Isolation of the Heterofullerene $C_{59}N$ as Its Dimer ($C_{59}N)_2$

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The heterofullerene ion $C_{59}N^+$ is formed efficiently in the gas phase during fast atom bombardment mass spectroscopy of a cluster-opened N-MEM (N-methoxyethoxy methyl) ketolactam. This transformation is shown to occur also in solution in the presence of strong acid, affording biazafullereny (C$_{59}$N)$_2$ in good yield. It is proposed that the azafullerene dimer is formed upon in situ reduction of the highly reactive azafullerion ion. The isolation and characterization of biazafullerényl opens a viable route for the preparation of other heterofullerenes in solution.

The introduction of heteroatoms into the fullerene cage leads to significant perturbations on the electronic and geometric character of the fullerene cluster (1); such heterofullerenes are expected to have applications in superconductivity, photoinduced electron transfer (photoelectric devices), and organic ferromagnetism. However, to date it has proved difficult to prepare and isolate heterofullerenes and thus to gain a more detailed understanding of their properties. In 1991, Smalley's group reported the gas-phase preparation of "dopy balls," molecular clusters consisting of C$_{60}$B$_n$ (2). The preparation followed the usual procedure of laser ablation of a graphite-heteroatom composite rod. Later in the same year, Rao reported the preparation of a number of C$_n$N$_m$ fullerenes (3) on the basis of mass spectroscopic observation of peaks in the range m/z (mass/charge) = 722 to 728 of toluene extracts of graphite arc soot, generated in the presence of nitrogen or ammonia. More recently, in attempts to prepare nanotubes in a nitrogen atmosphere, Zheng et al. (4) reported the preparation of C$_{59}$N. Neither of these groups reported exact mass measurements, nor did they comment on the possible fragmentation pattern. More recently, verification of the existence of C$_{59}$N and C$_{59}$N$_2$ in the gas phase was reported by Mattay et al. (5) and by Lamparth et al. (5).

Now we report that an efficient gas-phase preparation of azafulleronium C$_{59}$N$^+$, unrelated to that reported by Mattay et al. (5) and Lamparth et al. (5), can be mimicked in condensed phase by organic synthesis, resulting in the isolation and characterization of a dimer of the azafullerényl radical, biazafullerényl (C$_{59}$N)$_2$. Recently, we described opening a hole in the C$_{60}$ cage structure (6). FAB mass spectroscopy (FABMS) of the open cluster 1 revealed a base peak at m/z = 722; a high-resolution measurement showed an exact mass of 721.9991 atomic mass units (amu), in good agreement with the theoretical value of 722.003704 for C$_{59}$N$^+$. Further confirmation was found in the "shrink-wrap" fragmentation pattern of efficient loss of 26-amu (loss of CN, m/z = 696) and successive 24-amu (loss of C$_2$, m/z = 672, 648) fragments. A pattern of successive losses of C$_2$ fragments was reported for C$_{60}$ (7). There is, however, a marked difference between the shrink-wrap pattern of gas phase-prepared borafullerenes (for example, C$_{59}$B, reported by Smalley et al. (7), and the shrink-wrap pattern of the azafullerion ion. Whereas the borafullerenes exclusively lose C$_2$ fragments (down to C$_2$B), the azafullerion ion first loses a CN fragment and then C$_2$ fragments. The different behavior is likely due to the decreasing relative stability of the (neutral) CN, C$_2$, and CB fragments; the last is a carbene radical and is expected to be unstable. A relatively intense peak at m/z = 780 (95%) is due to loss of 2-methoxyethanol to yield the N-methyl carbonium ion 2 from 1 (Scheme 1).

Although the formation of a 1,3-oxazetidinium intermediate 3 (Scheme 1) may seem counterintuitive at first sight, it is plausible because the cyclopentanone carbonyl group and the N-methyl carbonium ion are parallel and buttressed against each other by the cage network. Support for this mechanism was obtained from the FAB mass spectrum of compound 5, a more complex N-MEM ketolactam derivative of C$_{60}$, synthesized recently (8).

The FAB mass spectrum with an o-dichlorobenzene/p-nitrobenzyl alcohol (ODCB/NBA) matrix of 5 showed a small M$^+$ peak at m/z = 958 (4%), a peak at m/z = 883 (17%), corresponding to the loss of 2-methoxyethanol, a peak at m/z = 853 (35%), corresponding to the subsequent loss of formaldehyde, and the base peak at m/z = 722. The shrink-wrap fragmentation pattern of the azafullerion ion was again observed.

