J. Am. Chem. Soc. **1995,** *117,* 8857–8858

C_{60} Derivative Covalently Linked to a Nitroxide Radical: Time-Resolved EPR Evidence of Electron Spin Polarization by Intramolecular Radical–Triplet Pair Interaction

Carlo Corvaja,[*,†] Michele Maggini,[*,‡] Maurizio Prato,[§]
Gianfranco Scorrano,[‡] and Maria Venzin[†]

Dipartimento di Chimica Fisica, Università di Padova
Via Loredan 2, 35131 Padova, Italy
Centro Meccanismi di Reazioni Organiche del CNR
Dipartimento di Chimica Organica, Università di Padova,
Via Marzolo 1, 35131 Padova, Italy
Dipartimento di Scienze Farmaceutiche
Università di Trieste
Piazzale Europa 1, 34127 Trieste, Italy

Received May 1, 1995

The chemical functionalization of fullerenes has provided a powerful access to a range of interesting new materials. The modified fullerenes, while retaining most of the properties of the pristine species, become more versatile in terms of solubility, photochemistry, and electrochemistry.[1,2]

We have recently reported a general procedure for the preparation of fulleropyrrolidines, fullerene derivatives in which the 3,4-bond of a pyrrolidine ring is fused with a 6,6 ring junction of C_{60}.[3] We describe herein the application of the same methodology to the synthesis of a fulleropyrrolidine in which a 2,2,6,6-tetramethylpiperidine-1-oxyl ring is spiro-linked to the pyrrolidine ring. This compound is unique in that it allows the study of the intramolecular interaction of a radical species with the C_{60} core. A detailed EPR investigation in the dark and under light exposure is reported.

The synthesis of 3,4-fulleropyrrolidine-2-spiro-4′-[2′,2′,6′,6′-tetramethyl]piperidine-1′-oxyl (**1**) (Scheme 1) was carried out by heating to reflux a toluene solution containing C_{60} (1 equiv), paraformaldehyde (4 equiv) and 4-amino-4-carboxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TOAC, 2 equiv).[4] Compound **1** was isolated in 40% yield after chromatography on a silica gel column using mixtures of toluene and ethyl acetate as eluant.[5]

The EPR spectrum of **1**[6] (Figure 1) is typical of a nitroxide radical, but for the unusual feature of having the low-field line ($M = 1$) hyperfine component narrower than the central one. This effect is accounted for by the anisotropy of the rotational diffusion tensor.[7]

The time-resolved EPR spectrum of **1** recorded at 200 K, 1 μs after the laser pulse is shown in Figure 2. It consists of five EPR lines in absorption and can be computer simulated as the superposition of three Lorentzian lines centered at $g = 2.0070$ separated by 15.20 G, and three other lines centered at higher field ($g = 2.0043$) having a separation of 5.05 G.

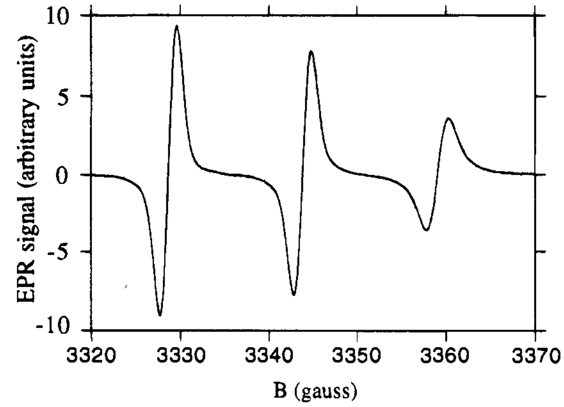


Figure 1. EPR spectrum of **1** in toluene at 210 K.

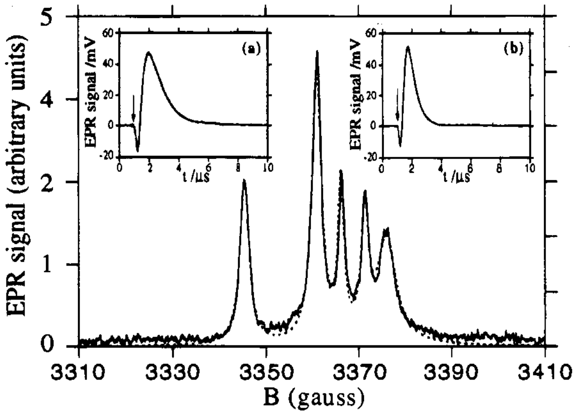
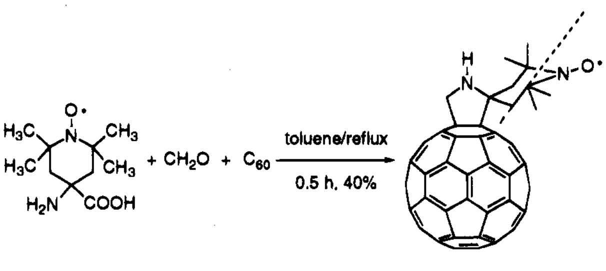


