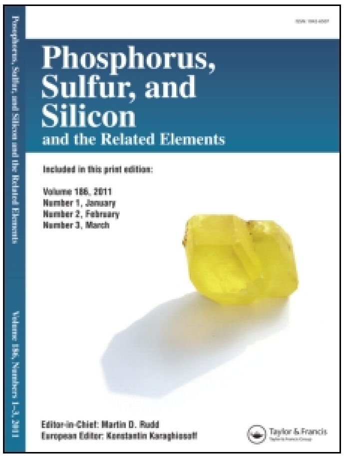

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Heterocyclic and Heteroatom Derivatives of Buckminsterfullerene C_{60}

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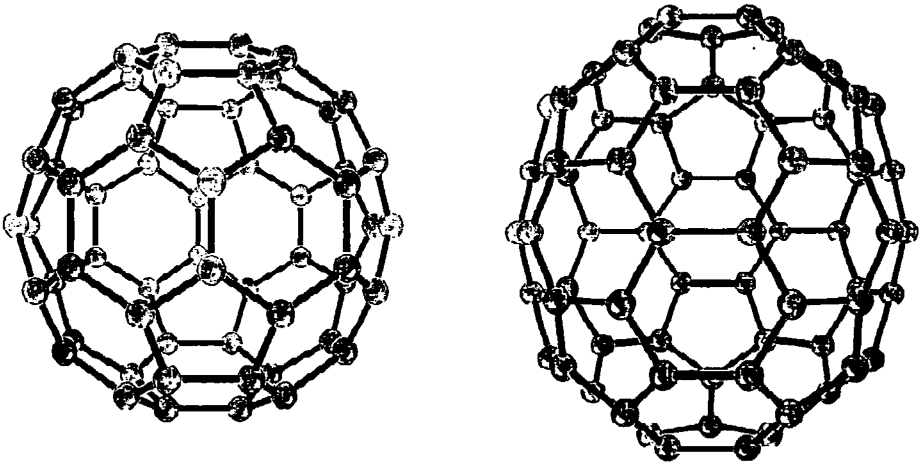
The synthesis of hydroazafullerene and the dimer of azafullerenyl are presented. The structures of these heterofullerene molecules were characterized with the use of proton and carbon NMR as well as C-H and C-^{15}N coupling constants.

KEY WORDS buckminsterfullerene, azafulleroids, azafullerenes.

INTRODUCTION

By now most scientists are familiar with the recently discovered allotrope of carbon, the fullerenes.[1-3] The most studied of these are C_{60} and C_{70}, shown below:



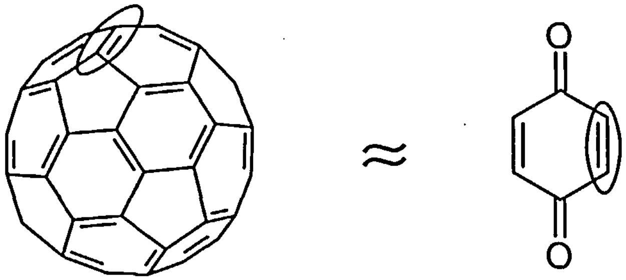
C_{60} C_{70}

FIGURE 1 The molecular structures of [60] fullerene and [70] fullerene.

Of these two fullerenes, the former, buckminsterfullerene, is the most studied, very likely because it is the most abundant by the current methods of preparation. As a result much more is known about the chemical, physical and materials properties of fullerene C_{60} and this presentation, as the title implies, will concentrate on heteroatom derivatives of the smaller fullerene.

In general, in a slightly oversimplified view, the chemistry of buckminsterfullerene can be modeled effectively by the chemistry of benzoquinone as depicted below:

Scheme 1



In this depiction, the encircled double bond of buckminsterfullerene ("[6,6] bond") is meant to have the same reactivity as that of benzoquinone. The sixty-carbon cluster is also almost as strong an oxidizing agent as benzoquinone. Since the quinone C=C bonds are electrophilic and are also dipolarophilic as well as dienophilic;[3, 4] the same can be said for the [6,6] bonds of the fullerene. In more general terms, the double bonds of C_{60} behave as electron poor, strained double bonds and the chemical reactivity can be summarized with the following eight reactions:

