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Getting a theoretical handle on fullerene ions: Quantum chemical calculations on the reactions of C_{60}^+, C_{60}^{2+} and C_{60}^{3+} with ammonia☆

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Abstract

Hybrid density functional theory calculations at the B3-LYP/6-31G** level of theory are used to explore the interactions between singly, doubly, and triply charged fullerene cations and ammonia. The calculations illuminate (and generally support) several aspects of the previously-reported experimental results for these systems. Primary adduct formation is exothermic but is hindered by an energetically costly localized distortion of the fullerene cage at the site of addition, as the 'chosen' carbon atom shifts from strained sp^2 to sp^3 coordination. The 50–75 kJ mol^{-1} 'deformation energy' is substantially larger than the residual strength of the bond between C_{60}^+ and NH_3. Although the deformation energy rises with increasing fullerene ion charge state, it does so less steeply than does the electrostatic attraction between C_{60}^{n+} and NH_3, so that the overall bond strength to NH_3 is progressively and substantially larger for the di- and tricationic adduct ions. For all charge states, a proton-bound structure is found to be the energetically preferred secondary adduct, but for dicationic and tricationic adducts formation of a secondary adduct is significantly less exothermic than proton transfer. It appears that the failure of C_{60}^+ to add measurably to nucleophiles weaker than NH_3 arises because such nucleophiles are not able to overcome the required deformation energy to effect bond formation. We find also that, in contrast to a simple electrostatically-driven model of 'handle' formation (in which it was proposed that the most strongly bound doubly-derivatized fullerene dications would be those for which the 'handles' were most widely separated across the fullerene framework) the lowest-energy double-handled adducts are in fact those for which the remaining resonance stabilization is greatest, with electrostatic considerations apparently taking a back seat on the question of relative stability. Similar considerations appear to apply to the double-handled tricationic adducts.

Keywords: Association reaction; C60; Hybrid density functional theory; Molecular polycation; Quantum chemical calculation; Proton transfer

1. Introduction

Buckminsterfullerene, C_{60}, the most well-rounded allotrope of carbon, has been subjected to an almost uncountable number of chemical inquisitions [1–8] since its discovery around 2 decades ago [9,10]. Various research groups have seen fit to strip it of an improbable number of electrons [11,12], to couple it with various inappropriate chemical partners [13,14], to stuff it with sundry unreasonable atoms and molecules [15–17], and to pummel it at frighteningly high velocities against a range of unrelenting surfaces [18]. In this context, the treatment that C_{60} has received at the hands of the Bohme group [19–22] can be seen to be comparatively benign. Using the selected-ion flow tube technique, Bohme and co-workers have systematically assessed the reactivity of fullerene ions, most frequently C_{60}^+, C_{60}^{2+}, and C_{60}^{3+}, with a broad range of gas-phase neutrals. Two somewhat surprising tendencies soon emerged from these studies. First, the multiply-charged fullerenes such as C_{60}^{2+} and C_{60}^{3+} were often distinctly less prone to exhibit single-charge transfer to reactant neutrals than was expected on the basis of a simple comparison of ionization energies [23–26]. For example, based on $IE(C_{60}^+) = 11.39 \pm 0.05$ eV [27] and $IE(C_2H_4) = 10.507$ eV, the reaction

$$C_{60}^{2+} + C_2H_4 \rightarrow C_{60}^+ + C_2H_4^+ \qquad (1)$$

is almost one eV exothermic, and yet this product channel was not detected at all, in competition only with a highly inefficient association process [24]. The second surprise was that highly inefficient association (or, so far as it could be established, no association whatsoever) was, it transpired, something

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☆ To Diethard, friend and mentor.

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which fullerene ions did extremely well. It began to seem that C_{60}^+, in particular, did nothing else. This author recalls that, during our first few days of assaying the reactivity of C_{60}^+, we had tested virtually the complete Bohme collection of lecture-bottles and volatile samples, running through H_2, N_2, NO, N_2O, CO, CO_2, OCS, CS_2, CH_4, C_2H_2, C_2H_4, C_2H_6, CH_3CCH, H_2O, H_2CO, CH_3OH, CH_3OCH_3, HCOOH, $HCOOCH_3$, CH_3CHO, CH_3COCH_3, *c*-C_2H_4O, HCN, and CH_3CN, without obtaining the slightest indication of a reaction of C_{60}^+ with any of these species. Ammonia and the amines we had left towards the end, because they were malodorous and would take longer to pump out of the vacuum system after their introduction. It transpired, however, that C_{60}^+ had a soft spot for amines, and would associate with them [28]. Under our reactive conditions of $T \sim 300$ K and $P \sim 0.35$ Torr (helium buffer gas pressure), we obtained effective bimolecular association rate coefficients of less than 1×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction:

