

Light-Induced ESR Studies of the Heterofullerene Dimers

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The recent condensed phase synthesis of the heterofullerenes $C_{59}HN$,¹ $(C_{59}N)_2$,² and $(C_{69}N)_2$ ³ gave rise to a new class of fullerenes with different electronic and geometric properties, compared to the parent molecules (C_{60} and C_{70} , respectively). Interest in these molecules arises from the fact that substitution of a carbon with a trivalent nitrogen is analogous to doping of semiconductors with an impurity. The addition of an impurity to such a small system (compared to a typical semiconductor) is a strong perturbation and might give rise to the formation of states deep within the gap. Thus, a route for variation of the electronic properties of fullerenes is made possible. Since the symmetry of the parent fullerene is lost in the heterofullerene, one can expect that the optical properties will be altered as well. Theoretical calculations of $C_{59}N$ have shown that lowering of the symmetry splits the triply degenerate t_{1u} state into one singlet and a 2-fold degenerate level, with the singlet being half occupied (and therefore paramagnetic).^{4,5} Therefore, the optical transitions will differ from those of C_{60} .

Calculations of the intermolecular bond strength between the two molecular fragments in $(C_{59}N)_2$ have shown that the binding energy is only ~ 18 kcal/mol.⁶ This bond might be expected to break easily upon UV or visible light irradiation to produce the radicals C_xN^{\bullet} ($x = 59$ or 69), isoelectronic with the radical anions $C_{60}^{\bullet-}$ and $C_{70}^{\bullet-}$. Therefore, information about the local structure of the binding sites in these dimers can be obtained from light-induced electron–electron spin resonance (LESR).⁷

Unlike in C_{60} , in C_{70} there are five distinguishable carbon atoms,⁸ and thus five different $C_{69}N^{\bullet}$ isomers can coexist. Simultaneous formation of all five radicals could lead to 15 distinct $C_{69}N$ dimers! We have recently demonstrated that the mechanism of azafullerene formation, i.e., $(C_{59}N)_2$, can be applied to higher fullerene analogs.³ In particular, the generation and decomposition of a specific [70]N-MEM-ketolactam isomer lead *selectively* to the formation of a specific $(C_{69}N)_2$ isomer.⁹ Here, we study two isomers, namely, $(C_{69}N)_2^A$ and $(C_{69}N)_2^B$.

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(9) Acid treatment of [70]N-MEM-ketolactam **1** in refluxing *o*-dichlorobenzene leads to $(C_{69}N)_2^A$. Under the same conditions, [70]N-MEM-ketolactam **2** gives rise to $(C_{69}N)_2^B$.^{3,10}

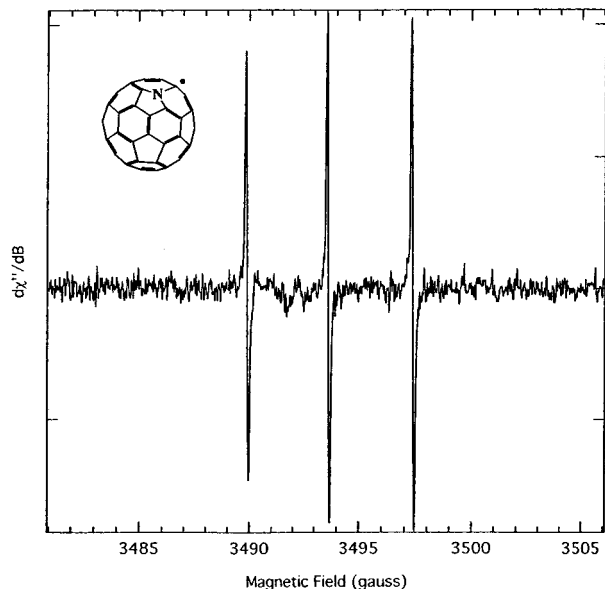
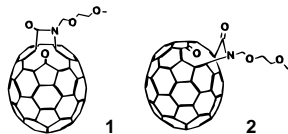


Figure 1. LESR spectra of photoexcited $(C_{59}N)_2$. Spectra were taken at room temperature at a microwave power of 0.5 mW.

