The effects of a pyrrolidine functional group on the magnetic properties of N@C$_{60}$

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Abstract

A new stable pyrrolidine functionalized fullerene derivative, C$_{69}$H$_{10}$N$_2$O$_2$, has been synthesized, purified by high performance liquid chromatography, and characterized by MALDI mass spectrometry, UV–vis spectroscopy, Fourier transform infrared, ^{1}H and ^{13}C nuclear magnetic resonance. The magnetic properties of the analogous endohedral species have been studied by both continuous wave (CW) and pulsed EPR. CW-EPR spectra indicated an anisotropic hyperfine interaction and a permanent zero-field-splitting (ZFS). Both CW and pulsed EPR showed the ZFS parameter D_{eff} to be around 17 MHz. Pulsed EPR revealed a biexponential decay in both T$_1$ and T$_2$, yielding a molecular tumbling correlation time τ_c of 31.4 ± 2.5 ps.

1. Introduction

Fullerenes which encapsulate atomic nitrogen (such as N@C$_{60}$) have been shown to contain an electron spin benefiting from long relaxation times and narrow linewidths in electron paramagnetic resonance (EPR) [1]. Such properties make N@C$_{60}$ an attractive candidate building block for a quantum information processing device [2] and a powerful spin probe for measuring environments such as the interior of nanotubes [3].

Relaxation in unmodified N@C$_{60}$ has been found to be driven by a vibrational Orbach mechanism [4]. If the fullerene is modified by a functional group in such a way as to introduce a zero-field-splitting (ZFS), the fluctuation of this ZFS due to molecular tumbling in liquid solution provides an additional relaxation pathway characterized by the magnitude of the ZFS, and the rotational correlation time of the molecule. Thus, by measuring T$_1$ and T$_2$,

respectively the spin-lattice and phase memory relaxation times, it is possible to probe the molecular dynamics of fullerene derivatives in solution.

The fluctuating ZFS mechanism is expected to produce a biexponential decay in both T$_1$ and T$_2$, assuming the molecule is not in the 'fast-tumbling' limit. Such a biexponential decay was not observed in earlier studies on fullerene derivatives, reportedly due to limited signal to noise and a relatively fast rotational correlation time. The effect of nuclear spins in the solvent may also have complicated the analysis by adding additional relaxation pathways [5]. The observation of a biexponential decay is simplified by choosing a bulky functional group, such as pyrrolidine, to slow down the rotation further.

In this Letter, we describe the synthesis of a new pyrrolidine-functionalized fullerene derivative, C$_{69}$H$_{10}$N$_2$O$_2$, and its analogous endohedral species, N@C$_{69}$H$_{10}$N$_2$O$_2$. The product is purified by high performance liquid chromatography (HPLC), characterized by MALDI mass spectrometry, ultraviolet-visible (UV–vis), Fourier transform infrared (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies. We measure the ZFS and hyperfine

interaction of the electron spin arising from the addition of the functional group to $N@C_{60}$ using continuous wave (CW) EPR. In contrast to previous reports of fullerene derivatives [6,7], including pyrrolidine-functionalized fullerenes, we observe an anisotropy in the ^{14}N hyperfine interaction in this species. Finally, we use pulsed EPR to measure T_1 and T_2 and thereby deduce the ZFS D_{eff} and rotational correlation time τ_c of $N@C_{69}H_{10}N_2O_2$ in carbon disulfide solution at room temperature.

