Convex *vs.* Concave π-Facial Binding of Metal Cations to a Semibuckminsterfullerene: an *Ab Initio* Study

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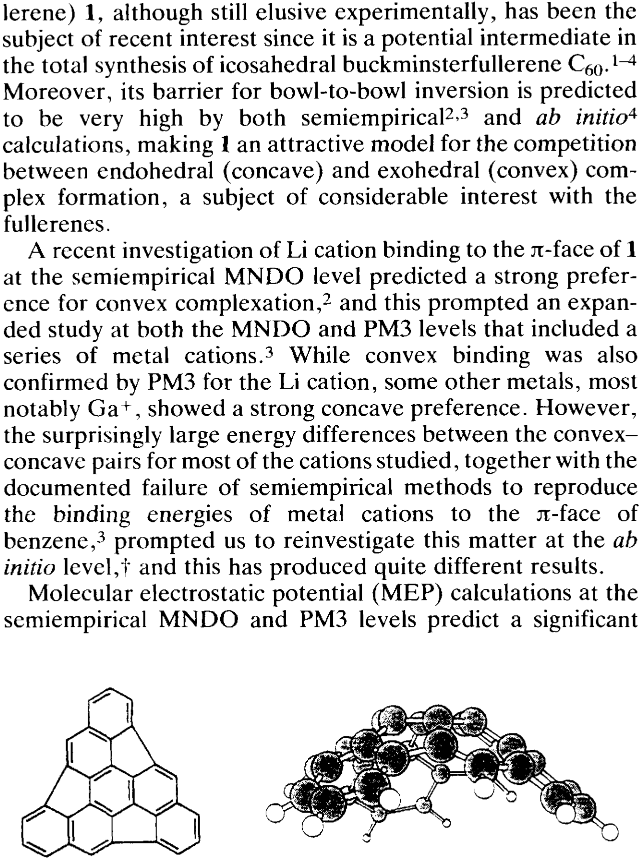
In contrast with both MNDO and PM3 semiempirical calculations that predict preferential binding of a number of metal cations to the convex face of triindenotriphenylene, *ab initio* calculations suggest modest to strong preference for the concave side in six of seven cases studied.

The bowl-shaped triindenotriphenylene (semibuckminsterfullerene) **1**, although still elusive experimentally, has been the subject of recent interest since it is a potential intermediate in the total synthesis of icosahedral buckminsterfullerene C_{60}.[1-4] Moreover, its barrier for bowl-to-bowl inversion is predicted to be very high by both semiempirical[2,3] and *ab initio*[4] calculations, making **1** an attractive model for the competition between endohedral (concave) and exohedral (convex) complex formation, a subject of considerable interest with the fullerenes.

A recent investigation of Li cation binding to the π-face of **1** at the semiempirical MNDO level predicted a strong preference for convex complexation,[2] and this prompted an expanded study at both the MNDO and PM3 levels that included a series of metal cations.[3] While convex binding was also confirmed by PM3 for the Li cation, some other metals, most notably Ga^+, showed a strong concave preference. However, the surprisingly large energy differences between the convex–concave pairs for most of the cations studied, together with the documented failure of semiempirical methods to reproduce the binding energies of metal cations to the π-face of benzene,[3] prompted us to reinvestigate this matter at the *ab initio* level,† and this has produced quite different results.

Molecular electrostatic potential (MEP) calculations at the semiempirical MNDO and PM3 levels predict a significant distortion of the negative component towards the convex face of **1**, which was attributed to decreased p_π–p_π overlap destabilizing the π system on this side.[3] With *ab initio* calculations, however, the MEP calculated along the C_3 symmetry axis as a function of the distance from the mean plane of the central six-membered ring (Fig. 1) is consistently more negative on the concave side of **1** at both 3-21G and 6-31G* levels. Accordingly, the total electron density calculated along the axis is higher on the concave side as well when points equally distant from the plane of the central ring are considered. Thus, unperturbed **1** is significantly more nucleophilic on its concave side, and concave-oriented approach of an electrophile should be favoured, at least along the axis of symmetry.‡



