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

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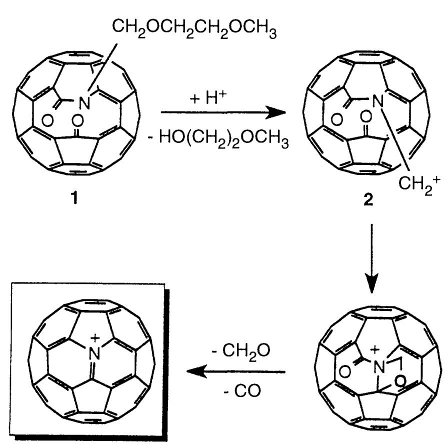
The heterofullerene ion $C_{59}N^+$ is formed efficiently in the gas phase during fast atom bombardment mass spectroscopy of a cluster-opened N-MEM (*N*-methoxyethoxy methyl) ketolactam. This transformation is shown to occur also in solution in the presence of strong acid, affording biazafullerenyl $(C_{59}N)_2$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

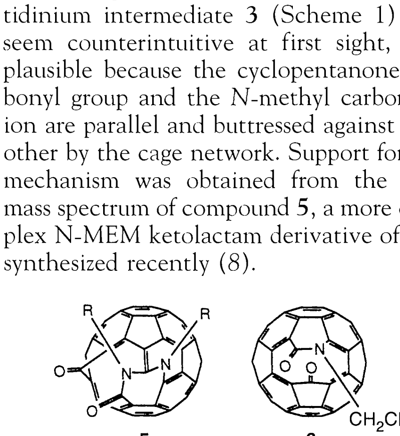
The introduction of heteroatoms into the fullerene cage leads to significant perturbations on the electronic and geometric character of the fullerene cluster (*1*); such heterofullerenes are expected to have applications in superconductivity, photoinduced electron transfer (photoelectric devices), and 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 $C_{60-n}B_n$ (*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_nN_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 $C_{69}N$ 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 azafullerenyl radical, biazafullerenyl $(C_{59}N)_2$. 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 722.003074 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 azafulleronium ion. Whereas the borafullerenes exclusively lose C_2 fragments (down to $C_{31}B$), the azafulleronium 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).



Scheme 1. Proposed mechanism for the gas-phase formation of azafulleronium $C_{59}N^+$ (**4**) from N-MEM ketolactam **1** in FABMS.

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*).



5 **6**

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 azafulleronium 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 carbonium 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 azafulleronium 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 (^{1}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*).

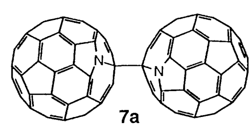
The absence of an electron spin resonance (ESR) signal excluded the possibility that the above product was a stable free radical. The compound also showed no signals in ^{1}H-NMR (both in CS_2 and in ODCB-d_4). The elemental analysis (C, 95.03; H, <0.5; N, 1.99) was considered consistent with a formula of $C_{59}N$ or $(C_{59}N)_2$ [calculated for $(C_{59}N)_2$: 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 $M(\cdot)^+$ of $C_{118}N_2$, presumably formed by electrochemical oxidation of the neutral species in the stainless steel electrospray capillary (*12*). Because neutral $C_{59}N$ 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.

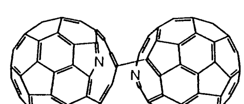
A strong argument for existence of the dimer was obtained from its cyclic voltammogram (CV) (1 mM solution in ODCB/0.1 M Bu_4NBF_4; ferrocene-ferrocenium couple, internal standard), which showed three overlapping pairs of reversible one-electron reductions within the solvent window (E_1 = −997 mV, E_2 = −1071 mV, E_3 = −1424 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_4 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 CS_2 (about 1.5 mg/ml, that is, 1 μM) 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_4 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*).

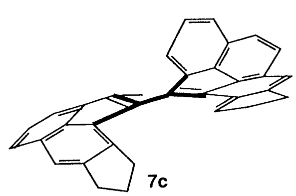
For the depicted dimer **7a**, the maximum



7a
6,6 Closed—6,6 closed



7b
6,6 Open—6,6 open



7c

number of carbon atom resonances would be 31, 30 sp^2, and 1 sp^3. 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^2-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^2-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 biazafullerenyl 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=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

