Selective π-Facial Binding of Metal Cations to Triindenotriphenylene as a Possible Catalytic Route to C_{60} Precursors: a MNDO, PM3 and *Ab initio* SCF-MO Study

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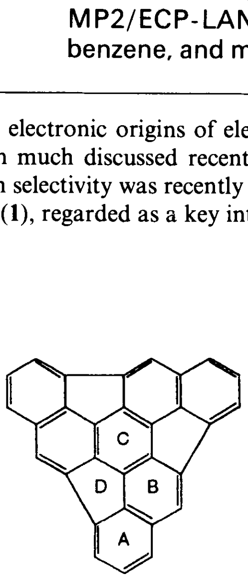
MNDO and PM3 SCF-MO calculations predict that in common with Li^+, larger ions such as Tl^+, Pb^+ or NH_4^+ are predicted to preferentially bind to the convex surface of **1** and hence are unlikely to encapsulate in any dimerisation reaction. The calculated molecular electrostatic potential of **1** also reveals the convex face to be the better electron donor. Concave binding is predicted at the MNDO level for Na^+ and K^+ and the PM3 level for Ga^+, but these results may be influenced by errors for these metals resulting in excessive stabilisation to π-faces. *Ab initio* calculations at the MP2/ECP-LAN1LDZ level predict that Ga^+ has the highest binding energy of all these metals to benzene, and may constitute the best candidate for synthetic efforts.

The electronic origins of electrophilic π-facial selectivity have been much discussed recently.[1] A particularly novel form of such selectivity was recently suggested[2] for triindenotriphenylene (**1**), regarded as a key intermediate in the total synthesis of C_{60} and its encapsulation complexes. Binding of a Li^+ ion was predicted on the basis of MNDO calculations to occur on ring C of the convex rather than concave face of **1**. Whilst a number of examples of Na^+, K^+, Rb^+ and Cs^+ complexes involving $\approx\mu^6$ binding to aromatic π-faces are well characterised structurally,[3] and symmetrical μ^6 coordination of Li^+ is known,[4] many Li^+ complexes show $\leqslant\mu^3$ binding to six-ring aromatic π-faces[5] as well as covalent binding at the Li^0 oxidation level.[6] Given this relatively anomalous behaviour of this element, we wished to verify whether the π-facial selectivity of **1** is dependent on either the nature of the metal or its oxidation state, and to investigate the potential for metal cations to act as catalysts for the dimerisation of **1** to form the $C_{60}H_{24}$ unit **2** in which the ion is encapsulated.



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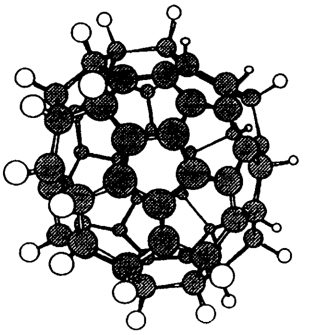

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Triindenotriphenylene **1** is predicted to be a highly non-planar molecule, with a calculated barrier to inversion of > 300 kJ mol^{-1} at three different levels of semi-empirical theory.[2] Our own MNDO and PM3 SCF-MO calculations‡ suggest that the origins of this large barrier are largely electronic, since molecular mechanics force fields (*e.g.* MM3) predict much lower barriers ($\approx$136 kJ mol^{-1}), arising largely from angle strain. We also note that a barrier of this magnitude appears not to be an artefact of the restricted Hartree–Fock procedure, since in our hands a PM3 spin-unrestricted (UHF) biradical calculation also predicts a significant barrier (383 kJ mol^{-1}).

The negative component of the calculated molecular electrostatic potential of **1** is significantly distorted towards the convex face,‡ an effect arising from a decreased p_π–p_π overlap destabilising the π system on this side, a distorsion which indeed may be a general phenomenon in inducing an electrophilic π-facial preference.

The original reported preference for Li^+ binding to the convex face[2] is also reproduced using recently published PM3 lithium parameters (Table 1).[7] Geometry optimisations starting with Li^+ bound to the concave face of any of the four rings A–D result in the ion 'creeping' to the outer rim of the system. Calculations on the convex face always gave μ^6 structures localised to any of rings A–D. The phenomenon did not depend on the oxidation state of the metal, the doublet $Li^{\bullet}$ complex showing the same behaviour.[4] The metals Li^+,[4] Na^+ and K^+ (ref. 9) all have a precedent for coordination exclusively by π-carbon ligands and hence the calculated preference of Na^+ and K^+ for a symmetrical structure with the ion lying in the concave face along the C_3 symmetry axis of the molecule did not seem unreasonable, particularly since the MNDO parameters published by Bock[8] for Na and K are reported to reproduce molecular geometries well. Only one experimental gas phase benzene binding energy to an alkali metal is available, for Na^+ (ΔH_{exp} 117 kJ mol^{-1}).[10] Whilst the predicted MNDO binding energy to benzene for Li^+ (ΔH_{calc} 207 kJ mol^{-1}) appears reasonable in this context, that for Na^+ (ΔH_{calc} 301 kJ mol^{-1}) and K^+ (ΔH_{calc} 362 kJ mol^{-1}) are excessive. This is confirmed by