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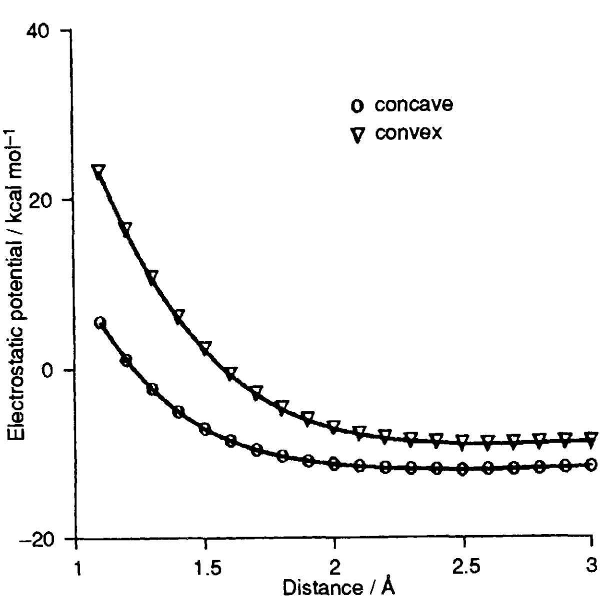

Fig. 1 6-31G*//3-21G electrostatic potential of **1** along the C_3 symmetry axis as a function of the distance from the central ring

A similar picture emerges from the model calculations of the pure coulombic interactions of a point charge with **1**. The 6-31G* binding energies of a +1 point charge located at 1, 2 and 3 Å, respectively, from the plane of the central ring on the symmetry axis are 75.6, 41.8 and 24.4 kcal mol^{-1} for the concave side, and 61.7, 40.6 and 20.6 kcal mol^{-1} for the convex side (1 cal = 4.184 J). Thus again, concave complexation of the positive charge is clearly preferred over convex.

Finally, we performed *ab initio* calculations for the series of $1\text{-}M^{n+}$ cations, with M = Li^+, Na^+, K^+, B^+, Ga^+, Be^{2+} and Mg^{2+}.§ The results, presented in Table 1, are generally in agreement with the simple electrostatic model discussed above, but again in sharp contrast with the semiempirical data. In all but one of the cases considered, concave preference is predicted at the HF *ab initio* level.¶ The calculated differences in stabilities of the convex *vs.* concave complexes are in most cases rather modest, usually in the range of 1–2 kcal mol^{-1}. The exceptions are **1**-K^+ and **1**-Be^{2+} for which significantly stronger preferences for the concave arrangement are predicted (Table 1). Moreover, our calculations do not confirm the exceptional behaviour of Ga^+ predicted by the semiempirical method. The Ga^+ complex exhibits the usual 1.7 kcal mol^{-1} preference for the concave arrangement without inordinately strong binding energy, at least at the HF level of theory.‖ From our results, the **1**-Be^{2+} complex seems to be the best candidate

Table 1 HF/6-31G*//3-21G calculated total energies E_{HF} (hartrees) and relative and binding energies (kcal mol^{-1}) for the concave and convex complexes **1**-M^+

	Concave		Convex		
	E_{HF}	R^a	$E_{re}{}^b$	R^a	Binding energy^c
Li^+	−1150.2917	1.92	+1.0	1.98	43.7
Na^+	−1304.6990	2.37	+1.2	2.35	33.0
K^{+d}	−1739.0375	2.85	+5.2	2.92	20.9
B^+	−1167.3007	1.86	−1.7	2.13	51.5
Ga^{+d}	−3056.7891	2.45	+1.7	2.22	33.1
Be^{2+}	−1157.0271	1.29	+18.6	1.47	269.9
Mg^{2+}	−1342.0435	1.92	+1.1	1.93	153.2

[a] Distance (Å) from the central six-membered ring of **1**. [b] E_{HF} (convex) − E_{HF} (concave). [c] Uncorrected for BSSE. The corrected values are *ca.* 2 kcal mol^{-1} lower. [d] 3-21G* basis set for the metal cation.[10c]

for the formation of the concave arrangement, since both the binding energy and the relative stability difference are largest among all of the complexes studied.