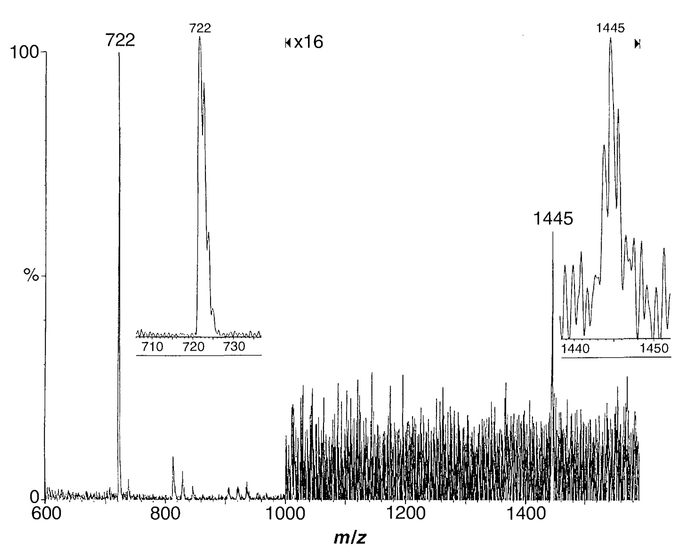
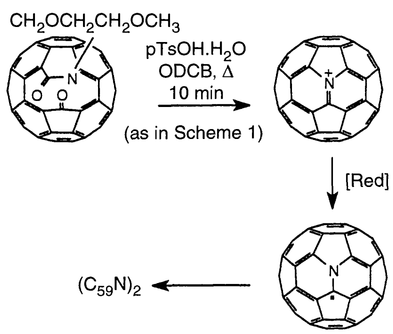


Fig. 1. Electrospray MS (+) spectrum of a 0.02 to 0.05 mM solution of $(C_{59}N)_2$ in toluene. The insets are expansions around the 722 and 1445 m/z peaks. The expanded patterns give an excellent fit to the calculated isotope mass ratios.

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 azafulleronium ion is formed first in a manner that mimics the gas-phase formation of azafulleronium 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 azafulleronium 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,



Scheme 2. Proposed cascade of events in the pTsOH.H_2O-initiated formation of $(C_{59}N)_2$ from N-MEM ketolactam **1** in refluxing ODCB.

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.

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10. The product was obtained in pure form by preparative high-performance liquid chromatography (Cosmosil 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 Cosmosil 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 dihydroxybenzoic 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.
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A Stable High-Index Surface of Silicon: Si(5 5 12)

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A stable high-index surface of silicon, Si(5 5 12), is described. This surface forms a 2 × 1 reconstruction with one of the largest unit cells ever observed, 7.7 angstroms by 53.5 angstroms. Scanning tunneling microscopy (STM) reveals that the 68 surface atoms per 2 × 1 unit cell are reconstructed only on a local scale. A complete structural model for the surface is proposed, incorporating a variety of features known to exist on other stable silicon surfaces. Simulated STM images based on this model have been computed by first-principles electronic-structure methods and show excellent agreement with experiment.

As the basis for a multibillion-dollar industry, the surfaces of silicon are the most widely studied of all semiconductors. Despite such scrutiny, only three stable surfaces of clean silicon have generally accepted structural models: the well-known low–Miller index (001) and (111) planes and the high-index (113) plane (*1–3*). As is common for covalently bonded materials, all of these clean surfaces reconstruct in order to reduce the energy associated with their surface dangling bonds. On Si(001), the surface atoms pair up as dimers to form a 2 × 1 reconstruction. On Si(111), a number of different reconstructions are observed, including the metastable 2 × 1 structure with the top two surface layers rearranged into π-bonded chains (observed on a cleaved surface), and the equilibrium 7 × 7 structure with a more complicated dimer-adatom-stacking fault (DAS) structure (observed after cooling from high temperatures). High-index Si(113), a surface consisting of alternating rows of atoms with (001) and (111) orientation, is stabilized by a 3 × 2 reconstruction composed of rebonded and dimerlike step edge atoms. Substrates oriented to (110), (331), and (015) also appear to have stable surfaces, but their structures have not been well established (*4–7*).

Although Si(001) is the dominant substrate for electronic device fabrication, high-index surfaces are being investigated as possible substrates for specialized applications (*8–10*). An ideally structured high-index surface (that is, bulk-terminated) would consist of a periodic array of low-index terraces separated by steps of monatomic height. Such a surface would provide a natural template for the growth of one-dimensional structures (*8*) and high-quality heteroepitaxial films (*9, 10*). However, the actual surface morphologies on high-index surfaces are usually not ideal, because of the influence of surface reconstructions, step and kink energies, and step-step interactions. In general, these surfaces may consist of a distribution of low-index terraces separated by variable-height steps or step bunches, or in the extreme case, may break up (facet) into planes of different orientations (*11*).

Whereas Si surfaces tilted only a few degrees away from (001) and (111) have been well characterized, less is known about high-index surfaces tilted farther away from these planes. Given the established stability of Si(113), which is oriented nearly midway between (001) and (111), high-index sur-

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