ESR Signal in Azafullerene (C$_{59}$N)$_2$ Induced by Thermal Homolysis

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Thermal homolysis of biazafullerenyl, (C$_{59}$N)$_2$, has been studied by CW ESR in the temperature range 290–829 K. The room-temperature ESR spectrum consists of a single sharp narrow line whose intensity is consistent with the presence of a low concentration of defect spins (1 spin per 600 C$_{59}$N units). Around 500 K, three sharp lines emerge on top of the impurity signal and are assigned to the $^{14}$N($I = 1$) hyperfine spectrum with a hyperfine coupling constant, $a_{iso} = 3.60(1)$ G and a g-factor of 2.0004(2). The intensity of the observed $^{14}$N hyperfine spectrum directly measures the fraction of the C$_{59}$N$^+$ radicals formed as the temperature increases, growing from $\sim$50 ppm at 516 K to $\sim$300 ppm at 740 K. The temperature evolution of this fraction allows us to extract an estimate of the binding energy as 7(1) kcal/mol. The high temperature treatment of the sample eventually results in the partial decomposition and formation of C$_{60}$.

Substitution of one of the carbon atoms of the fullerene skeleton by nitrogen$^1$ leads to the formation of the azafullerenyl radical, C$_{59}$N$^+$, which is isoelectronic with the C$_{60}$ radical anion. The additional electron introduced by nitrogen, as a result of its trivalency, provides a simple way for intrinsic on-ball doping of C$_{60}$ without substantial perturbation of its electronic and geometric character.$^2$ However, C$_{59}$N$^+$ is a very reactive radical, which is readily found either to dimerize$^1$ to yield biazafullerenyl, (C$_{59}$N)$_2$, or to form hydroazafullerene, C$_{59}$HN, in the presence of reducing agents.$^3$ Solid (C$_{59}$N)$_2$ comprises dimeric molecular units,$^4$ linked by C–C bonds formed by C atoms neighboring the N atom on each monomer and a binding energy of 18 kcal/mol (Figure 1).$^5$ It is a diamagnetic, ESR silent, insulating solid with a band gap$^6,7$ of 1.4 eV (ca. 0.4 eV smaller than that of C$_{60}$). Its susceptibility shows a temperature-dependent diamagnetic term, $\chi_0$, of the order of $\sim$7(8) $\times$ 10$^{-4}$ emu/mol.$^8$ A low concentration of defects (1 spin per 250–300 molecules)$^8$ present in solid (C$_{59}$N)$_2$ is responsible for the observation of an ESR signal whose intensity is strongly dependent on the heat treatment of the sample.

Breaking of the C–C bond between the two C$_{59}$N units in biazafullerenyl can be achieved by UV or visible light irradiation to produce C$_{59}$N$^+$ radicals, which are detectable by the ESR technique. The CW$^9$ or pulsed$^{10}$ ESR signal of light irradiated (C$_{59}$N)$_2$ in solution consists of three equidistant sharp lines of equal intensity, implying a single $^{14}$N hyperfine splitting with a hyperfine coupling constant, $a_{iso} = 3.73$ G. Its g-factor (2.0013(2) (ref 9) and 2.0011(1) (ref 10)) has a slightly larger value that that reported for the C$_{60}^-$ radical anion, $g = 1.9991$.$^11$ This has been explained in terms of symmetry lowering following the heteroatom substitution in the cage.$^9$ Attempts to observe the radical in the powder or film of the dimer failed,$^9$ possibly because of spectral broadening. In the present study, we have explored the thermal stability of the (C$_{59}$N)$_2$ solid by using the ESR technique. Temperature-dependent Raman work$^{12}$ had shown that biazafullerenyl is stable to laser irradiation to temperatures as high as 500 K. In the present study, the stability of the dimer is followed up to 829 K. Thermal excitation at high temperatures does lead to the breaking of the C–C bond in a small fraction (ca. 1 in 2 $\times$ 10$^5$ at 500 K) of (C$_{59}$N)$_2$ dimer units, with the resulting C$_{59}$N$^+$ radicals easily detectable by ESR.

The fraction of biazafullerenyl units undergoing thermal homolysis increases with increasing temperature, following a Boltzman distribution. The lower limit of the binding energy of (C$_{59}$N)$_2$ is found to be 7(1) kcal/mol, in reasonable agreement with the value predicted by theoretical calculations.$^3$ However, chemical analysis of the resulting material after the high-temperature treatment also reveals that a large fraction of (C$_{59}$N)$_2$ transforms to C$_{60}$.

The ESR spectrum of the (C$_{59}$N)$_2$ powder$^{13}$ at room-temperature comprises of a narrow line with a peak-to-peak width of 1.9 G. Its intensity is $\sim$2 $\times$ 10$^{-6}$ emu/mol, corresponding to approximately 1 spin per 600 C$_{59}$N units, a value considerably smaller than the values found for earlier samples. This small value is consistent with the origin of the ESR signal from impurities or defects present in the sample. On heating, three new lines appear at approximately 500 K, superimposed on the main defect line. As the temperature increases, they become even more pronounced, as it is apparent in Figure 2a which displays the ESR spectrum of (C$_{59}$N)$_2$ at 636 K. The measured spectra were fitted using three Lorentzian lines together with the defect line present at all temperatures. The amplitude and width of the Lorentzian lines were constrained.