2. Experimental details

$C_{69}H_{10}N_2O_2$: A mixture of C_{60} (MER corporation, 99.5+%) (70.0 mg, 0.1 mmol), 4-nitrobenzaldehyde (98%, Aldrich) (75.5 mg, 0.5 mmol), and *N*-methylglycine (98%, Aldrich) (17.8 mg, 0.2 mmol) in toluene (50 mL) was heated under reflux for 2 h under a nitrogen atmosphere. The resulting reaction mixture was collected, filtered, and purified by HPLC (5PBB, 20×250 mm, toluene eluent, 18 mL/min) to give the pure product in 31% yield. MALDI *m/z*: 898.2 (M^+, $C_{69}H_{10}N_2O_2$ requires 898.1). UV–vis (toluene): λ_{max} nm 314 ($\varepsilon = 3658.9$ m^2 mol^{-1}), 433 ($\varepsilon = 300.66$ m^2 mol^{-1}). FTIR (KBr): 527 cm^{-1} (s, C_{60} cage); 790–859 cm^{-1} (w, out-of-plane aromatic C–H bending); 1343 cm^{-1} (s, nitro group symmetric stretching vibration), 1424 cm^{-1}, 1462 cm^{-1}, and 1600 cm^{-1} (w, aromatic C–C stretching); 1522 cm^{-1} (s, nitro group asymmetric stretching vibration); 2776–2941 cm^{-1} (w, br, aromatic C–H stretching)(s-strong, w-weak, br-broad). ^1H NMR(500 MHz, CS_2:$CDCl_3$ = 3:1): δ(ppm) = 2.83 (s, 3H, H-3), 4.33 (d, J = 9.5 Hz, 1H, H-2), 5.02 (d, J = 9.5 Hz, 1H, H-2), 5.07 (s, 1H, H-1), 7.10 (d, J = 8 Hz, 1H, H-5 or H-9), 7.18 (d, J = 7 Hz, 1H, H-9 or H-5), 8.04 (band, 1H, H-6 or H-8), 8.30 (d, J = 9 Hz, 1H, H-8 or H-6). ^{13}C NMR(125.8 MHz, CS_2:$CDCl_3$ = 3:1): δ(ppm) = 155.65, 153.48, 152.37, 151.85, 148.06, 147.45, 147.42, 146.46, 146.44, 146.36, 146.30 (1C, C-7), 146.27, 146.22, 146.10, 145.79, 145.75, 145.55, 145.53, 145.50, 145.48, 145.47, 145.39, 145.35, 145.33, 144.84, 144.65, 144.55, 144.42, 143.32, 143.20, 142.89, 142.80, 142.78, 142.73, 142.34, 142.31, 142.30, 142.27, 142.18, 142.07, 141.98, 141.90, 141.85, 141.73, 140.45, 140.19, 139.75,

137.26, 136.42, 136.23, 135.68, (50 peaks from sp^2 C_{60} carbon) 130.10 (2C, C-5 and C-9), 128.40 (1C, C-4), 124.02 (2C, C-6 and C-8), 82.75 (1C, C-1), 70.18 (1C, C-2), 69.06 (1C, C-11), 68.05 (1C, C-10), 40.14 (1C, C-3).

$N@C_{69}H_{10}N_2O_2$: Method as for $C_{69}H_{10}N_2O_2$ using $N@C_{60}/C_{60}$ (1/100) as starting material, the reaction was carried out in the absence of light. The nitrogen EPR signal intensity of the product mixture is approximately 73% of the initial signal.

EPR sample preparation: $N@C_{69}H_{10}N_2O_2$/$C_{69}H_{10}N_2O_2$ (around 7/1000) sample was dissolved in CS_2, degassed, and sealed in quartz EPR tubes (3 mm diameter).

CW EPR measurements were performed on a Magnettech Miniscope MS200 using a 2G modulation, 270 s scan time, and 99 scans at room temperature. Spectral simulation was performed using the EASYSPIN software package [8].

Pulsed EPR measurements were performed using an X-band Bruker Elexsys580e spectrometer. Spin lattice relaxation time T_1 and spin dephasing time T_2 were measured by an inversion recovery sequence and Hahn echo sequence, respectively. The $\pi/2$ and π pulse durations were 56 and 112 ns, respectively. Phase cycling was used to eliminate the contribution of unwanted free induction decay (FID) signals.

3. Results and discussion

3.1. Synthesis and characterization

A nitrobenzene functionalized fullerene, $C_{69}H_{10}N_2O_2$, was synthesized according to the pyrrolidine functionalization method [9] (Fig. 1). Briefly, *p*-nitrobenzaldehyde, *N*-methylglycine, and C_{60} were heated under reflux in toluene for 2 h and subsequently purified by HPLC (Fig. 2). $C_{69}H_{10}N_2O_2$ elutes approximately 2 min earlier than C_{60}. Recycling mode HPLC was used to purify the product to greater than 95%.

