Semibuckminsterfullerene: MNDO Study of a Hemispherical Triindenotriphenylene

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Semiempirical geometry optimization of triindenotriphenylene predicts a rigid cup-shaped structure with strain-induced bond alternation in the central benzenoid ring; model studies of the corresponding Li complex suggest that metal coordination occurs preferentially from the convex side of the bowl.

Bowl-shaped polycyclic aromatic hydrocarbons (PAHs) whose carbon frameworks constitute cross-sections of buckminsterfullerene[1] are attractive synthetic targets because of their potential as reference compounds for spherical carbon clusters and, more importantly, because their topology provides the opportunity to model the endohedral chemistry of the fullerenes. Recent efforts have focused on corannulene,[2] the structural prototype of this class of PAHs. Only the second example can be envisaged in triindeno-[4,3,3a,2,1-

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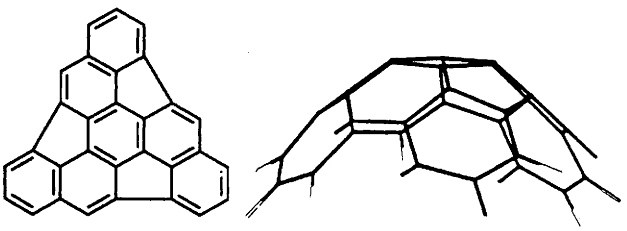
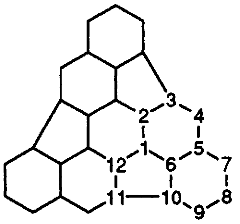


Fig. 1 Structure and MNDO-optimized geometry of triindenotriphenylene **1**



cdef:4′,3′,3a′,2′,1′-*ijkl*:4″,3″,3a″,2″,1″-*opqr*]triphenylene **1**, whose carbon skeleton was previously suggested by McKee and Herndon[3] as a possible intermediate in the formation of C_{60}. As part of a programme directed at the synthesis of **1** we now report the results of our computational investigation of this system.

Geometry optimization of **1** (C_3 symmetry constraints imposed) using the MNDO parameter set[4]‡ clearly predicts the cup-shaped topology as a minimum on the $C_{30}H_{12}$ potential energy surface (Fig. 1) with a deviation from planarity of 39°. This clearly surmounts the degree of non-planarity observed in corannulene (26.8°)[5] and is somewhat closer to the value found in C_{60} (31°).[6] The planar C_{3h} structure of **1** is estimated to be 77.3 kcal mol^{-1} higher in energy than the equilibrium C_3 geometry (Table 1), thereby essentially excluding a bowl inversion along this pathway. In fact, frequency analysis of the C_{3h} conformation disclosed three negative eigenvalues characteristic for a stationary point of higher order. Interestingly, the corresponding process for corannulene was experimentally determined [7] to have an activation energy of only 10.2 kcal mol^{-1} and is believed to proceed through a planar transition state.[2c] This finding, well reproduced computationally at various levels of theory, suggests that it is the higher degree of pyramidalization[8] of the central ring carbons in **1** that enforces its superior rigidity relative to corannulene.

Inspection of CC bond lengths of **1** reveals that its strained carbon framework can be expected to exhibit bond alternation in the central benzenoid ring, with bonds calculated to be elongated along the side of five-membered ring fusion and contracted adjacent to it. Thus, $R_{1\text{–}2}$ (1.385 Å) is computed to be 0.067 Å shorter than $R_{1\text{–}12}$ (1.452 Å), which compares to a MNDO value for unperturbed benzene of 1.407 Å, intermediate between the two. Similar patterns have been observed in triphenylene[9] (bond lengths of 1.411 and 1.470 Å in the central benzene ring), C_{60}[10] (1.388 and 1.432 Å), and corannulene[5] (CC distance along six–six juncture: 1.391 Å; along six–five juncture: 1.413 Å). Thus, the extent to which bond alternation is predicted to occur in **1** significantly exceeds the values observed in related compounds, and although MNDO calculations tend to overestimate slightly aromatic internuclear distances, those computed for **1** are a potential source for novel, strain-driven chemistry.

