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A Possible Synthesis and the Unusual Electronic Properties of Endofullerene $\text{NH}_4^+@C_{60}$ and Its Reduced Forms

Pavlo O. Dral,^[a] Tatyana E. Shubina,^[a] Laura Gagliardi,^[b] Dirk M. Guldi^[c] and Timothy Clark^[a]

^[a]Computer-Chemie-Centrum and Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen

^[b]Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, USA

^[c]Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen

1 Introduction

The inner wall of fullerenes is essentially chemically inert because of its concave shape. Many species including nitrogen atom, noble-gas atoms, hydrogen and nitrogen molecules, carbon monoxide, methane, metal atoms, carbides, nitrides, oxides and intermetals have been incorporated into fullerenes to give stable endofullerene derivatives.[2]

Most of the above examples of the endofullerenes were synthesized by constructing or reclosing the fullerene cage in the presence of the moiety to be incorporated. Only the noble gases@ C_{60} were obtained by bombarding the closed fullerene with atoms at high temperatures.[2]

Encapsulating guests inside fullerenes can be used to modulate the desired (opto)electronic and magnetic properties of fullerenes.[2] Usually metal-containing guests are used.[2] Here we present a study on the electronic properties and possible synthesis of non-metallic endofullerene with ammonium cation inside the C_{60} cage.[1]

2 Methods

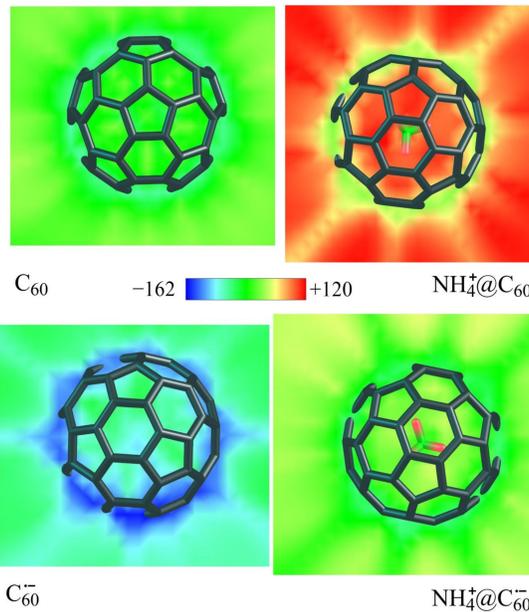
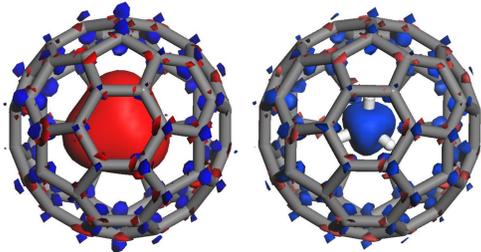
Geometries of all structures were fully optimized without symmetry constraints at the B3LYP level of theory using the 6-31G(d) basis set. Stationary points were confirmed to be minima or transition states by calculating the normal vibrations within the harmonic approximation. Additional single-point (SP) calculations were performed at the MP2 level of theory on the DFT-optimized geometries (denoted MP2/6-31G(d)//B3LYP/6-31G(d)). DFT densities were used as initial guess for MP2 calculations because of instability of HF wavefunctions. The Gaussian 03 and 09 MO program packages[3] were used for DFT and MP2, VAMP 11[4] and EMPIRE 2013[5] for semiempirical and MOLCAS[6] for CASSCF and CASPT2 calculations.

3 Results and Discussion

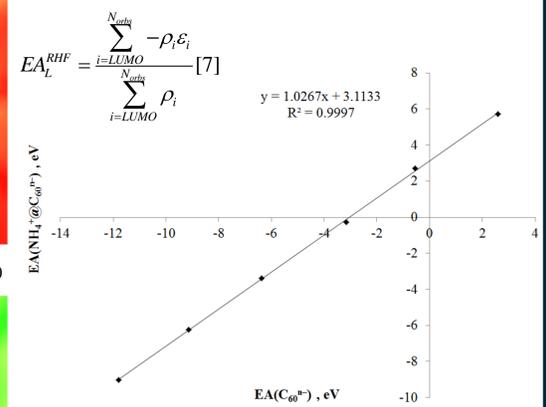
3.1 Electronic Properties of $\text{NH}_4^+@C_{60}$

Encapsulating ammonium cation inside the C_{60} cage increases the electron accepting properties of C_{60} drastically. $\text{NH}_4^+@C_{60}^{n-}$ with $n = 1...5$ represent ion pairs rather than Rydberg radicals $[(\text{NH}_4^+)(e^-)_{\text{Rydberg}}]$ inside $C_{60}^{(n-1)-}$. However, single-electron excitation of the radical ion pair $\text{NH}_4^+@C_{60}^-$ can lead to $[(\text{NH}_4^+)(e^-)_{\text{Rydberg}}]@C_{60}$. [1]

Molecular electrostatic potentials of the ground (left) and charge transfer (right) states of $\text{NH}_4^+@C_{60}^-$ at the AM1 CIS level