MALDI mass spectrometry revealed the expected molecular ion peak at *m/z* 898.2 and an isotopic distribution pattern in agreement with that calculated. UV–vis spectrum features at 314 nm and 433 nm are indicative
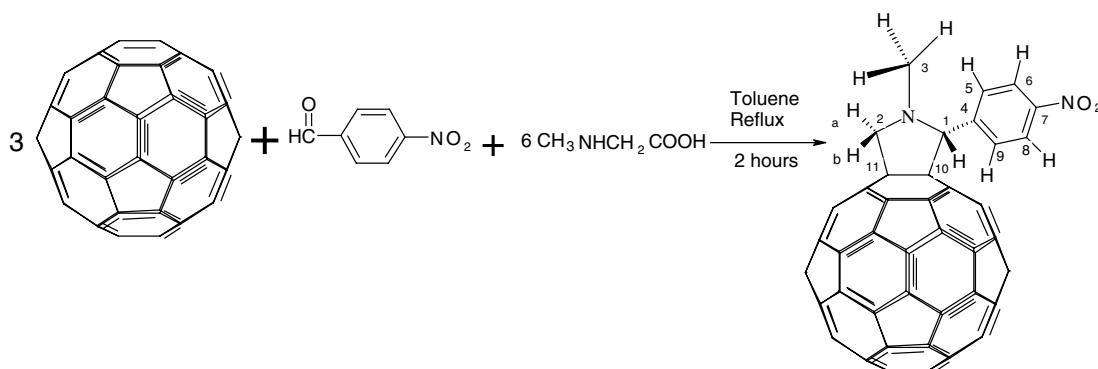

Fig. 1. Scheme of the synthesis of the pyrrolidine functionalized fullerene derivative.
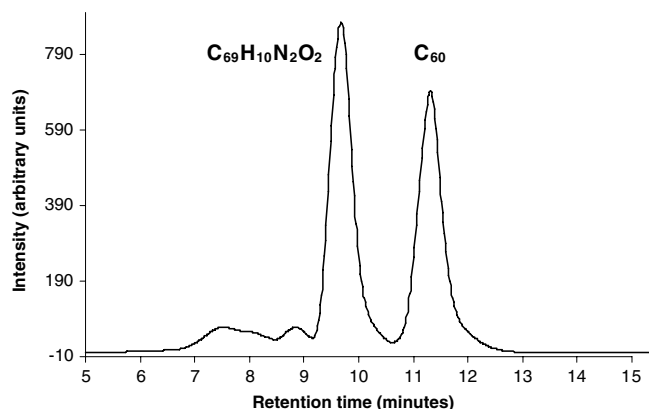
Fig. 2. HPLC chromatogram of the product mixture from synthesis, HPLC (5PBB, 20×250 mm, toluene eluent, 18 mL/min).

of pyrrolidine functionalization and consistent with other pyrrolidinization compounds [9–12]. Nitro group symmetric and asymmetric stretching vibrations were observed in FTIR at 1343 cm^{-1} and 1522 cm^{-1}. Finally, ^{1}H and ^{13}C NMR provide confirmation of the structure. Four different proton environments were found in the pyrrolidine ring. The two proton environments, H-2a and H-2b, were found to be stereo different and consistent with other pyrrolidinization compounds [11,12]. Four inequivalent aromatic proton environments were also observed, one of which was found to be broad resonance consistent with previously reported compound [10]. The ^{13}C NMR spectrum of compound revealed 50 sp^2 and 2 sp^3 environments relating to the C$_{60}$ cage and an additional 3 pyrolidine sp^3 and 4 nitrobenzene sp^2 carbon environments as expected.

The endohedral fullerene species N@C$_{69}$H$_{10}$N$_2$O$_2$ (Fig. 3) was prepared in an analogous fashion using N@C$_{60}$/C$_{60}$ (around 1/100).