1. OSMYLATION[5]

2. NUCLEOPHILIC ADDITION[3, 4]

3. CYCLOADDITION REACTIONS[3, 4]

4. ELECTROPHILIC ADDITION[3]

5. FREE RADICAL ADDITION[3, 6]

6. HALOGENATION[3].

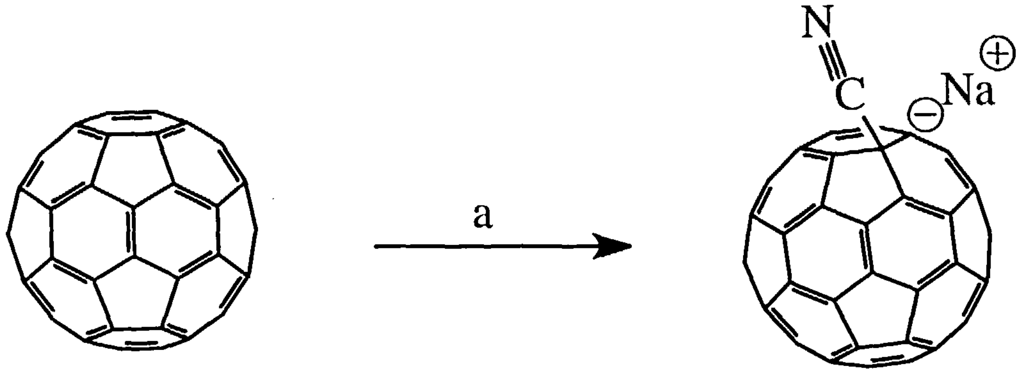
7. HYDROXYLATION[3, 7]

8. TRANSITION METAL COMPLEXES[3, 8, 9]

The order of the reactions is not in terms of usefulness or ease but more-or-less in order of their chronological discovery. Of these, reaction 7 gives mixtures of isomers, commonly known as fullerols, where the exact position of the hydroxyl groups is currently unknown. From a mechanistic point of view, reactions 1, 4 and 6 are somewhat puzzling since they normally are carried out on electron rich, not electron deficient double bonds. For fullerene modification, the most efficient and facile are reactions 2 and 3, and of these, the latter affords the cleanest monoadditon products.[3]

Polyaddition to C_{60} is, in general, a serious problem[10] and can proceed uncontrollably in reactions 2, 4, and 7 but to a much lesser extent in reactions 2 and 3. However, a case where nucleophilic monoaddition can be the major product was published recently:[11]

Scheme 2

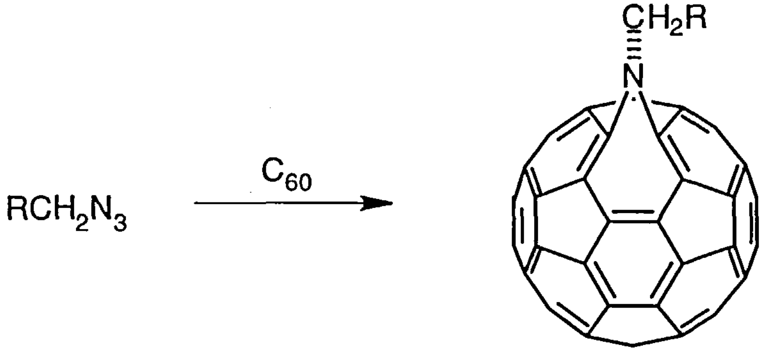


(a) NaCN, *o*-dichlorobenzene (ODCB)/DMF, 25° C

RESULTS AND DISCUSSION

Many dipolar cycloadditions have been carried out over the years on buckminsterfullerene. In our group we have emphasized the addition of diazoalkanes and azides. A typical azide addition[12] is shown below in Scheme 3. The reaction shown in Scheme 3 is a moderate temperature thermal addition. At higher temperatures, or under photolysis, fulleroaziridines, the products of nitrene addition are observed. The azafulleroid formed in Scheme 3 is usually accompanied by bisazafulleroid, shown in Scheme 5.