Local electron affinities (EA_L) at AM1

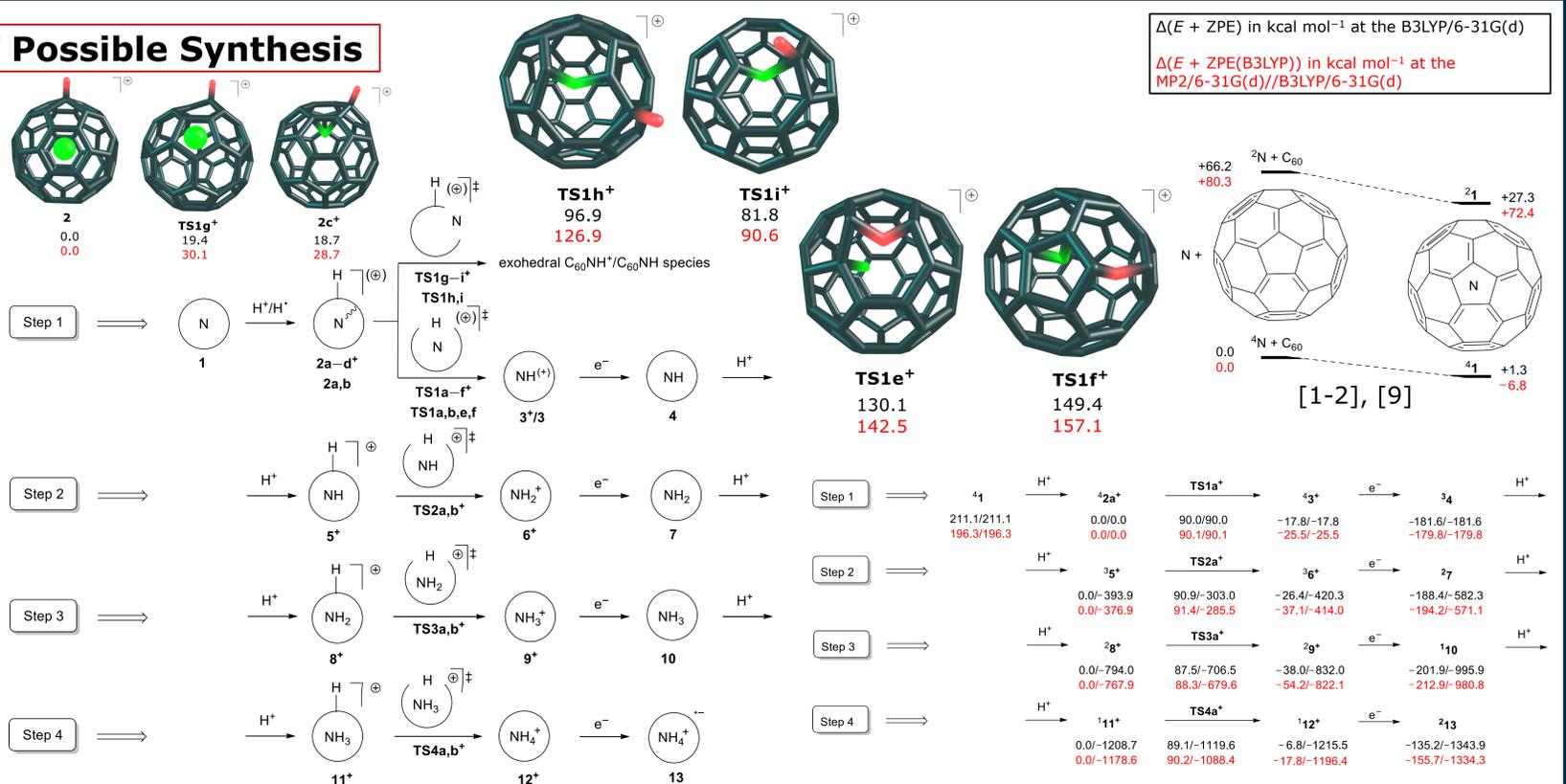


$$EA_L^{UHF} = \frac{\sum_{i=N^{n-}+1}^{N_{\text{orb}}} -\rho_i^\alpha \epsilon_i^\alpha + \sum_{i=N^{n-}+1}^{N_{\text{orb}}} -\rho_i^\beta \epsilon_i^\beta}{\sum_{i=N^{n-}+1}^{N_{\text{orb}}} \rho_i^\alpha + \sum_{i=N^{n-}+1}^{N_{\text{orb}}} \rho_i^\beta} \quad [1]$$

Vertical EAs at B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)

3.2 Mechanism of Possible Synthesis

Energy gains during proton transfer to $\text{NH}_x@C_{60}$ from H_3^+ as proton carrier are about 30 kcal mol⁻¹ larger than the subsequent barriers.[1] Taking into account the large barriers and potential danger of nitrogen escape from $\text{N}@C_{60}$, the proposed approach is of more interest for fundamental research, while a more practical and economical synthesis can be synthesis of some of discussed endofullerenes including $\text{NH}_4^+@C_{60}$ via molecular surgery of fullerene as, for instance, $\text{H}_2\text{O}@C_{60}$ was synthesized in 2011.[8]



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