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‡ MNDO or PM3 calculations were carried out at the restricted Hartree–Fock level (RHF) using the MOPAC93 program. Parameters for sodium and potassium were those recently reported.[8] Structures were optimized using the eigenvector following method and the XYZ keyword. *Ab initio* calculations were carried out using the GAUSSIAN92 program.[15] Searches of the Cambridge structural database for coordinated metal cations were performed using release 5.6 of the Quest software.[16] Computer readable files for Apple Macintosh and Microsoft Windows systems in Quicktime™ and MPEG video animation format illustrating the three dimensional molecular electrostatic isopotential calculated for **1** are available for general access from the Gopher + server Gopher.ch.ic.ac.uk. [A printed copy of the diagram has been deposited; for details of the Supplementary Publication Deposition Scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1 (Supp. Pub. No. 56999 2 pp.)] These files will reside in the Royal_Society_of_Chemistry/Perkin_Transaction_2/3_07186C directory for a period of at least two years from the publication of this paper. A description of how to visualise such material, together with appropriate programs is available from the same source. An on-line version of this paper is available from the world-wide-webb server as http://www.ch.ic.ac.uk/RSC/P2/3_07186C.html.

Table 1 MNDO and PM3 calculated energies (kJ mol^{-1}) of concave and convex binding of **1**–M$^+$

	MNDO			PM3		
	Concave	Convex^a	ΔH^b	Concave	Convex^a	ΔH^b
	1054	–	–14	1065	—	3
$Li^{\bullet}$	854 A	–72 B	—	1133 D	–51 B	—
Li^+	1532 A	–93 C	68	1684 A	–36 C	211
NH_4^+	1740 S	–42 C	160	1679 C	–43 C	–34
Na^+	1170 S	42 C	–135	—	—	—
K^+	812 S	243 C	–318	—	—	—
Pb^+	1800	–115	387	1890	–73	263
Pb^{2+}	2847	–25	468	2929	–127	264
Ga^+	—	–	—	1287 S	141	–161
Tl^+	--	–	—	1848	0	1023

^{a} Energy relative to the concave face. ^{b} **1** + **1**–M$^+$→**2**–M$^+$

the results at the RHF *ab initio* level;* Li$^+$ 170, Na$^+$ 113 (6-31G* basis) or Na$^+$ 83, K$^+$ 58, Rb$^+$ 49 (ECP-LAN1LDZ basis) and at the MP2/ECP-LAN1LDZ level; Na$^+$ 87, K$^+$ 58, Rb$^+$ 48 kJ mol^{-1}. We note that the LAN1LDZ basis does not include polarisation functions, and hence probably underestimates the binding energies.

We therefore investigated other metal ions likely to bind to the π-face of **1** for which MNDO or PM3 calculations are possible. Several particularly well characterised examples of Ga$^+$ binding are known, including a cyclophane in which tris μ^6 coordination is the only binding to the metal.[11] Only PM3 parameters are available for this metal, for which a clear concave preference is revealed (Table 1). As with K$^+$ however, the calculated binding enthalpy of Ga$^+$ to benzene appears excessive (400 kJ mol^{-1}) in comparison to the *ab initio* values (Ga$^+$ 97 at RHF/ECP-LAN1LDZ, 124 kJ mol^{-1} at MP2/ECP-LAN1LDZ, the corresponding values for Tl$^+$ being 80 and 117 kJ mol^{-1}). The magnitude of these values do indicate that Ga$^+$ may bind much more strongly than K$^+$ to a π-face, and hence may be the most likely candidate for encapsulation. Both thallium[12] and ammonium[13] ions are known to exhibit bis μ^6 coordination to benzene rings, and mono μ^6 coordination for Pb^{2+} is known.[14] For Pb$^+$ there is also an experimental gas phase binding energy to benzene,[10] which is reproduced at the PM3 level (ΔH_{calc} 100, ΔH_{exp} 109 kJ mol^{-1}). The calculated semi-empirical preference for all these ions is convex binding. The result for thallium reveals the lowest energy isomer to be effectively bound to the rim rather than the edge (Table 1).

Since **1** can potentially dimerise to $C_{60}H_{24}$ *via* a series of six [2 + 4] Diels–Alder cycloadditions, we considered it of interest to calculate the energy of this reaction. In the absence of a metal ion, the dimerisation is approximately thermoneutral (Table 1). With the exception of Na$^+$, K$^+$ and Ga$^+$, the larger metal ions are not predicted at the semi-empirical level to strongly enhance the dimerisation reaction (Table 1). In particular, Tl$^+$ inhibits the dimerisation, presumably because of its steric bulk. We suggest that Ga$^+$ may be the best candidate for encapsulation, both because of the strength of its π-ligand interactions, and its relatively small size.

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* Calculated RHF (MP2) energies using the LAN1LDZ/ECP basis set for metal–benzene complex in Hartree; Na –230.6727 (231.1697), K –230.6631 (–231.1588), Rb –230.6594 (–231.1551), Ga –232.4177 (–232.9442), Tl –280.6299 (–281.2270). The size of **1** precludes such calculations.

Acknowledgements

We thank the European Erasmus scheme for a travel grant (to F. S. and S. S.).

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Paper 3/07186C
Received 6*th December* 1993
Accepted 17*th January* 1994