These differ in the position of the nitrogen atom: on the pole in *A* and one bond toward the equator in *B* (see Figures 2a and b, respectively).

Azafullerene samples¹⁰ in 1-chloronaphthalene were degassed by several freeze–pump–thaw cycles on a vacuum line and sealed under vacuum. Samples were illuminated with a Xe lamp through a 50% transmission grid in the cavity.

The LESR spectrum of $(C_{59}N)_2$, shown in Figure 1, exhibits clear evidence of radical formation. The three sharp (70 mG) lines are typical of a single ^{14}N hyperfine splitting (hfs) with a hyperfine coupling constant (hfc) of 3.73 G. Such spectra can be detected only in the fluid phase of the solvent, indicating a motionally narrowed signal. Attempts to detect the radical in the powder or film of the dimer failed, probably because of spectral broadening or the inhibition of motion, making the reverse reaction too favorable. The integrated intensity of the lines increases linearly with increase in the lamp power, as expected for a monomolecular process. The signal disappears immediately upon blocking of the light and can be observed

(10) Chromatographically pure materials, $(C_{59}N)_2$, $(C_{69}N)_2^A$, and $(C_{69}N)_2^B$ (>96% purity), were obtained by HPLC (semipreparative Cosmosil Buckyprep Column, UV/326 nm, toluene, 5mL/min, retention times 14.1, 34.5, and 41.0 min, respectively). Selected Spectroscopic Data: (1) 1H NMR ($CDCl_3$, 500 MHz) 5.70 (2H, AB, $d_A = 5.85$, $d_B = 5.55$, $J_{AB} = 11$ Hz), 4.15 (m, 1H), 4.08 (m, 1H), 3.75 (m, 2H), 3.51 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz) 194.2, 163.4, 155.2, 153.3, 151.7, 151.5, 151.1, 151.0, 150.8, 150.7, 150.3, 149.9, 149.4, 149.2, 149.0, 148.9, 148.8, 148.4, 148.3, 148.31, 147.8, 147.8, 147.4, 147.1, 147.0, 146.96, 146.7, 146.7, 146.66, 146.6, 145.7, 145.6, 145.6, 145.3, 145.2, 144.4, 144.2, 144.1, 143.7, 143.7, 143.5, 142.4, 140.2, 139.1, 137.3, 136.4, 136.3, 136.0, 135.2, 135.1, 134.4, 1134.3, 134.2, 133.1, 132.6, 132.2, 131.3, 131.1, 130.5, 129.4, 79.2, 76.7, 70.2, 59.5 ppm; (2) FAB-MS (chloroform/NBA) m/z 976 (M)⁺, 842 ($C_{69}N$)⁺; 1H NMR ($CDCl_3$, 400 MHz) 5.57 (2H, AB, $d_A = 5.72$, $d_B = 5.42$, $J_{AB} = 11$ Hz), 3.81 (m, 2H), 3.50 (m, 2H), 3.28 (s, 3H) ppm; ^{13}C NMR (D_2O/CS_2 , 125 MHz) 161.2, 154.4, 153.5, 152.5, 151.8, 151.6, 151.5, 151.2, 150.8, 150.4, 150.2, 150.1, 149.7, 149.6, 149.5, 149.4, 149.3, 148.9, 148.7, 148.4, 148.3, 148.0, 147.9, 147.4, 147.0, 146.5, 145.7, 145.6, 145.5, 144.2, 144.8, 144.7, 144.6, 144.4, 144.35, 144.35, 144.3, 143.7, 143.4, 141.9, 140.5, 139.4, 138.5, 135.7, 135.3, 133.6, 132.6, 132.5, 132.3, 131.9, 131.4, 131.2, 131.1, 129.0, 126.6, 123.5, 122.9, 78.4, 71.8, 70.0, 58.7 ppm; (($C_{69}N$)₂)⁺ FAB-MS (chloroform/NBA) m/z 976 (M)⁺, 842 ($C_{69}N$)⁺; ^{13}C NMR (ODCB-*d*₄, 125 MHz) 156.7, 153.1, 151.8, 151.7, 151.5, 151.1, 150.6, 150.4, 149.8, 149.7, 149.2, 148.6, 148.5, 147.9, 147.0, 146.6, 146.5, 145.8, 144.3, 143.0, 142.1, 141.1, 140.7, 139.6, 139.3, 138.5, 135.1, 134.8 ppm; (($C_{69}N$)₂)^B FAB-MS (toluene/NBA) m/z 842 ($C_{69}N$)⁺; ESI (toluene) m/z 1684, 842; ^{13}C NMR (ODCB-*d*₄, 125 MHz) 157.7, 157.1, 151.7, 151.6, 151.5, 151.45, 151.4, 150.7, 150.4, 150.3, 149.4, 149.35, 148.8, 148.7, 148.6, 147.8, 147.4, 147.1, 147.05, 146.5, 146.2, 146.0, 144.1, 144.05, 142.6, 142.1, 141.5, 137.4, 136.8, 133.3 ppm; FAB-MS (toluene/NBA) m/z 842 ($C_{69}N$)⁺; ESI (toluene) m/z 1686, 842.