The retention time of N@C$_{69}$H$_{10}$N$_2$O$_2$ is slightly longer than that of C$_{69}$H$_{10}$N$_2$O$_2$ in the same way that N@C$_{60}$ elutes more slowly than C$_{60}$ [13]. This was demonstrated by measuring the EPR spin signal of the two halves of the pure product eluting from HPLC. The first half was found to be spin silent and the second half spin active.
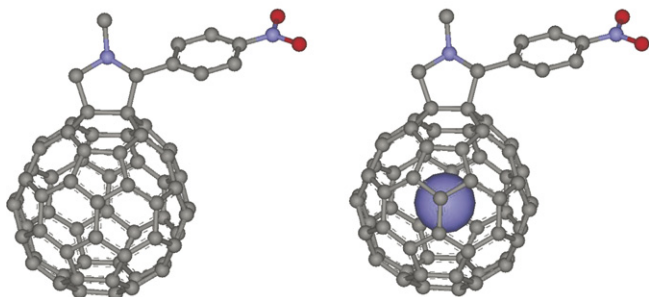

Fig. 3. Structural models of fullerene derivatives: C$_{69}$H$_{10}$N$_2$O$_2$ and N@C$_{69}$H$_{10}$N$_2$O$_2$.

3.2. Continuous wave EPR

The CW EPR spectrum of N@C$_{69}$H$_{10}$N$_2$O$_2$ powder at room temperature is shown in Fig. 4. Satellite peaks on either side of the three principle lines are indicative of a ZFS. Due to the low concentration of N@C$_{69}$H$_{10}$N$_2$O$_2$ within C$_{69}$H$_{10}$N$_2$O$_2$, the spin exchange interaction between different molecules can be ignored.

The data is fitted using the spin Hamiltonian:

$$\mathscr{H}_0 = \omega_e S_z - \omega_I I_z + \vec{S} \cdot A \cdot \vec{I} + \vec{S} \cdot \vec{D} \cdot \vec{S}, \qquad (1)$$

where $\omega_e = g\mu_B B_0/\hbar$ and $\omega_I = g_I \mu_N B_0/\hbar$ are the electron and ^{14}N nuclear Zeeman frequencies, g and g_I are the electron and nuclear g-factors, μ_B and μ_N are the Bohr and nuclear magnetons, $\hbar = h/2\pi$, h is Planck's constant and B_0 is the magnetic field applied along z-axis in the laboratory frame. A is the hyperfine interaction tensor, and $\vec{D}$ is the ZFS tensor. The ZFS parameters D and E correspond to the eigenvalues (x, y, z) of $D = 3z/2$, $E = (y - x)/2$.

The hyperfine coupling in N@C$_{60}$ is isotropic and approximately 15.8 MHz – about 50% greater than that of a free nitrogen atom [14]. The fact that the central hyperfine line ($M_I = 0$) in the spectrum shows higher intensity as compared to the two outer hyperfine lines ($M_I = \pm 1$) indicates that the ^{14}N hyperfine coupling is anisotropic.

The spectrum is simulated (red line in Fig. 4) with ZFS parameters $D = 17.0$ MHz and $E = 0.8$ MHz (consistent with reports on other pyrrolidine-functionalized fullerenes [6]) and hyperfine terms $A_{xx} = A_{yy} = 14.2$ MHz, $A_{zz} = 18.5$ MHz. The functional group induces a distortion of the fullerene cage, removing the degeneracy of the encased nitrogen p-orbital, resulting in an asymmetric electron density distribution. This produces the ZFS and an anisotropy in the hyperfine interaction. The ZFS is about twice that of the methano-fullerene derivative N@C$_{61}$(COOC$_2$H$_5$)$_2$ [7],

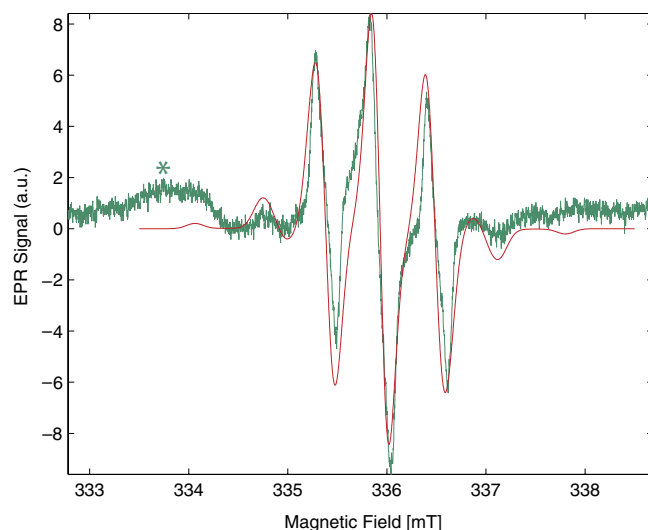Fig. 4. X-band CW-EPR spectra of N@C$_{69}$H$_{10}$N$_2$O$_2$ (powder, 2G modulation, 270 s scan time, 99 scans, room temperature) and their fitting lines ($D = 17.0$ MHz, $E = 0.8$ MHz, $A_{xx} = A_{yy} = 14.2$ MHz, $A_{zz} = 18.5$ MHz) (* = impurity).