In a search for a synthetic organic method to obtain macroscopic quantities of 4 (or a derivative) that would mimic the events observed in FABMS and in the process of attempting to remove the whole MEM group with a concomitant improved access to the orifice in this molecule, we observed that reaction of 1 with excess TiCl$_4$ in ODCB at room temperature yields the N-chloromethyl ketolactam 6 in 47% yield, instead of the expected fully deprotected lactam (9). Compound 6 was anticipated to be a good precursor for the corresponding N-methyl carbonion ion. Its FAB mass spectrum (toluene/NBA) contained a base peak at m/z = 722, accompanied by shrink-wrap peaks at m/z = 696, 672, 648, and 624. However, the only significant peak between the (M + H)$^+$ peak at m/z = 816 and 722 was at m/z = 768, corresponding to the protonated, deprotected ketolactam. This result indicates that in the case of 6, a different pathway to the azafullerion ion is followed than in the cases of 1 and 5. Compound 6, the third analog in our series of C$_{60}$ derivatives with an opening in the cage structure, was fully characterized by proton nuclear magnetic resonance (H-NMR), $^{13}$C-NMR, ultraviolet-visible spectrophotometry (UV-vis), and Fourier transform infrared (FT-IR) spectrophotometry.

In a second attempt at deprotection, a fast and remarkable reaction was observed when N-MEM ketolactam 1 was treated with a large excess (15 to 20 equivalents) of p-toluenesulfonic acid monohydrate in ODCB at reflux temperature under nitrogen. The formation of a very apolar major product, accounting for 85

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to 95% of starting material, was obtained by column chromatography (silica gel/toluene) of the crude reaction mixture (10).

The absence of an electron spin resonance (ESR) signal excluded the possibility that the above product was a stable free radical. The compound also showed no signals in $^1$H-NMR (both in C$_5$D$_5$ and in ODCB-d$_5$). The elemental analysis (C, 95.03; H, <0.5; N, 1.93) was considered consistent with a formula of C$_{59}$N$_3$ or (C$_{58}$N$_3$), [calculated for (C$_{58}$N$_3$): C, 98.06; N, 1.94]. Although the value for carbon is low (by ~ 3%), it is not unusual for fullerene derivatives; most fullerenes do not burn properly and consistently give results that are 1 to 4% below the calculated values. Our confidence rests with the nitrogen and hydrogen analytical results.

Electrospray MS (+) (positive mass spectroscopy) of a 0.02 to 0.05 mM solution in toluene showed, besides a strong peak at m/z = 722 (11), a weak ion cluster at m/z = 1445 (Fig. 1), corresponding to free radical cation M⁺ of C$_{59}$N$_3$, presumably formed by electrochemical oxidation of the neutral species in the stainless steel electrospray capillary (12). Because neutral C$_{59}$N$_3$ can only exist as a radical (1) (and therefore by itself cannot be our product) and because molecular clusters, observed in MS, are always a result of cation clustering with neutrals, it is unlikely that the m/z = 1445 peak was the result of molecular clustering.

A strong argument for existence of the dimer was obtained from its cyclic voltamogram (CV) (1 mM solution in ODCB/0.1 M Bu$_4$NBF$_4$; ferrocene-ferrocenium couple, internal standard), which showed three overlapping pairs of reversible one-electron reductions within the solvent window (E$_1$ = -997 mV, E$_2$ = -1071 mV, E$_3$ = -1242 mV, E$_4$ = -1485 mV, E$_5$ = -1979 mV, and E$_6$ = -2089 mV). A combination of linear sweep voltammetry and chronoamperometry (13) established that all overlapping waves are two-electron reductions. There is also an irreversible two-electron oxidation with a peak potential at +886 mV, that is, 0.2 V more negative (easier to oxidize) than C$_{60}$ (14). The appearance of closely spaced pairs of waves in the CV suggests that our system consists of two (identical) weakly interacting electrophores, similar to the dianthrylalkanes (15).

In the $^{13}$C-NMR spectrum of (C$_{59}$N)$_2$, 30 lines were observed in the region between 157 and 124 parts per million (ppm) (16). No other resonances (that is, for expected sp$^3$-hybridized carbon atoms) were observed. ODCB was the only solvent in which a reasonably high concentration of (C$_{59}$N)$_2$ could be obtained. Although the resonances for ODCB-d$_5$ are usually just outside the region of C$_{60}$ derivatives, the possibility that a few signals were lost under the solvent peaks existed.

A second $^{13}$C-NMR spectrum (8 days of acquisition) in C$_5$D$_5$ (about 1.5 mg/ml, that is, 1 $\mu$M) consisted of a similar pattern of 28 lines and, within the experimental constraints of the spectrum noise, there were no resonances in the ODCB-d$_5$ region. From the observation of only 30 lines for (C$_{59}$N)$_2$, we conclude that the molecule is highly symmetric and has two planes of symmetry (or one inversion center and one plane of symmetry), one between the two balls and one through the length of the dimer. On the basis of this symmetry argument, the two balls can only be connected through carbon atoms C$_1$ (adjacent to the N atom in a "6,6" fashion, where the C$_1$-N bond is between two six-membered rings of the azafullerene, as in 7a, in agreement with calculated relative electron densities (1).