Comparison of the calculated binding energies of the alkali metal cations to **1** (Table 1) with the recently published results for metal cation–benzene interactions performed at a very similar level of theory** shows that **1** is slightly more basic than benzene, especially on the concave side. Moreover, all of the *ab initio* studies predict a constant decrease in the binding of alkali metal cations to the π-face of an aromatic system with increasing radius of the cation, a trend that is not reproduced at the semiempirical level of theory.[3] The available experimental gas-phase binding energies of Li^+, Na^+ and K^+ to benzene, 38.3,[5,6] 28.0[7] and 18.3[8] kcal mol^{-1}, respectively, provide convincing evidence for the adequacy of the computational model employed in this study.

In conclusion, a general concave preference for **1**-M^+ complex formation is found at the HF/6-31G*//3-21G level in contrast with predictions based on semiempirical calculations. The failure of the MNDO and PM3 methods to adequately describe the metal cation–aromatic system complexes may be caused not only by the parametrization available for the metals, but also by a general failure of these methods to describe the π-electron density distribution in nonplanar systems.††

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Footnotes

† Gaussian92[9] was used throughout the study. 3-21G[10a] and 6-31G*[10b] basis sets were employed. Due to the size of **1** the study was limited to the Hartree–Fock level.

‡ Inspection of the MEP maps of the planes parallel to the central six-membered ring at various distances proves that the cross-points of the planes with the symmetry axis represent the electrostatic potential minima.

§ Partial geometry optimization was performed at the HF/3-21G level with the cation kept on the C_3 symmetry axis on either the concave or convex side, and only the distance between the cation and the central six-membered ring being optimized while the geometry of **1** was frozen. The validity of this approach was confirmed for both convex and concave **1**-Li^+ and **1**-Na^+ complexes which were reoptimized fully within C_3 symmetry constraints. Very limited lowering of the total energies was found (less than 0.001 Hartree or 0.6 kcal mol^{-1}, at both 3-21G//3-21G and 6-31G*//3-21G levels) with virtually no change in the calculated relative energies of the concave *vs.* convex complexes. The resulting complexes were not characterized by the force calculations, due to the size of the systems studied. However, the assumption of the C_3 symmetry to represent genuine potential energy minima seems to be justified,‡ particularly for the larger cations.[2,3] The basis set superposition error (BSSE) was estimated at both 3-21G and 6-31G* levels by counterpoise calculations, replacing the cations with a ghost set of the appropriate orbitals. The BSSE seems to be of some importance at the 3-21G level where the ghost orbitals serve as polarization functions for the carbon atoms in **1**. However, at the 6-31G* level, BSSE errors are estimated to affect the results only very slightly with overestimation of the binding energies by less than 2 kcal mol^{-1}, and differences in the relative concave *vs.* convex energies of less than 0.3 kcal mol^{-1}.

¶ We expect electron correlation effects to slightly enhance concave preferences. The detailed *ab initio* studies of benzyllithium suggest that the structures with more close contacts of the metal cation with the carbon atoms are slightly favoured by post-HF treatment.

‖ It should be noted, however, that for the benzene–Ga^+ complex a significant electron correlation contribution to the binding energy was found at MP2/ECP-LAN1LDZ level.[3]

** The *ab initio* calculated binding energies for benzene to Li^+, Na^+ and K^+, are 39.5, 24.4 and 19.2 kcal mol^{-1}, respectively, at the 6-31G*(C,H)-3-21G*(M^+) level,[7] and 40.6 and 27.0 kcal mol^{-1} at the 6-31G* level[5] for Li^+ and Na^+ (only).[3]

†† Recent *ab initio* studies of the π-facial selectivity in nucleophilic addition to norbornen-7-ones shows that the MNDO method erroneously predicted the favoured direction of the nucleophile, even if the point charge calculations were employed.[11]

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