Figure 2. Solid line: transient EPR spectrum of **1** at 200 K recorded 1 μs after the laser pulse excitation. Dotted line: spectrum analysis (see text). Insets show the time evolution of the EPR lines at 3346 G (a) and 3366 G (b), microwave power = 10 mW. The arrows indicate the start of the laser pulse.

Scheme 1



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The first 1:1:1 triplet occurs at the field positions corresponding to the EPR transitions of the nitroxide free radical.

[†] Dipartimento di Chimica Fisica, Università di Padova.

[‡] Dipartimento di Chimica Organica, Università di Padova.

[§] Dipartimento di Scienze Farmaceutiche, Università di Trieste.

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(5) Satisfactory analytical data (MALDI-MS, UV–vis and combustion analysis) were obtained for compound **1**.

(6) Toluene solutions of derivative **1** (1.7×10^{-6} M) contained in 5 mm quartz tubes were carefully deoxygenated by bubbling pure nitrogen for several minutes. The samples were illuminated inside the cavity of a Bruker ER 200D X-band EPR spectrometer by 308 nm, 20 ns light pulses from a Lambda Physik LPX 100 excimer laser. The temperature was controlled by a standard nitrogen flow cryostat. The transient EPR signal was recorded without field modulation with an EG & G boxcar integrator; the gate (0.5 μs duration) was set at different delay times from the laser pulse. The time evolution of the EPR signal was recorded with a Nicolet 4094 digital oscilloscope with a maximum acquisition rate of 200×10^{6} sample/s. For the time-resolved experiments, a cylindrical cavity (TE_{011}) provided with an 8 mm optical access was used. The time resolution of the complete EPR apparatus is of the order of 150 ns.

(7) Calculations, performed according to the theory (Nordio, P. L. *Chem. Phys. Lett.* **1970**, *4*, 250–252) developed to account for the EPR line shape of very elongated molecular structures (Corvaja, C.; Giacometti, G.; Kopple, K. D.; Ziauddin *J. Am. Chem. Soc.* **1970**, *92*, 3919–3924), agree with the observed line width pattern if an axial symmetric rotational diffusion tensor is assumed with the principal axis of fast diffusion along the direction shown in Scheme 1 (dotted line). We used the hyperfine and *g* tensors obtained by single-crystal EPR (Griffith, O. H.; Cornell, D. W.; Mc Connell, H. M. *J. Chem. Phys.* **1965**, *43*, 2909–2910) and ENDOR (Brustolon, M.; Maniero, M.; Corvaja, C. *Mol. Phys.* **1984**, *51*, 1269–1281) measurements on a similar nitroxide. The minimum-energy structure, calculated using the Spartan 3.1 program running on an IBM Risc/6000 250 workstation with the PM3 semiempirical method, was used for **1**. The six-membered-ring conformation is in agreement with X-ray diffraction studies on a series of TOAC derivatives and peptides containing the same nitroxide unit (Toniolo, C., personal communication).

0002-7863/95/1517-8857$09.00/0

Moreover, the line widths follow the same trend as in the spectrum of Figure 1. The low-field line of the second triplet coincides with the central line of the first triplet. The spectrum analysis in terms of six Lorentzian lines is shown in Figure 2 by the dotted line. The relative intensities of the two triplets change with the temperature.

Figure 2 shows also the time evolution of the EPR signals recorded at the field positions corresponding to the maximum intensity of the low-field line of the nitroxide spectrum (inset a) and of the central line of the second species (inset b). The two curves can be fitted by a linear combination of two exponential decay functions with coefficients having opposite signs, convoluted by the exponential response function of the EPR apparatus. The signal, in emission during the early times after generation, changes into enhanced absorption and eventually decays to the Boltzmann equilibrium value. Both species behave in the same way, though with different time constants. The time constants change with the temperature and, as expected, with the microwave power level.[8,9]

Chemical induced dynamic electron polarization (CIDEP) of short-lived free radicals has been explained in terms of radical pair mechanism (RPM) and of triplet mechanism (TM).[10,11] Recently a new mechanism has been proposed which could act on transient as well as on stable radical species.[12] It consists of the interaction of a doublet state species D, as a free radical with an excited triplet species T. The T···D encounters produce triplet quenching and spin polarization of the radical species because the quenching rate depends on the doublet spin component.

