

## Photolysis of $(C_{59}N)_2$ Studied by Time-Resolved EPR

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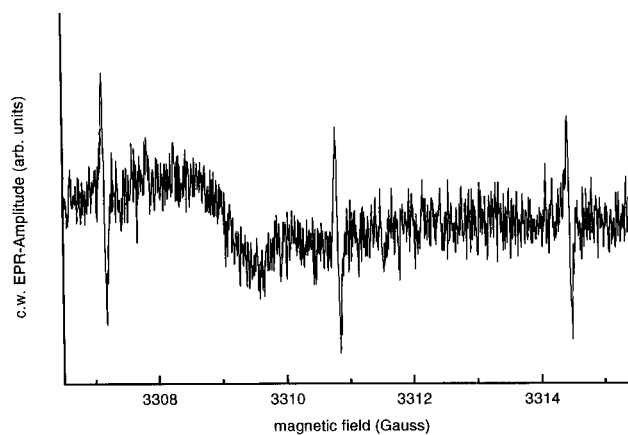
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The incorporation of heteroatoms into the fullerene cage is expected to modify the electronic properties of the molecule and in particular to lead to localization of charge and spin densities. Attempts to synthesize  $C_{59}N^*$  in bulk quantities led to the formation of its dimeric form.<sup>1–2</sup> According to Bellavia-Lund et al.,<sup>3</sup> the dimer undergoes thermo- or photoinduced homolysis, yielding  $C_{59}N^*$  radicals. This reaction scheme was postulated from observed derivatives, although the radicals evaded direct detection by continuous-wave (cw) EPR, probably because of their short lifetime.

Time-resolved EPR techniques such as Fourier-transform EPR (FT-EPR)<sup>4</sup> or transient nutation-detected EPR (TN-EPR),<sup>5</sup> however, are ideally suited for the detection of radicals on the microsecond time scale, and furthermore, these techniques are capable to monitor radicals in a non-Boltzmann state, as is frequently found after photolysis. From the analysis of the time dependence of the EPR signal intensity of resolved hyperfine components in a spectrum, information about the spin multiplicity of the educt can be obtained. In the case of the azafullerene dimer, such an analysis was expected to answer the question if intersystem crossing into a metastable triplet state of the dimer precedes fission of the weak (18 kcal/mol) C–C bond.

Samples of  $(C_{59}N)_2$  were prepared by the method described in ref 2. A saturated solution of the dimer in 1-chloronaphthalene (Aldrich) was prepared on a high vacuum line after thoroughly degassing the solvent. For all experiments, samples sealed in 4 mm (o.d.) quartz tubes were used.

In Figure 1, the cw EPR spectrum is shown which is obtained by repetitively exciting the sample with 532 nm laser pulses (10 mJ/pulse, 10 Hz). The EPR spectrum with three equidistant lines of equal intensity is indicative for  $^{14}N$  hyperfine interaction (hfi). The observed isotropic coupling constant of 10.4 MHz is similar to the value reported by Wudl et al.<sup>6</sup> for  $C_{69}N^*$ , and we therefore assigned it to the  $C_{59}N^*$  radical. Its  $g$  factor was determined by direct comparison with that of  $^3C_{60}$



**Figure 1.** Cw EPR spectrum of  $C_{59}N^*$  obtained by pulsed laser irradiation of  $(C_{59}N)_2$  at room temperature. The signal was detected during a scan of 40 min using 1 mW microwave power and a modulation amplitude of 50 mG.

and found as  $g = 2.0011(1)$ . The absence of additional line splittings and the narrow width of only 60 mG (peak-to-peak) can be taken as further evidence that the observed signal does not originate from an addition product. This line width is significantly larger than that determined by FT-EPR (see below) because for recording of the very weak signal high microwave power and conditions of slight overmodulation had to be used. Under conditions of repetitive optical excitation in a slowly scanned cw EPR spectrum, the time average of the time-dependent EPR absorption is detected, and from the apparently unpolarized spectrum, it can be concluded that the lifetime of the radicals must by far exceed their spin–lattice relaxation time. The broad signal at slightly higher  $g$  factor is also detected under “light-off” conditions, and its origin still remains unknown.

In Figure 2, a sequence of spectra is compiled, observed by FT-EPR with different delay times of the microwave pulse to the laser pulse. As can be seen, the spectra are spin-polarized at early delay times, but an absorptive spectrum is observed for delay times larger than 100  $\mu s$ . At early times, the high-frequency hyperfine component (hfc) (corresponding to the “low field” transition in a cw field-swept spectrum) is emissively polarized, whereas the low-frequency line appears in absorption. The center line is weakly absorptive even for short delay times. (Its unexpected intensity variation most probably has to be attributed to the bad signal-to-noise ratio.) The observed polarization scheme, termed E/A\* in the literature,<sup>5</sup> gives clear proof that the precursor state is a spin triplet. First, only with a paramagnetic precursor state, “triplet mechanism”, leading to electron spin polarization independent of nuclear spin states, can lead to a nonvanishing spin polarization of the  $M_I = 0$  hfc at short delay times. Second, an emissively polarized high-frequency hfc is indicative of a triplet precursor. For this argument we only have to assume that the exchange coupling between the two radicals is negative, leading to a singlet ground state. Here, this assumption is certainly justified.