$$C_{60}^+ + NH_3(+M) \rightarrow C_{60}NH_3^+(+M^*) \quad (2)$$

ranging up to near-collision-rate values for the analogous association reactions with di- and trimethylamine [28]. Furthermore, although the primary association reactions with methylamine and with ethylamine were comparatively slow ($k = 1.5 \times 10^{-11}$ and 5.0×10^{-11} cm^3 molecule^{-1} s^{-1}, respectively), a subsequent secondary addition of another amine was found to be efficient in these systems, as was also observed for dimethylamine (but *not* for trimethylamine). The observed reactivity of C_{60}^{2+} and C_{60}^{3+} with ammonia and the amines was, fittingly, more 'highly charged': reactions invariably occurred at close to the collision rate, with addition often competing with charge transfer (and, from the multiply-charged adducts, proton transfer) [28–30].

The present work revisits the reactivity of fullerene ions with amines, this time from the fresh standpoint of computational chemistry, with the hope of rationalizing aspects of the fullerene ion/amine reaction mechanism. For the sake of computational expediency, ammonia is the only ligand surveyed here: its reactivity with C_{60}^+, C_{60}^{2+}, and C_{60}^{3+} is explored in the context of association and proton transfer processes.

2. Theoretical methods

The present work uses hybrid density functional theory calculations, namely the combination of Becke's three-parameter exchange functional [31] with the correlation functional of Lee, Yang, and Parr [32] (B3-LYP), to characterize stationary points on various potential energy surfaces appropriate to the interaction of fullerene ions with ammonia. In concession to the large size of the species involved, results are reported using a comparatively modest basis set, 6-31G**. Calculations were pursued with the imposition of at least C_s symmetry. Nonetheless, despite the use of a small basis set and the recourse to symmetric structures, it did not prove possible to obtain fundamental vibrational frequencies or zero-point energy (ZPE) corrections for the species concerned. A further limitation of the computational method is that basis set superposition error (BSSE) [33] was not addressed. With these limitations in mind, it is anticipated that the computed bond strengths and other relative energies are unlikely to be highly accurate: neglect of both ZPE and BSSE is likely to result in some exaggeration of adduct ion bond strengths.

All calculations were performed using the GAUSSIAN98 program suite [34].

3. Results and discussion

3.1. Reaction of NH_3 with C_{60}^+

The energetic and structural data obtained for the interactions of C_{60}^+ with one or two NH_3 molecules are summarized in Table 1, while depictions of the optimized geometries are shown in Fig. 1. All calculations were pursued only on the doublet electronic state surface, since the reactant ion C_{60}^+ has one unpaired electron: spin contamination was found to be minor in all calculations, with expectation values $\langle s^2 \rangle$ consistently below 0.78 (which compares with the value of 0.75 expected for a pure doublet).

Of the parameters detailed in Table 1, some require further explanation. The angle $\theta(NCC_\alpha)$ is defined as the mean of the three values for the angle between *N*, the *ipso* carbon, and an α carbon. This value provides a measure of the pyramidalization

Table 1
Energetic and structural details obtained, at the B3-LYP/6-31G** level of theory, for species relevant to the reactions of C_{60}^+ and secondary ions with ammonia

Species	$E_e(C_{60}X^{n+})$[a] (hartree)	E_{rel}[b] (kJ mol^{-1})	r(C–N) (Å)	$\theta(NCC_\alpha)$[c] (°)	$q_{Mull}(N)$[d]	E_{deform}[e] (kJ mol^{-1})	Other parameters
$C_{60}^+ + 2NH_3$	−2285.910695	0.0	–	101.5	–		
$(C_{60}\cdot NH_3)^+$ ($^2A'$) + NH_3	−2342.4777205	−24.3	1.616	108.9	+0.52	52.5	
$(C_{60}\cdot NH_3\cdot NH_3)^+$ ($^2A'$)	−2399.0725034	−121.5	1.558	110.0	+0.49(α); +0.13(β)		$r(N_\alpha\text{–}H) = 1.095$; $r(H\text{–}N_\beta) = 1.670$
$(H_3N\cdot C_{60}\cdot NH_3)^{2+}$ ($^2A''$)	−2399.0436002	−45.6	2.862	101.8	+0.07 × 2		
$C_{60}NH_2 + NH_4^+$	−2342.0985531	+57.3			−0.06		

[a] Total energy for the identified fullerene-containing species, excluding zero-point vibrational energy.

[b] Energy of the indicated combination of species (at 0 K), expressed relative to the total energy of the three reactants $C_{60}^+ + 2NH_3$.

[c] Pyramidalization angle of the anchorage carbon atom(s), defined as detailed in the text.

[d] Calculated Mulliken charge on the nitrogen atom(s), with contributions from H atoms incorporated into N.

[e] Energy of deformation of the anchorage carbon atom, defined as detailed in the text.