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

Ferenc Simon,[†] **Denis Arčon,**[‡] **Nikos Tagmatarchis,**[#] **Slaven Garaj,**[†] **Laszlo Forro,***[,†] **and Kosmas Prassides***[,‡]

Ecole Polytechnique Federale de Lausanne, CH-1051 Lausanne, Switzerland, and School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.

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$^{\bullet}$ radicals formed as the temperature increases, growing from ∼50 ppm at 516 K to ∼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$^{\bullet}$, which is isoelectronic with the C$_{60}^{-\bullet}$ 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$^{\bullet}$ 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-independent diamagnetic term, χ_0, of the order of $-(7-8) \times 10^{-4}$ 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$^{\bullet}$ 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$_{60}^{\bullet-}$ 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
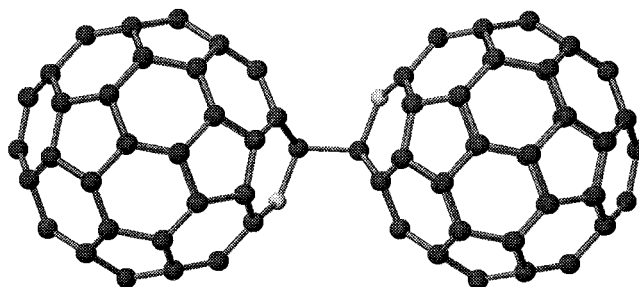

Figure 1. The structure of the (C$_{59}$N)$_2$ molecule.

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 × 10^4 at 500 K) of (C$_{59}$N)$_2$ dimer units, with the resulting C$_{59}$N$^{\bullet}$ 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.[5] 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 ∼2 × 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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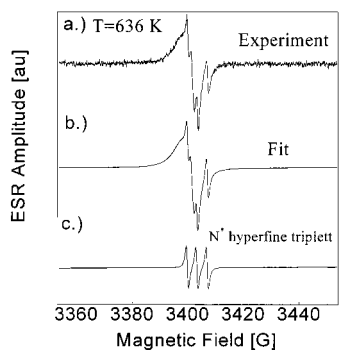† Ecole Polytechnique Federale de Lausanne.
‡ University of Sussex.

Figure 2. (a) X-band ESR spectrum of solid $(C_{59}N)_2$ measured at $T = 636$ K. The positions of the ^{14}N hyperfine lines, emerging at high temperature, are marked with asterisks. (b) Fit of the ESR spectrum with parameters explained in text. (c) The extracted ^{14}N hyperfine triplet lines.
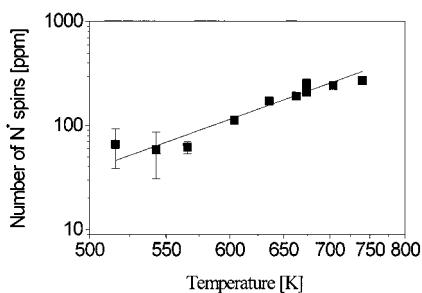

Figure 3. Temperature dependence of the calculated number of $C_{59}N^{\bullet}$ spins per $C_{59}N$ unit. The solid line is the fit to the Boltzman distribution function, leading to a value of the binding energy of $(C_{59}N)_2$, $E_{bind} = 7(1)$ kcal/mol.

to be equal, while their centers were separated by the ^{14}N hyperfine coupling constant a_{iso}. As seen in Figure 2b, this model reproduces well the experimentally observed spectrum with the deconvoluted ^{14}N hyperfine spectrum, shown in Figure 2c.

The isotropic hyperfine constant extracted from these data is $a_{iso} = 3.60(1)$ G, in excellent agreement with the values reported earlier for the $C_{59}N^{\bullet}$ radical, following light-induced homolysis of $(C_{59}N)_2$ in solution (3.73 and 3.7 G).[9,10] The assignment of the new lines to the ^{14}N 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 $(C_{59}N)_2$ can be broken, following thermal treatment to high temperatures, the intensity of the observed triplet line ($\chi_s \sim 2 \times 10^{-8}$ 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 2×10^4 $(C_{59}N)_2$ dimers breaks into $C_{59}N^{\bullet}$ radicals by thermal homolysis in the vicinity of 500 K. On further heating, the intensity of the ^{14}N hyperfine triplet lines increases by a factor of 4 from 540−740 K. This means that, in the same temperature interval, the number of $C_{59}N^{\bullet}$ 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 Boltzman distribution function, $p \propto \exp(-E_{bind}/k_B T)$ to estimate the binding energy of $(C_{59}N)_2$ dimers as $E_{bind} = 7(1)$ kcal/mol, in reasonable agreement with the results of theoretical calculations (18 kcal.mol).[5] 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 C_{60} (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 $(C_{59}N)_2$ begins to occur. This result implies that the molar susceptibility and thus the number of $C_{59}N$ 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.

Calculations[2] have shown that impurity doping of solid C_{60} by $C_{59}N$ monomers would induce deep donor states, lying 0.27 eV below the t_{1u} LUMO level. Similar doping of the insulating $(C_{59}N)_2$ solid by $C_{59}N$ monomers could thus lead to the injection of electrons in the band formed by the LUMO levels of the $(C_{59}N)_2$ 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 $(C_{59}N)_2$ solid.

In conclusion, we have shown that thermal homolysis is indeed a possible channel for cleaving the C−C bond in the $(C_{59}N)_2$. The observed ^{14}N hyperfine triplet structure is identified as the ESR signal of $C_{59}N^{\bullet}$ free radicals by its close resemblance to the ESR signal of the $C_{59}N^{\bullet}$ radicals produced in solution by light irradiation. The binding energy has been estimated from the temperature evolution of the fraction of $C_{59}N^{\bullet}$ 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 C_{60}.

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(13) The powder $(C_{59}N)_2$ sample was prepared by dissolving a cluster opened MEM-substituted ketolactam of C_{60} (MEM = methoxyethoxymethyl) in 1,2-diclorobenzene (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 (~9.5 GHz). Typically, a microwave power of 100 μW 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 $CuSO_4$• $5H_2O$ single crystals were used.