Spin–lattice relaxation establishes thermal equilibrium between the spin sublevels on a time scale of approximately 100  $\mu s$ . The zero crossing of the signal intensity of the high-frequency hfc can be simulated by assuming  $T_1 = 50 \mu s$ . Because of the weak signal intensity even obtained after accumulating  $10^4$  free induction decay (FID), a full kinetic analysis of the data which would also reveal the decay rate of the azafullerenyls could not yet be performed. It is noteworthy, however, that even prolonged irradiation of the sealed sample

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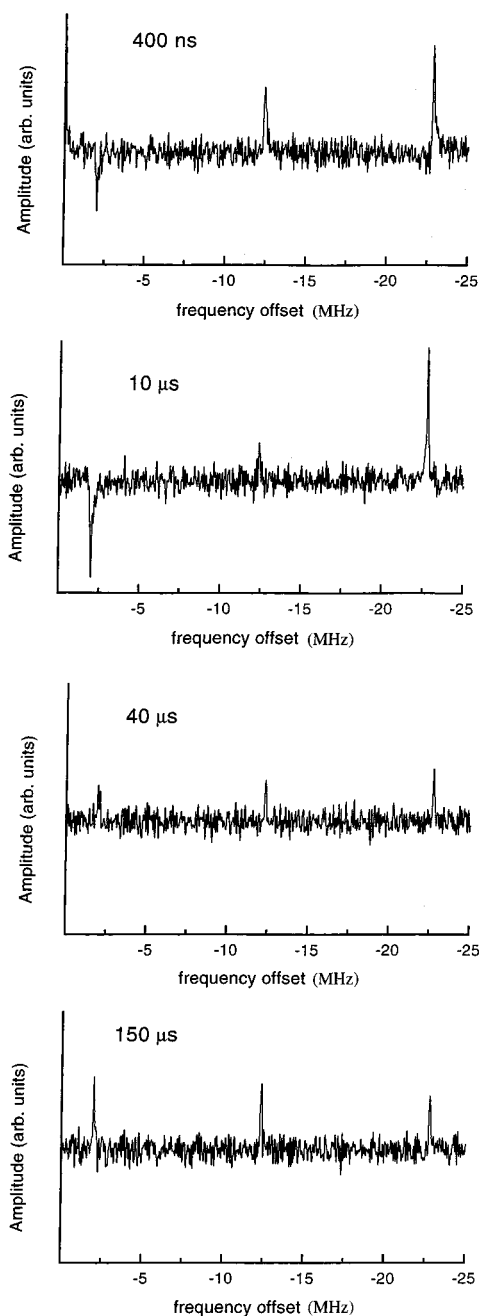
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**Figure 2.** FT-EPR spectra observed with different delay times of the  $\pi/2$  microwave pulse to the laser pulse. The spectrum observed with a delay of  $150 \mu\text{s}$  results from Boltzmann-equilibrated radicals. The slight difference in intensities originates from increasing off-resonance excitation.

of approximately  $200 \mu\text{L}$  by more than  $10^5$  laser pulses did not noticeably decrease the signal intensity, which is clear evidence that the major chemical decay channel of the azafullerenyl radicals must be redimerization.

The width of the lines (taken at half-maximum) as deduced from the FT-EPR spectra amounts to only  $\nu_{1/2} = 110(10)$  kHz (fwhm). Using this value a peak width limit of 25 mG is predicted using cw detection assuming a Lorentzian line shape. As instrument-limited line widths of 50 kHz have been observed in our spectrometer under similar conditions, we assume that we can assign this value to the homogeneous line shape function of the radical and that we can deduce the spin dephasing time via  $T_2 = (\pi\nu_{1/2})^{-1} = 3 \mu\text{s}$ . Both relaxation times  $T_1$  and  $T_2$  are unusually long for a nitrogen-containing radical which would indicate that the anisotropic terms of the nitrogen hyperfine interaction are quite small. Relaxation rates resulting from rotational tumbling might also be reduced by taking into account that the rotational correlation time of fullerenes in solution is close to the “free rotator” value of a few picoseconds.<sup>7</sup>

To rationalize the observed  $^{14}\text{N}$  hfi, a quantum chemical calculation of the spin density distribution in the  $\text{C}_{59}\text{N}^{\bullet}$  radical was performed. First, the geometry was optimized with ROHF utilizing a STO-3G basis set. Subsequently, the isotropic hyperfine splitting constant (hfsc) at nitrogen and carbon positions were calculated with GAUSSIAN94 at the 3-21G/LSDA level. For this geometry, we could reproduce the observed nitrogen hfsc only within a factor of 2 (7.8 G calculated vs 3.7 G observed). In a second approach, the geometry was optimized using a STO-3G/BLYP (unrestricted) routine. The use of a density functional theory (DFT) technique for optimization changed the local geometry at the nitrogen site considerably. A subsequent single-point 3-21G/LSDA spin density calculation resulted in a much improved value of 4.6 G for the nitrogen hfsc. A final judgment about the reliability of the prediction of spin densities by the various DFT approximations will only be possible when also  $^{13}\text{C}$  coupling constants have been determined and assigned. It should be noted, however, that the calculated spin density is always mainly located at the a carbon position as expected by comparing with results obtained for the isoelectronic  $\text{HC}_{60}^{\bullet}$  radical.<sup>8</sup>

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