Scheme 3



a, R = $OCH_2CH_2SiMe_3$ (SEM)

b, R = C_6H_5

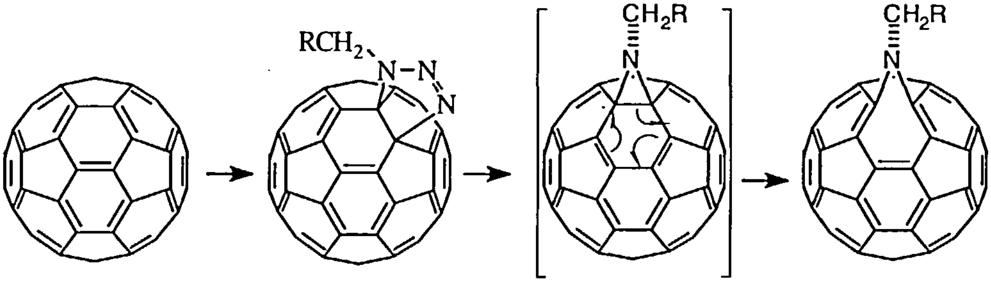
c, R = 4-C_6H_4-OMe

d, R = 4-C_6H_4-Br

e, R = $OCH_2CH_2OCH_3$ (MEM)

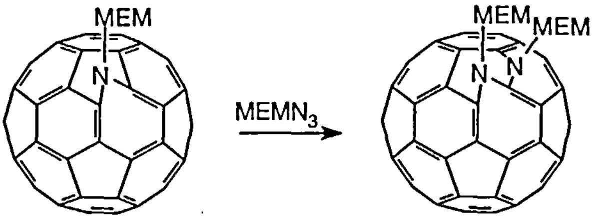
The reaction involves an addition followed by a rearrangement, concomitant with nitrogen loss:

Scheme 4



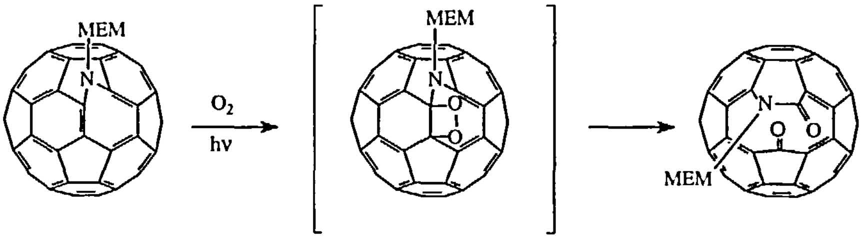
The product, known as an azafulleroid has the unusual property of rendering the C=C bonds adjacent to the nitrogen atom more reactive than the rest of the fullerene bonds. As a consequence, subsequent cycloadditions to the azafulleroid are regiospecific. For example, an additional mole of MEM-N_3 adds regiospecifically to form a bisazafulleroid, as shown below:[13]. The formation of bisazafulleroids is simple as depicted; at least two isomeric bisazafulleroids, of which the one depicted below is the major one, are formed.[13]

Scheme 5



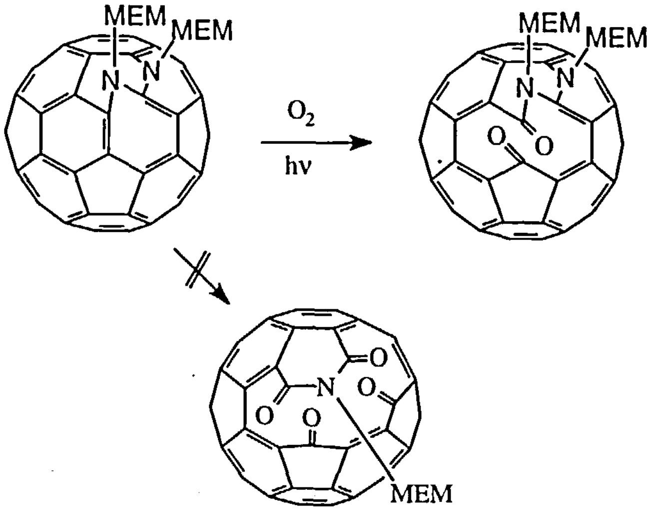
Another reagent for cycloaddition can be singlet oxygen which can be generated by self-sensitization; where the azafulleroid acts as sensitizer, as observed with C_{60}[14] to convert ground state triplet to excited state singlet oxygen as shown below:

Scheme 6



We call the product of this reaction a holey bucky because it is the first case of a fully characterized fullerene derivative with an eleven-membered ring on its surface.[15] Interestingly, the bisazafulleroid in Scheme 7 only reacts with one mole of singlet oxygen to afford a new holey bucky:

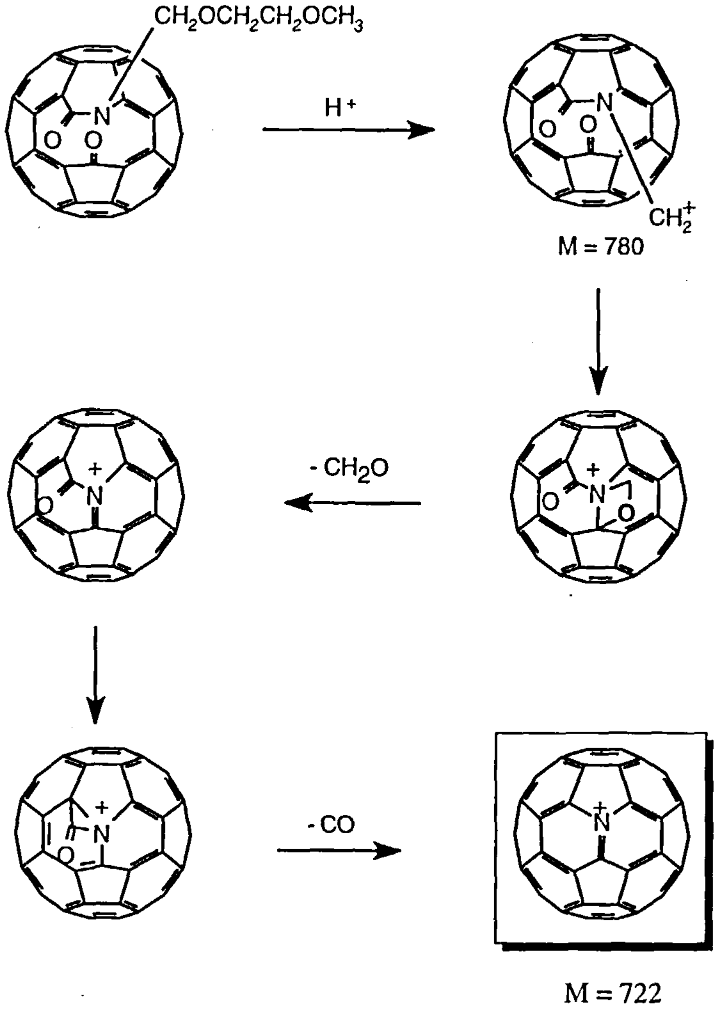
Scheme 7



Had the bisazafulleroid reacted with two moles of singlet oxygen, it would have formed the largest orifice on the surface of a fullerene; a fifteen-membered ring.

Mass spectrometric examination of the ketolactams of Schemes 6 and 7 revealed that the base peak was at 722 amu. An exact mass measurement revealed that this peak was due to $C_{59}N$. At this point we realized that we had a very efficient method for the preparation of a heterofullerene in the gas phase and conjectured that the most likely course of events upon mass spectrometric analysis was as depicted in Scheme 8.