repeatedly without loss of intensity, indicating that there is no photochemical change. Indeed, following illumination, the sample purity (checked by HPLC) was found to be identical to the starting material. The g -value of the radical, measured with a crystal of DPPH as reference, was found to be 2.0013(2). This value is higher than that reported for the C_{60} radical anion, 1.9991.¹¹ The unusually low g -value of $C_{60}^{\bullet-}$ was explained in terms of a Jahn–Teller distortion that splits the triply degenerate t_{1u} states, thus leading to quenching of angular momentum.¹² The positive g -shift in the heterofullerene radical can originate from two sources. First, the lower symmetry of $C_{59}N^{\bullet}$ relative to that of $C_{60}^{\bullet-}$ removes the distortion; second, the nitrogen heavy atom effect increases spin–orbit coupling in the heterofullerene. A positive shift in g -value was also observed for photochemically generated allyl radicals R_nC_{60} and was explained in terms of an oxygen heavy atom effect.¹³ Attempts to detect the same radicals by photolysis of the heterofullerene monomer, $C_{59}HN$, failed, even though the hydrogen is expected to be only weakly bound to the fullerene. This result is surprising since the absorption spectra of both dimer and monomer are almost identical,¹ indicating a similar electronic structure. We can assume, thus, that the interfullerene C–C bond cleavage in the dimer is a complex process, involving at least two steps. A plausible model could be one where the excitation is localized first on the heterofullerene spheres, followed by funneling to the dimer bond via energy transfer or vibronic coupling mechanisms. For photoexcited $C_{59}HN$, the bond to H does not rupture with equal ease because (1) the resulting H^{\bullet} is much less stable than $C_{59}N^{\bullet}$ and (2) the excitation remains delocalized all over the molecule, which relaxes back to the ground state without bond rupture. Thus, the potential energy surface for photolysis of these molecules is expected to be different especially in the vicinity of the interball C–C bond in one case and the C–H bond in the other.