which is consistent with the higher symmetry of that molecule compared with $N@C_{69}H_{10}N_2O_2$.

3.3. Pulsed EPR

It has been shown that nuclear spins in the solvent environment provide a mechanism for electron spin relaxation [5]. To probe the effects of the functional group on spin relaxation, it is important to use a solvent in which there are no naturally abundant nuclear spins, such as carbon disulfide.

Fig. 5 shows relaxation measurements of T_1 and T_2 of $N@C_{69}H_{10}N_2O_2$ in CS_2 solution at room temperature, taken using the central ($M_I = 0$) hyperfine line. In both cases, the data were not well fitted by purely monoexponential decay. Both T_1 and T_2 have two components corresponding to the 'inner' ($M_S = +1/2{:}-1/2$) and 'outer' ($M_S = \pm3/2{:}\pm1/2$) transitions in the $S = 3/2$ multiplet. The relative amplitudes of the 'inner' and 'outer' contributions to the total measured echo signal are 2:3. In the case

of an $S = 3/2$ spin system, a fluctuating ZFS term will lead to the following relaxation times [4,15]:

$$(T_{2,i}^{-1})_{ZFS} = \frac{4}{5}D_{eff}^2\left[\frac{\tau_c}{1+\omega_e^2\tau_c^2} + \frac{\tau_c}{1+4\omega_e^2\tau_c^2}\right] \tag{2}$$

$$(T_{2,o}^{-1})_{ZFS} = \frac{4}{5}D_{eff}^2\left[\tau_c + \frac{\tau_c}{1+\omega_e^2\tau_c^2}\right], \tag{3}$$

$$(T_{1,i}^{-1})_{ZFS} = \frac{8}{5}D_{eff}^2\left[\frac{\tau_c}{1+\omega_e^2\tau_c^2}\right] \tag{4}$$

$$(T_{1,o}^{-1})_{ZFS} = \frac{8}{5}D_{eff}^2\left[\frac{\tau_c}{1+4\omega_e^2\tau_c^2}\right] \tag{5}$$

where $D_{eff}^2 = D^2 + 3E^2$, τ_c is the correlation time of the fluctuations, and ω_e is the electron spin transition frequency.

The measured T_2 was fitted to a biexponential decay, $y_0 + A_i\exp(-2\tau/T_{2,i}) + A_o\exp(-2\tau/T_{2,o})$, which produced two components with decay rates $12.3 \pm 0.7\ \mu s$ and $2.8 \pm 0.2\ \mu s$, and relative amplitudes ($A_i/A_o \approx 2/3$). The coherence time (T_2) of pristine $N@C_{60}$ in these conditions is 80 μs. Hence, the results suggest an additional relaxation mechanism affecting the 'inner' and 'outer' rates differently, such as that provided by a fluctuating ZFS.

Both T_1 and T_2 decays shown in Fig. 5 were fitted using the above Eqs. (2)–(5), yielding a molecular rotation correlation time of $\tau_c = 31.4 \pm 2.5$ ps and a ZFS term $D_{eff} = 17.1 \pm 0.5$ MHz, matching well with that measured using CW EPR. The correlation time τ_c is longer than that of reported fullerene derivatives and three times that of $N@C_{60}$ in toluene [7], showing that the bulky functional group slows down the tumbling of the fullerene cage. The rotation correlation time of a somewhat larger nitroxyl derivative of C_{60} in a benzene–ethanol mixture was reported to be 98 ps [16], measured by EPR of the nitroxyl radical. This much longer rotational time illustrates the role of a solvent–solute interaction as an additional factor in molecular tumbling rates, in which the polar nitroxyl group plays a likely part. Thus, in molecular dynamics studies of fullerene derivatives, the use of an endohedral $N@C_{60}$ spin, rather than a nitroxyl group, as the effective spin label avoids introducing potentially undesirable interactions with the solvent.

