the same as the ESE values of Table 2, which also contain zero-point and thermal energy corrections.

Regarding heats of formation, $\Delta H_f^\circ = 812$ for the D_{5d} isomer, as calculated from reaction 8.

$$10C_{18}H_{10} \rightarrow C_{60}H_{20}\ (\mathbf{10}) + 10C_{12}H_8 \tag{8}$$

This value is close to 820, twice the value for $C_{30}H_{10}$ (**9**), two of which also contain 10 angular rings. The smaller $\Delta H_f^\circ = 781$ of the C_{5v} isomer **6** is attributable to its less strained, more aromatic terminal rings.

D_{5d} $C_{60}H_{20}$ plays a role in homocyclic reaction 9a, the reactants and products of which each contain 20 branched and 10 angular six-membered rings, and 30 four-membered rings. From the ΔH_f° values of Table 2, this reaction is thermoneutral ($\Delta H^\circ = 0$).

$$C_{72}H_{12} + C_{108}H_8 \rightarrow C_{60}H_{20}\ (D_{5d}) + C_{120} \tag{9a}$$

In contrast is the significant exothermicity of reaction 9b, $\Delta H^\circ = -31$ kcal/mol, which arises from the imbalance of angular and terminal rings, that is, reaction 9b is not homocyclic.

$$C_{72}H_{12} + C_{108}H_8 \rightarrow C_{60}H_{20}\ (C_{5v}) + C_{120} \tag{9b}$$

There is a series of relationships among the ΔH_f° values of Table 2. Archimedene can be prepared by hypothetically "splicing" $C_{108}H_8$ (**3**) and biphenylene, $C_{12}H_8$, extruding 16 hydrogen atoms (as $8H_2$) to form the requisite four additional four-membered rings (Table 1), with four angular and two terminal six-membered rings becoming six branched rings in the process. The enthalpy change of this splice is estimated to be $\Delta H_f^\circ(\mathbf{3}) + \Delta H_f^\circ(\text{biphenylene}) + 6H_b - 4H_a - 2H_t$ or $1858 + 100.5 + 6 \times 99.15 - 4 \times 73.80 - 2 \times 50.25 = 2158$ kcal/mol. This value is only slightly smaller than $\Delta H_f^\circ = 2191$ for C_{120} (**1**), as would be expected for H-increments pertaining to planar rather than bent moieties.

Another such splice forms archimedene from two $C_{60}H_{12}$ (**7**) bowls. In this instance, six additional four-membered rings are formed and 12 angular six-membered rings become 12 branched rings. Its enthalpic change, $2 \times 927 + 12 \times (99.15 - 73.80) = 2158$ kcal/mol, again somewhat smaller than 2191. Archimedene may be formed by joining other members of Table 2, including two $C_{60}H_{20}$ (**6**, C_{5v}); $C_{90}H_{10}$ (**4**) with $C_{30}H_{10}$ (**9**); $C_{72}H_{12}$ (**5**) with $C_{48}H_{12}$ (**8**); and $C_{60}H_{20}$ (**10**, D_{5d}) with two $C_{30}H_{10}$ (**9**), one above and one below (the first step forming $C_{90}H_{10}$). The ΔH_f° values of **1** thereby obtained are similarly smaller than those computed by means of homocyclic reaction 5.

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References and Notes

(1) (a) Haymet, A. D. J. *Chem. Phys. Lett.* **1985**, *122*, 421. (b) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1996**, *262*, 813.

(2) (a) Miljanić, O. Š.; Vollhardt, K. P. C. [*N*]Phenylenes: A Novel Class of Cyclohexatrienoid Hydrocarbons. In *Carbon Rich Compounds: Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2005; pp 000−000. (b) Iglesias, B.; Cobas, A.; Pérez, D.; Guitián, E.; Vollhardt, K. P. C. *Org. Lett.* **2004**, *6*, 3557. (c) Dosche, C.; Kumke, M. U.; Löhmannsröben, H.-G.; Ariese, F.; Bader, A. N.; Gooijer, C.; Miljanić, O. Š.; Iwamoto, M.; Vollhardt, K. P. C.; Puchta, R.; Hommes, N. J. R. v. E. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5476. (d) Kumaraswamy, S.; Jalisatgi, S. S.; Matzger, A. J.; Miljanić, O. Š.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 3711. (e) Bruns, D.; Miura, H.; Vollhardt, K. P. C.; Stanger, A. *Org. Lett.* **2003**, *5*, 549. (f) Han, S.; Bond, A. D.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3223. (g) Han, S.; Anderson, D. R.; Bond, A. D.; Chu, H. V.; Disch, R. L.; Holmes, D.; Schulman, J. M.; Teat, S. J.; Vollhardt, K. P. C.; Whitener, G. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 3227. (h) Bong, D. T.-Y.; Gentric, L.; Holmes, D.; Matzger, A. J.; Scherhag, F.; Vollhardt, K. P. C. *Chem. Commun.* **2002**, 278. (i) Dosche, C.; Löhmannsröben, H.-G.; Bieser, A.; Dosa, P. I.; Han, S.; Iwamoto, M.; Schleifenbaum, A.; Vollhardt, K. P. C. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2156. (j) Dosa, P. I.; Whitener, G. D.; Vollhardt, K. P. C.; Bond, A. D.; Teat, S. J. *Org. Lett.* **2002**, *4*, 2075.

(3) (a) Schulman, J. M.; Disch, R. L. *J. Phys. Chem. A* **2003**, *107*, 5223. (b) Schulman, J. M.; Disch, R. L.; Jiao, H.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8051. (c) Schulman, J. M.; Disch, R. L. *J. Phys. Chem. A* **1997**, *101*, 5596. (d) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1996**, *118*, 8470. (e) Maksić, Z. B.; Kovaĉek, D.; Eckert-Maksić, M.; Böckmann, M.; Klessinger, M. *J. Phys. Chem. A* **1995**, *99*, 6410. (f) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583. (g) Trinajstić, N.; Schmalz, T. G.; Živković, T. P.; Nikolić, S.; Hite, G. E.;

Klein, D. J.; Seitz, W. A. *New J. Chem.* **1991**, *15*, 27. (h) Aihara, J. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 57.

(4) Projected structures are tipped forward (except for **6**, tipped backward, and **1**, slightly twisted away from an S_{10} axis) by rotation about an axis through the center of mass (surrounded by a circle of diameter 0.5 Å) in order to reveal the base ring, all other atoms, and almost all bonds. Shaded atoms are behind the plane of projection; shaded bonds include those passing through the plane.

(5) (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2383. (c) Schleyer, P. v. R. *Pure Appl. Chem.* **1996**, *68*, 209. (d) Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669. (e) For a recent extension, see Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. v. E. *Org. Lett.* **2001**, *3*, 2465.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

(8) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(9) (a) Wolinski, K.; Hinto, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(10) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1984**, *113*, 291.

(11) (a) *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, November, 1998, National Institute of Standards and Technology, Gaithersburg, MD 20899 (http://webbook.nist.gov). (b) Beckhaus, H.-D.; Faust, R.; Matzger, A. J.; Mohler, D. L.; Rogers, D. W.; Rüchardt, C.; Sawhney, A. K.; Verevkin, S. P.; Vollhardt, K. P. C.; Wolff, S. *J. Am. Chem. Soc.* **2000**, *122*, 7819.

(12) Schulman, J. M.; Disch, R. L. *J. Comput. Chem.* **1998**, *19*, 189.