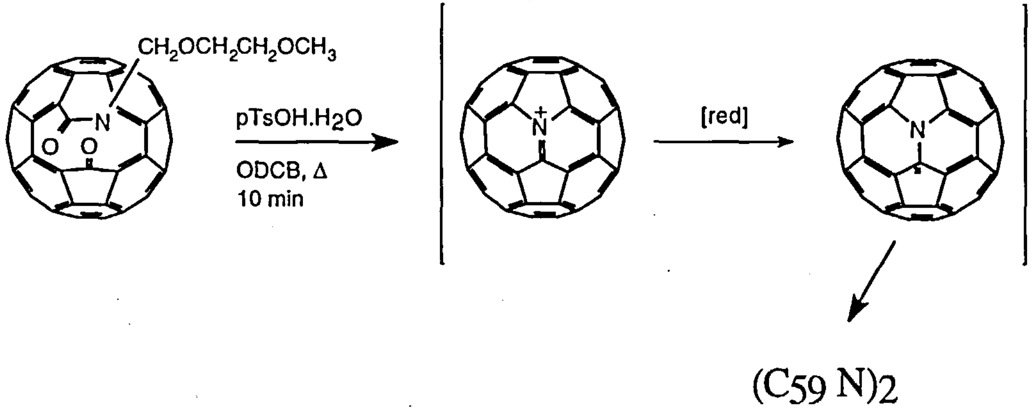
Scheme 8



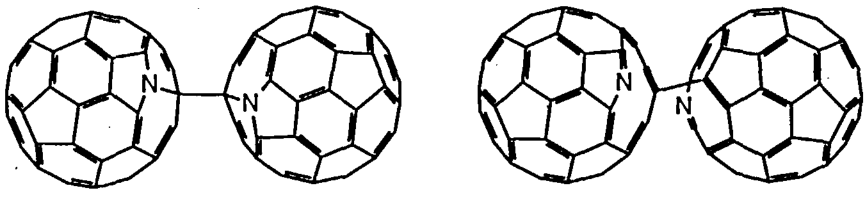
In the above mechanistic scheme,[16] the carbocation of the M = 780 amu fragment finds itself in very close proximity to the keto-carbonyl and is trapped by it to form the depicted oxazetidinium ion which upon loss of formaldehyde is converted to a lactonium ion. The latter is ready to undergo a hexatriene-cyclohexadiene rearrangement leading to an alpha lactone which immediately decarbonylates to the azafulleronium ion of mass 722.

Using this hypothetical scheme, Dr. Hummelen discovered, after some frustrating experimentation, that simply toluenesulfonic acid/o-dichlorobenzene (ODCB) converted the ketolactam to the azafullerene dimer [$(C_{59}N)_2$] as shown in the scheme below.

Scheme 9



In Scheme 9, we assume that the reducing agent "[red]" is the 2-methoxyethanol produced as side product from the acid-cleavage of the MEM group. The dimer obtained in this way was characterized by electrospray mass spectrometry, FTIR, electronic spectroscopy and ^{13}C - NMR spectroscopy. The latter showed 30 resonances in the sp^2 but none in the sp^3 region of the spectrum. Because of this we were forced to leave the absolute structure characterization unresolved, suggesting that either the "open" or "closed" form were possible:



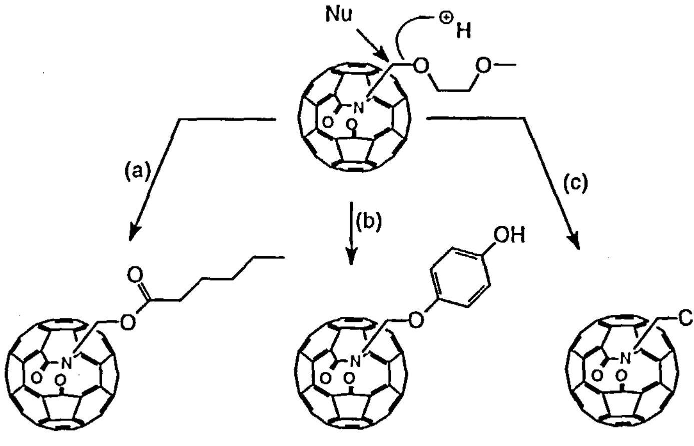
6,6 CLOSED - 6,6 CLOSED

6,6 OPEN - 6,6 OPEN

FIGURE 2 Possible structures of $(C_{59}N)_2$.

We believed that we would get a better handle on the structure solution problem if we had a simpler system such as $C_{59}HN$. Dr. Keshavarz decided to investigate the mechanistic proposal of Scheme 8 and to prove the first step, he decided to trap the cationic species with a number of nucleophiles:

Scheme 10



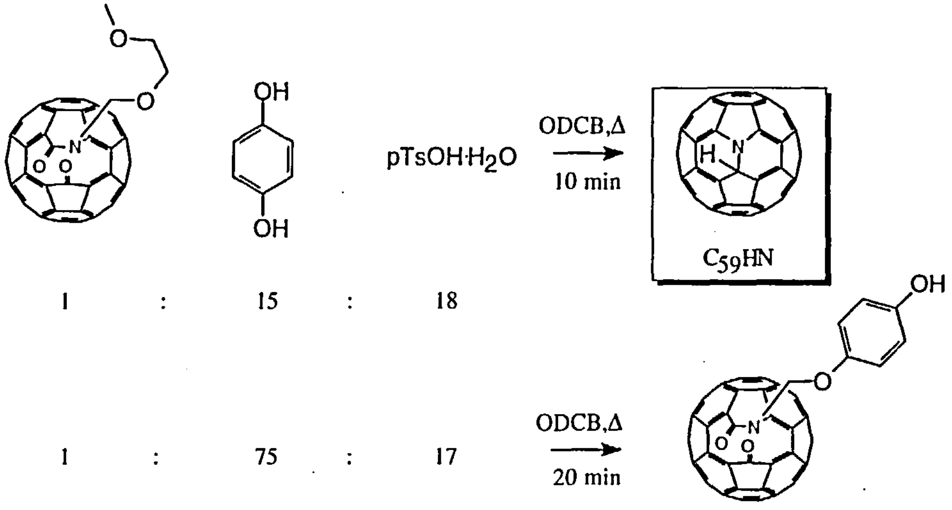
(a) pTsOH H_2O, Hexanoic acid, ODCB, 180 C, 35%