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Figure 1. The structure of the (C$_{59}$N)$_2$ molecule.
temperatures, the intensity of the observed triplet line (approximately every 2
further heating, the intensity of the 14N hyperfine triplet lines
radicals by thermal homolysis in the vicinity of 500 K. On
to be equal, while their centers were separated by the 14N
isotropic hyperfine constant extracted from these data is
3.60(1) G, in excellent agreement with the values reported
earlier for the C59N radical, following light-induced homolysis
of (C59N)2 in solution (3.73 and 3.7 G).9,10 The assignment
of the new lines to the 14N hyperfine spectrum is further supported
by the value of the g-factor of the central line, g = 2.0004(2),
which is again in good agreement with the previous ESR
results.9,10 Consistent with the powder nature of the present
sample, the line width of the observed triplet is ~0.5 G,
significantly broader than the value of 60 mG found in solution.

Even though it is clearly apparent that the C–C bond in
(C59N)2 can be broken, following thermal treatment to high
temperatures, the intensity of the observed triplet line (\(\chi_s \approx 2 \times 10^{-8} \ \text{emu/mol at 540 K}\)) is still very small, representing
only ~0.5% of the total ESR signal. In other words, only 1 in
approximately every 2 \(\times 10^8\) (C59N)2 dimers breaks into C59N\(^*\)
radicals by thermal homolysis in the vicinity of 500 K. On
further heating, the intensity of the 14N hyperfine triplet lines
increases by a factor of 4 from 540–740 K. This means that,
in the same temperature interval, the number of C59N free
radicals increases by a factor of 6, because of the Curie
dependence of the radical signal (Figure 3). Thus at 740 K, 1
in every ~6000 dimers has cleaved into monomer fragments.
Assuming thermal equilibrium at each temperature, we can use
the Boltzmann distribution function, \(p \propto \exp(-E_{\text{bind}}/k_B T)\)
to estimate the binding energy of (C59N)2 dimers as \(E_{\text{bind}} = 7(1)\)
kcal/mol, in reasonable agreement with the results of the
theoretical calculations (18 kcal/mol).3 In the same temperature
interval, the line width of the triplet increases from 0.5–1.45
G possibly as a result of dipolar contributions. Above 740 K,
further broadening prevents the reliable observation of the triplet
structure.

On cooling from 829 K to room temperature, the triplet
structure redevelops but it retains the significant line width
which is frozen in by the high-temperature treatment and
implying a possible degradation of the sample. At the same time,
the total intensity of the ESR signal remains higher (by a factor
of 4) than that observed on heating, implying a substantial
increase of the defect concentration, following the high-
temperature treatment of the sample. The sample was thus
checked after the end of the experiment by X-ray diffraction,
mass spectrometry, and HPLC measurements. The X-ray
diffraction profile showed a large increase in the presence of
an amorphous background, while both the mass spectrum and
the HPLC chromatogram (Cosmosil column, \(\lambda = 235\) nm,
toluene as eluent) showed the presence of large amounts of C60
(approaching almost 50% of the sample mass). A substantial
increase in the total susceptibility had been already observed
on heating above 740 K, suggesting that it is in vicinity of these
temperatures that decomposition of (C59N)2 begins to occur.
This result implies that the molar susceptibility and thus the number
of C59N monomers are underestimated at high temperatures.
We thus believe that the value of the experimentally determined
binding energy 7(1) kcal/mol represents a lower limit of its value.

Calculations2 have shown that impurity doping of solid C60
by C59N monomers would induce deep donor states, lying 0.27
eV below the \(E_{1u}\) LUMO level. Similar doping of the insulating
(C59N)2 solid by C59N monomers could thus lead to the injection
of electrons in the band formed by the LUMO levels of the
(C59N)2 dimer. The level of donor doping at 800 K (ca. 300
ppm) determined from our experiment is similar to the values
commonly encountered in semiconductors. However, at this low
electron density level, strong correlation effects are expected
to lead to the retention of the insulating character of the (C59N)2
solid.

In conclusion, we have shown that thermal homolysis is
indeed a possible channel for cleaving the C–C bond in the
(C59N)2. The observed 14N hyperfine triplet structure is identified
as the ESR signal of the C59N\(^*\) radical by its close resemblance
to the ESR signal of the C59N\(^*\) radicals produced in solution by
light irradiation. The binding energy has been estimated from
the temperature evolution of the fraction of C59N\(^*\) radicals
present to be ~7(1) kcal/mol, in reasonable agreement with
theoretical predictions. Decomposition of biazafullerenyl occurs
at high temperatures (above 740 K) principally leading to the
production of C60.

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References and Notes
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The powder (C$_{59}$N)$_2$ sample was prepared by dissolving a cluster opened MEM-substituted ketolactam of C$_{60}$ (MEM = methoxyethoxy-methyl) in 1,2-dichlorobenzene (ODCB). The solution was then degassed with Ar for 60 min and then treated with a large excess of $p$-toluenesulfonic acid for 20 min at 220 °C. After cooling to room temperature, the obtained solution was passed through a silica gel column with toluene as eluent. The solvent was evaporated and the black precipitate was then recrystallised from a CS$_2$/diethyleter 2/1 solution. The recrystallisation procedure was repeated four times. The resulting material was then dried under the vacuum and finally degassed at 140 °C (dynamic vacuum was about $10^{-4}$ Pa) for 30 h. The purity of the sample was checked by HPLC, which showed the presence of small amounts of C$_{60}$. Phase purity of the powder was established by X-ray diffraction measurements on a Siemens D5000 diffractometer. ESR experiments were performed on a Bruker ESP 300E spectrometer in X-band ($\approx$9.5 GHz). Typically, a microwave power of 100 $\mu$W and a modulation field of 0.1 G were used. A commercial Bruker high temperature cavity (ER 4114 HT) was used in the temperature range between 300 and 829 K. For calibration of the susceptibility, freshly prepared CuSO$_4$·5H$_2$O single crystals were used.