For the depicted dimer 7a, the maximum number of carbon atom resonances would be 31, 30 sp$^3$, and 1 sp$^2$. We have seen only signals in the 157 to 124 ppm region; it is possible that the signal due to the quaternary sp$^3$ carbon atoms (expected chemical shift of 50 to 110 ppm) is too weak to be detected under the Fourier transform NMR (FT-NMR) conditions required to record the remaining signals. Because the signals in the 157- to 124-ppm region correspond to 118 carbon atoms (30 signals, of which 1 integrates to 8 C, 26 to 4 C (104 carbons), and 3 to 2 C (6 carbons)), an alternative structure (7b), in which all carbons are sp$^3$-hybridized, could be considered. This rather unusual structure was initially not expected to be favored because (i) it requires a "6,6 open" arrangement (with concomitant intra-annular pentagon double bonding) and (ii) it was thought to require an unusual bond angle at the interball bonding atoms. However, a combination of the above NMR results and FT-IR and UV-vis results (see below) strongly suggest that 7b be given serious consideration. In addition, construction of a three-dimensional model, as well as computer modeling (17), show that the sp$^3$-hybridized carbons that are involved in the interball bonding are less strained in 7b than in C$_{60}$, because they are coplanar with the cage carbon atoms to which they are bonded, as shown schematically by "bold" bonds in 7c.

The FT-IR (transmittance; KBr pellet) and neat powder DRIFT (diffuse reflectance infrared technique) spectra of biazafullerene are virtually identical and show, besides multiple absorptions in the four areas where C$_{60}$ shows single peaks (that is, at 1428, 1182, 576, and 527 cm$^{-1}$), a strong peak at 845 cm$^{-1}$ and medium strong peaks at 837 and 821 cm$^{-1}$. Furthermore, there are three weaker absorptions at 1584, 1565, and 1551 cm$^{-1}$. The latter absorptions could be assigned to C=C-N or C=C or both (from C=C=C=N) stretching in the bis 6,6 open structure 7b.

Besides the stronger absorption at 328 nm in its UV-vis spectrum, the molecule features weak absorptions with maxima at 442, 596, 720, and 800 nm and no more absorptions in the near-IR region (up to 2000 nm). The broad, rounded band at 442 nm...
nm is typical of fullerenes with a double-bond endocyclic to a pentagon (18), in agreement with structure 7b.

We propose (see below) that the azafullerium ion is formed first in a manner that mimics the gas-phase formation of azafullerium as shown in Scheme 1: The acid protonates the MEM moiety, inducing the loss of 2-methoxyethanol; the N-methyl carbonium ion thus formed rearranges to the four-membered 1,3-oxazetidinium ring compound, which in turn loses formaldehyde and carbon monoxide to yield the azafulleronium ion. The azafullerium ion, expected to be a very strong oxidant, can apparently be reduced ([Red] in Scheme 2, by either 2-methoxyethanol or water) to the azafullerenyl radical, which dimerizes to yield biazafullerenyl. Preliminary results indicate that the title dimer readily dissociates to the monomer, which can be trapped to produce organic derivatives of C_{59}N (19). We are currently investigating the chemical reactivity, physical properties, and possible applications of this intriguing first member of the class of heterofullerenes.

REFERENCES AND NOTES

8. J. C. Hummelen, unpublished results.
10. The product was obtained in pure form by preparative high-performance liquid chromatography (Cosmosis Buckyprep Semiprep column toluene). From the chromatographic behavior it was clear that this material is apolar and that it has a “Bucky” character: Despite its apolarity it shows a remarkably high affinity to Cosmosis Buckyprep column material.
11. Four different MS techniques-FABMS (ODCB, NBA (+) and (-)); desorption electron ionization [DEI (+)]; matrix-assisted laser desorption ionization [MALDI(+)] through use of either an α-cyanocinnamic acid/1-methylnaphthalene matrix or a dinitrobenzoic acid/fucose matrix and a nitrogen laser (wavelength λ = 337 nm) at threshold power, and atmospheric pressure chemical ionization [APCI, both (+) and (-); toluene]-showed peaks at m/z = 722 or broad ion-cluster peaks with maximum at m/z = 723, depending on the resolving power of the technique. In none of the above methods were ions with a higher mass detected.

Scheme 2. Proposed cascade of events in the pTsOH.H$_2$O-initiated formation of (C$_{59}$N)$_2$ from N-MEM ketolactam 1 in refluxing ODCB.