The radical triplet polarization mechanism (RTPM) process has been found to occur in solution[13,14] and also in the solid state.[15,16] RT pairs are formed by the encounters either in a quartet or in a doublet state. The two states have energies separated by the electron exchange interaction J. The theory[12] predicts a full emissive transient EPR spectrum of the radical if the pair quartet state has a higher energy than the pair doublet state ($J < 0$) while, if $J > 0$, an enhanced absorption is expected.

C_{60} triplet quenching by stable nitroxide radicals was observed by flash photolysis and attributed to a charge-transfer mechanism.[17] However, CIDEP effects observed by laser-flash irradiation of toluene solutions of C_{60} containing the free radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) were consistent with the RTPM.[18]

Our observations of the spin polarization of the nitroxide spectrum can be explained within the frame of the RTPM if, in the excited state of **1**, one electron localized on a π MO in the fullerene moiety is promoted to an antibonding π^* MO also localized on the fullerene. In this case the excited state of **1** can be described as a "localized" singlet or triplet excitation interacting with the nitroxide doublet state.

The time evolution of the nitroxide transient signal is accounted for by a two-step polarization process. In a first phase, compound **1** absorbs a light quantum and eventually passes to the first excited doublet state D_1 (corresponding to excited singlet fullerene S_1 and doublet nitroxide). From this state, either the molecule decays to the ground state by fluorescence and nonradiative processes or it undergoes an intersystem crossing (ISC) into the first excited quartet state Q_1 (corresponding to fullerene triplet plus nitroxide doublet). D_1 to Q_1 ISC occurs because these states are mixed by the electron–electron dipolar interaction. If $J > 0$, the largest mixing occurs for the D_1 spin component $-1/2$ which is therefore depleted faster than the $1/2$ component. Therefore, the ISC process produces spin polarization and causes the nitroxide EPR transition to occur initially in emission as observed.

The second step consists of Q_1 deactivation to the doublet ground state, which is also expected to be spin selective and to follow the same preferred route to the $-1/2$ ground state sublevel, producing enhanced absorption. Our work on derivative **1** provides the first example of intramolecular RT interaction producing spin polarization.

The three-line spectrum with 5.05 G splitting is to be attributed to **1** in the excited quartet state. In a quartet state three $\Delta m_s = 1$ EPR transitions are expected. However, we observe only one of them ($-1/2 \leftrightarrow 1/2$) since in a liquid solution the other two are expected to be broadened by the modulation of the electron dipolar interaction caused by the rotational diffusion. The field position of the $-1/2 \leftrightarrow 1/2$ transition does not depend on the molecule orientation[19] and therefore remains sharp. The separation into three lines is accounted for by hyperfine interaction with the nitrogen nucleus. The quartet state hypothesis explains the value of the hyperfine separation. In fact, for a system containing three unpaired electrons and a single coupled ^{14}N nucleus, if the exchange integral J is larger than the hyperfine coupling a_N, the line separation is only $a_N/3$, since each unpaired electron spends only one-third of its time on the nitroxide group.[20] Furthermore, we note that also the measured g (2.0043) factor is in agreement with the above model, since it corresponds to the average (2.0041) of the g factors of the $^3C_{60}$ triplet (2.0012)[18,21] and of the nitroxide (2.0070). To the best of our knowledge, EPR of an excited quartet state in solution was not observed before.

A radical species produced by intramolecular electron transfer from the nitroxide group to the fullerene moiety would not explain the hyperfine coupling nor the g factor, because the transfer of one electron to the fullerene would result in a free radical to be considered formally as a fullerene radical anion having as the counterion a positive N=O group. This transient species is expected to have a spin distribution typical for radical anions of fulleropyrrolidines. However, the chemically generated radical anion of unsubstituted *N*-methylfulleropyrrolidine[3] shows a nitrogen splitting of 0.23 G and G = 2.0016.[22]

Acknowledgment. This work was in part developed within the Progetto Strategico Materiali Innovativi of the CNR. Partial support by the Centro Studi sugli Stati Radicalici ed Eccitati of the CNR is gratefully acknowledged.

JA951381X

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