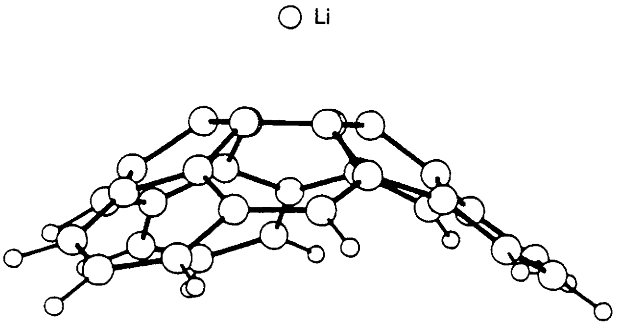


Fig. 2 MNDO-optimized geometry of the convex Li–arene complex **2**

Table 1 Energies and selected bond lengths of triindenotriphenylenes **1** and **2**[a]

	1	**2**[b]
ΔH_f°	252.5[c]	344.6[d]
R(1–2)	1.385	1.411
R(1–6)	1.430	1.432
R(1–12)	1.452	1.478
R(2–3)	1.470	1.470
R(3–4)	1.395	1.400
R(4–5)	1.467	1.462
R(5–6)	1.414	1.417
R(5–7)	1.442	1.443
R(6–10)	1.466	1.464
R(7–8)	1.392	1.392
R(8–9)	1.442	1.443
R(9–10)	1.383	1.385
R(10–11)	1.505	1.502
R(Li–Bz)[e]		1.827[f]

[a] MNDO-values (C_3-symmetry constraints imposed). Heats of formation in kcal mol^{-1} (1 cal = 4.184 J), bond lengths R in Ångstroms. *Cf.* CC bond length in D_{6h} benzene (MNDO): 1.407 Å. For reasons of clarity, the numbering scheme deviates from IUPAC recommendations. [b] Convex coordination of Li$^+$ to **1**. [c] ΔH_f° of planar C_{3h} geometry: 329.8 kcal mol^{-1}. [d] ΔH_f° of concave isomer: 389.3 kcal mol^{-1}. [e] Distance between Li and midpoint of the central benzene ring. [f] Corresponding value of concave isomer: 2.048 Å.

Examination of the energy levels of the HOMO (−8.39 eV) and the LUMO (−1.18 eV, both doubly degenerate) indicates a facile reduction of **1** to form stable anions with up to four negative charges. Further computational characterization of such charged species was not attempted.

The hemispherical geometry of **1** offers two topologically different coordination sites and thereby provides the opportunity to mimic exo-[6,10] and endo-hedral[11] metal complexes of C_{60}. Of the possible symmetry-unique locations for metal attachment only those along the molecule's C_3 axis were examined computationally by coordinating Li$^+$ to **1** (Table 1). Surprisingly, it was found that complexation from the outside of the bowl as in **2** (Fig. 2) is favoured by 44.7 kcal mol^{-1} over the alternative concave arrangement, in which the metal resides inside the hemisphere. Since the interaction between Li$^+$ and **1** is purely electrostatic, this result implies that the electron density is greater on the outside of the bowl than on the inside. Preferential convex coordination can thus be explained by pyramidalization (or rehybridization) of central ring carbons in a fashion that increases the spatial extentions of the p-type atomic orbitals on the outside of the bowl. This phenomenon has its aliphatic analogy in alkenes of facial differentiality such as norbornene, where *exo*-attack by electrophiles is favoured over *endo*-addition.[12] In addition to such stabilizing rehybridization effects, a convex arrangement of cation and arene benefits to a larger extent from induced dipole interactions than the concave alternative.

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‡ Results from calculations employing the AM1 or the PM3 parameter sets are in qualitative agreement with those reported here.

The weak bonding between Li^+ and **1** in the concave configuration is revealed by the long distance between the metal and the midpoint of the central benzene ring (R_{Li-Bz}: 2.048 Å). In the more stable convex coordination of **2**, Li^+ is located only 1.827 Å away from the arene, indicative of stronger binding interactions. Under the imposed symmetry constraints, the geometric changes upon metal complexation are largest for carbon centres 1, 2 and 12, where depletion of electron density causes an increase in their respective bond lengths. Structural effects at locations more remote from the coordination site are only minor. Interestingly, a similar preferred lithium complexation pattern has been suggested for tetralithiated corannulene,[13] in which case semiempirical calculations support the notion of four Li cations attached to the convex side of the negatively charged bowl. Thus, synthesis of a metal fragment coordinated to cup-shaped PAHs in a concave fashion appears to be a formidable challenge.

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