Photolysis of $(C_{69}N)_2$ is expected to give similar results, based on the analogy between the two dimers. Indeed, as shown in Figure 2a, the LESR spectrum of isomer A also exhibits a ^{14}N hfs, ($C_{69}N^A$) that has a more positive g -value [2.0024(2)] and larger hfc (4.74 G), compared to those of $C_{59}N$. This indicates that the unpaired electron and nitrogen wave functions overlap to a greater extent in this radical and, thus, the electron is more localized in the vicinity of the nitrogen. The identical line width in both cases, ~ 70 mG, indicates a similar relaxation mechanism. The spectrum of $C_{69}N^B$ is more complicated as it exhibits two ^{14}N hfs (Figure 2b). The first is identical to that of $C_{69}N^A$ in both the g -value and hfc [2.0025(2), 4.78 G]. The second signal can be attributed to a different radical, based on its low g -value of 1.9973(2). Its hfc (0.49 G) is an order of magnitude smaller than the high g -signal, indicating that spin density on the nitrogen is small. Since C_{70} has five different symmetry sites,⁸ a possible origin for this signal is a $C_{69}N^{\bullet}$ radical where there is a higher unpaired electron density probability at the equatorial site (site d or e in ref 8). This can explain the small hfc arising from a larger separation between the carbon and nitrogen atoms, leading to small overlap between their wavefunctions. Since intermolecular bonding in these dimers is due to the reactivity of the carbon adjacent to the nitrogen, it is

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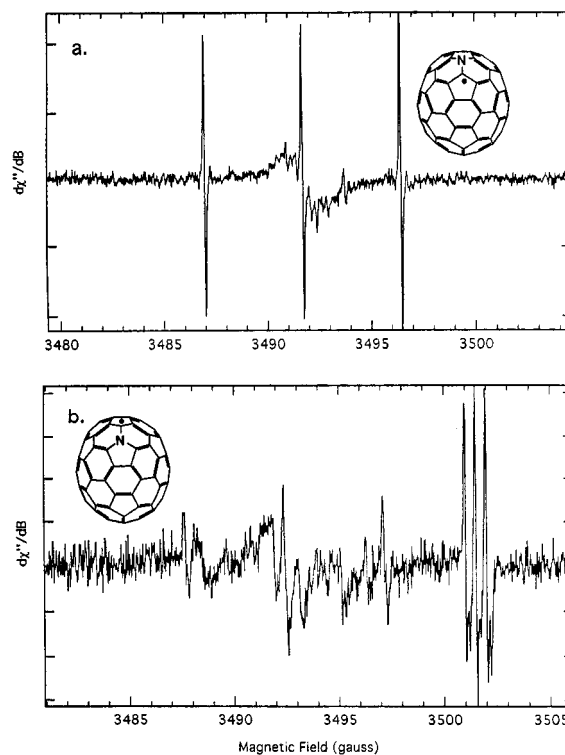


Figure 2. LESR spectra of photoexcited (a) $(C_{69}N)_2^A$ and (b) $(C_{69}N)_2^B$. Experimental conditions are as in Figure 1.

unlikely that, in this case, the detected radical is the photolysis product of a dimer where the bonding is between equatorial carbons while the nitrogen is in the pole of the molecule. A more reasonable explanation is that the radical of isomer B has two different electron localization sites, where in one of them the unpaired electron is forced to be on the equatorial site because of structural strain in the molecule. The occurrence of two different electron localization sites in radical B and only one site in radical A, might be attributable to difference in strain energy in different regions of the parent C_{70} molecule. Structure calculations on C_{70} have shown that the most strained regions in the molecule are the poles. Substitution of the carbon in radical A with a nitrogen should stabilize the molecule since a longer C–N bond replaces the shorter C=C bond. On the other hand, a similar substitution in radical B has a smaller stabilization effect since that site is less strained to begin with. Thus, we can assume that radical B is less stable than radical A and is more prone to undergo structural deformation. One such deformation could be the shifting of the unpaired electron to the equatorial site, giving rise to the low g -value signal in Figure 2b. The identical g -value and hfc of $C_{69}N^A$ and the low-field signal in $C_{69}N^B$ indicate that, in this case, the unpaired electron is highly localized on the C α to N and is not as sensitive to geometry.

In conclusion, we have shown that photolysis of the heterofullerene dimers leads to formation of the azafullerene radicals. Using LEPR, direct information on the nature of these radicals can be obtained.

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Supporting Information Available: Spectral data (8 pages). See any current masthead page for ordering and Internet access instructions.

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