(b) pTsOH H_2O, Hydroquinone, ODCB, 180 C, 50%

(c) $TiCl_4$, CH_2Cl_2, ODCB, 25 C, 47%

Next, he wanted to determine if overwhelming the reaction mixture with hydroquinone, a better reducing agent than methoxyethanol and resistant to the acidic conditions of the reaction, would allow the isolation of $C_{59}HN$. As Scheme 11 shows, he was able to reach his goal.

Scheme 11



The hydroazafullerene was isolated and purified by high performance liquid chromatography (HPLC) to afford a dark material, green in solution. All attempts to record an NMR spectrum (^{13}C or ^{1}H) failed until we realized that the sample may have

$C_{59}N\cdot$ as an impurity. Indeed, a relatively strong electron spin resonance (ESR) spectrum could be recorded. To avoid relaxation of the NMR signal by the unpaired spin species, the pulse delay was changed from eight seconds to four seconds; this allowed the successful recording of clean spectra. The hydrogen appeared at a resonance of 8.2 ppm and the elusive sp^3 carbon atom at 72.1 ppm; the C-H coupling constant was 162 Hz. The chemical shift of this carbon atom is considered "normal" for a fullerene sp^3 hybridized carbon but the coupling constant is larger than expected as shown in the comparison below:

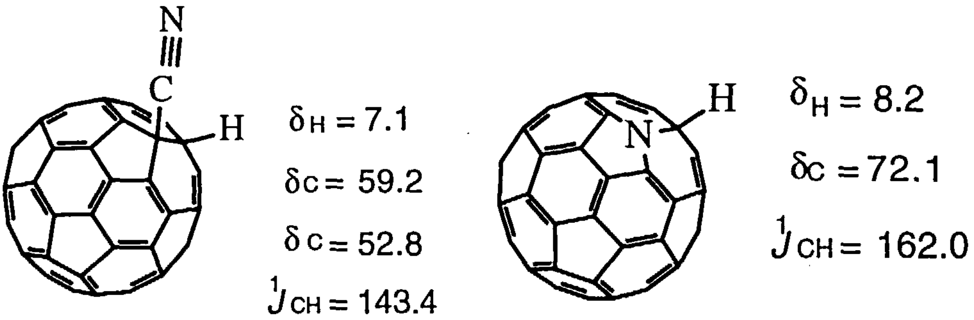
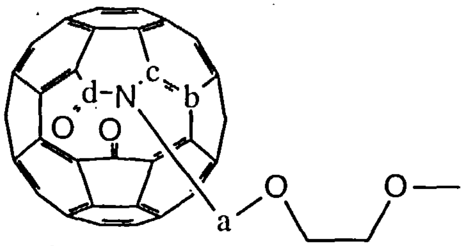


FIGURE 3 Comparative NMR values of hydroazafullerene and cyanohydrofullerene.

It was clear that the characterization of $C_{59}HN$ was on firm ground. Comparison of the ^{13}C NMR spectra of it and the dimer, $(C_{59}N)_2$, revealed that the fullerene region of both molecules was essentially superimposable, yet the latter was clearly missing the resonance corresponding to the sp^3 hybridized carbon atoms. This demanded we search for the missing carbon of the interdimer bond in the fullerene region of the spectrum. To facilitate this, Ms. Bellavia-Lund decided to use ^{13}C - ^{15}N coupling as a tool. She first prepared the 50%-labeled MEM azide, followed by the synthetic sequences outlined above to produce the labeled ketolactam, where the carbon resonances at 80.8, 128.1, 139.7, and 163.8 ppm were coupled to the labeled nitrogen atom. These, were ascribed to the MEM-methylene, one of the β-carbons, the carbon directly attached to nitrogen, and the carbonyl carbon, respectively. The reason for the 50% labeling stems from the fact that the sodium azide employed for the preparation of MEM azide by reaction with MEM chloride, had only one of its terminal nitrogen atoms labeled.



a = 80.8 ppm

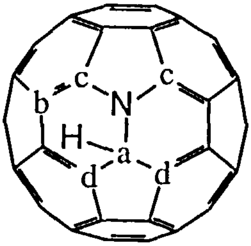
b = 128.0 ppm

c = 139.7 ppm

d = 163.8 ppm

FIGURE 4 Assignment of carbon atoms coupled to ^{15}N in the ketolactam.