Molecular tumbling in the presence of an anisotropic hyperfine interaction (HFI) provides an additional relaxation mechanism, which can be observed by studying the outer hyperfine lines ($M_I = \pm1$). Based on the hyperfine tensor extracted from CW EPR, the contribution to phase relaxation from this mechanism is estimated to be of the order of 100 μs [17,18].

T_2 was measured on the low-field ($M_I = +1$) hyperfine line and found to have a biexponential decay, with components $T_{2,i} = 10.2 \pm 0.7\ \mu s$ and $T_{2,o} = 2.9 \pm 0.3\ \mu s$. While the effect on the faster $T_{2,o}$ component falls within experimental error, the effect on $T_{2,i}$ is clear and consistent with the additional relaxation mechanism of fluctuating hyperfine anisotropy. The effect of ESEEM on this outer hyperfine line [4] is negligible at these short relaxation times.
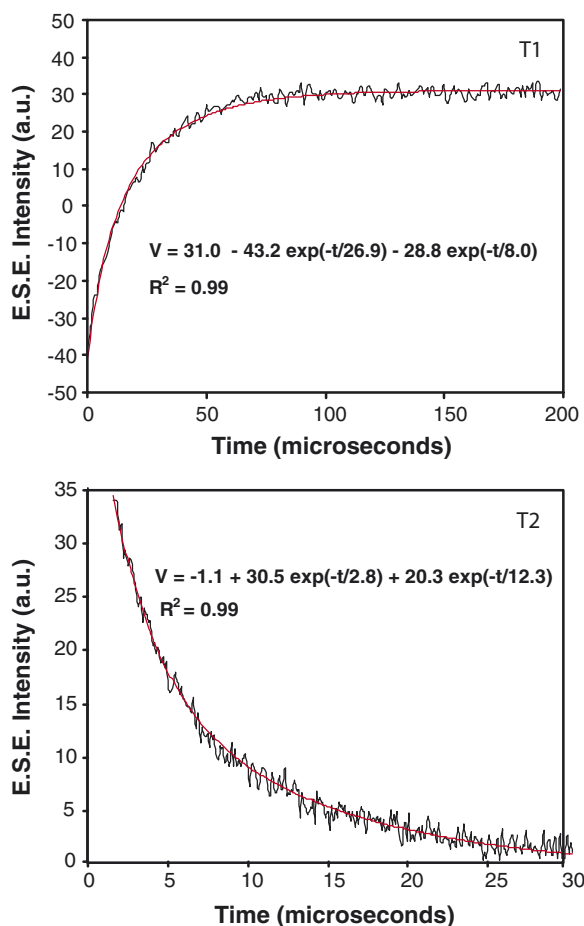

Fig. 5. Pulsed EPR measurements of $N@C_{69}H_{10}N_2O_2$ in CS_2 solution at room temperature. Biexponential fitting lines are derived using Eqs. (2)–(5), and a common set of parameters $D_{eff} = 17.1 \pm 0.5$ MHz and $\tau_c = 31.4 \pm 2.5$ ps.

4. Conclusions

A new pyrrolidine functionalized fullerene derivative, $C_{69}H_{10}N_2O_2$, was synthesized and purified by HPLC. The structure was confirmed by MALDI mass spectrometry, UV–vis, FTIR, ^1H NMR, and ^{13}C NMR spectroscopies. The magnetic properties of the analogous species, $N@C_{69}H_{10}N_2O_2$, were measured both by CW and pulsed EPR at room temperature. CW EPR spectra indicate that the functional group introduces a permanent ZFS $D = 17.0$ MHz and an anisotropy in the hyperfine interaction. The presence of a ZFS and hyperfine anisotropy was confirmed by the observation of biexponential decays in both T_1 and T_2 measurements using pulsed EPR. The nitro functional group was found to slow down the molecular tumbling in solution, with a correlation time τ_c of 31.4 ± 2.5 ps at room temperature, three times that of $N@C_{60}$ in toluene.

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