The above ketolactam was then converted to both $C_{59}HN$ and $(C_{59}N)_2$ and their spectra were recorded. The former heterofullerene showed three carbon resonances coupled to nitrogen at 71.7, 134.9, and at 155.3, which could easily be assigned to the sp^3 hybridized carbon bearing hydrogen ("a"), the two β ("b"), and the remaining two α carbons ("c"), respectively. The resonance at 147.1 ppm is β-coupled to H.



a = 71.7 ppm

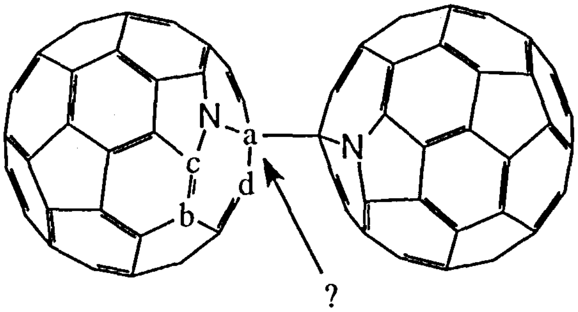
b = 134.9 ppm

c = 155.3 ppm

d = 147.1 ppm

FIGURE 5 Assignment of carbon atoms coupled to ^{15}N ("a-c") and H ("d") in hydroazafullerene

Armed with this information, we examined the spectra of the dimer to finally establish whether it is "open" or "closed" but much to our chagrin could find only one ^{13}C resonance that split into a doublet at 156 ppm, one that broadened at 138 ppm and one that broadenned to a lesser extent at 149 ppm. Our interpretation of these results is pictured below.



b (a?) = 138 ppm

c = 156 ppm

d = 149 ppm

FIGURE 6 Assignment of carbon atom coupled to ^{15}N in $(C_{59}N)_2$.

The figure above shows that, whereas we are certain about the assignment of one out of the possible two α as well as the β sites, we are still uncertain about the crucial sp^3 α carbon ("a"). It is possible that, as is well known in fullerene chemistry, when a fullerene is a substituent, it has a strong deshielding effect. In $(C_{59}N)_2$, each half of the molecule acts as a deshielding group on the other; also, the interball bonding carbons ("a") are pressed against the opposite ball's nitrogen atom's lone pair, which causes further deshielding. An additional complication is that the "a" carbons are α to their own ball's nitrogen but β to the adjacent ball's nitrogen. This could cause a further broadening of the line. The fact that we do not observe a resonance in the region normally assigned to the sp^3 region for the dimer is further supported by quantum calculations at the LDF (local density functional) level, which reveal that the hybridization of "a" is between sp^2 and sp^3.[17]

Since (1) the electronic spectra of the $(C_{59}N)_2$ and $C_{59}HN$ were essentially superimposable, (2) the infrared spectra were very similar, and (3) the fullerene region of the ^{13}C NMR spectra were very similar, we were forced to conclude that the structure of the dimer is "closed" (as depicted above). The ultimate proof of structure will have to rest with a single crystal X ray structure.

CONCLUSION

We have shown above that by making use of one of the more versatile fullerene functionalization reactions, polar cycloaddition of MEM azide; one can, in three steps, replace a carbon atom of buckminsterfullerene with a nitrogen atom and produce the first heterofullerene in bulk quantity. Because a tetravalent element was substituted by a trivalent element, the molecule was left with a dangling bond, if the bonding scheme of buckminsterfullerene is retained. The dangling bond is a free radical so $C_{59}N^{\bullet}$ is an open shell molecule which is unstable at room temperature and dimerizes to produce the stable dimer $(C_{59}N)_2$.

The synthetic procedure for the formation of the dimer was modified by addition of an acid-stable reducing agent, hydroquinone, resulting in the formation of the "monomer" $C_{59}HN$, where a hydrogen atom quenched the reactive unpaired spin. Whereas it was relatively easy to determine the structure of the monomer by a combination of proton, carbon and carbon - ^{15}N coupling NMR experiments, the structure of the dimer had to be garnered only by inference from comparative spectroscopies (UV-vis, FTIR, NMR) between the monomer and the dimer.

ACKNOWLEDGMENT

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