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## Liquid Crystals

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# Unexpected high ordering of a [60]Fullerene nitroxide in the nematic phase of 4-4'-azoxyanisole

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A nitroxide [60]fullerene adduct containing a pyrrolidine-1-oxyl group has been synthesized. Its orientational order in the nematic phase of the liquid crystal solvent 4,4'-azoxyanisole (PAA) has been measured from the variation of the EPR spectral parameters on passing from the isotropic to the nematic phase. Highly resolved EPR lines allow for precise evaluation of the shifts of the  $g$ ,  $a_N$  and  $a_H$  values. Since the  $g$  and the hyperfine tensors are known, the order matrix could be obtained. This is compared with the one calculated with a theoretical model based on short range solute–solvent interactions, which predicts a considerable degree of orientation of the molecular axes, despite the almost spherical shape of the molecule. The agreement with experimental findings is quite good and it is further improved if a bent structure of the pyrrolidine ring is taken into account.

## 1. Introduction

Because of their property of being aligned by a magnetic field, nematic liquid crystals have been used as solvents for orienting solute molecules and studying the anisotropy of their molecular properties [1]. When free radicals are dissolved in liquid crystal solvents, information on the  $g$  tensor and on the electron nucleus hyperfine interaction tensor can be obtained from EPR [2, 3]. For biradicals, the spectrum depends also on the electron–electron dipolar coupling, which is directly related to the radical distance [4].

Even if knowledge of the complete tensors is not available from such studies, they are of particular interest in those cases when diluted single crystals suitable for EPR cannot be grown.

On the other hand, if the magnetic interaction tensors of a particular radical are known, from the spectrum recorded in the nematic phase the orientational order of the radical can be inferred. Free radicals have been used also for probing the local orientation of the nematic phase director in samples subjected to motion [5, 6].

In the course of our EPR investigations on  $C_{60}$  derivatives and on their properties in liquid crystal solvents,

we have synthesized a symmetric nitroxide derivative **1** in which a 2,2,5,5-tetramethylpyrrolidine-1-oxyl ring is fused on a 6,6-junction of  $C_{60}$ , and have measured its EPR spectrum in solution in 4-4'-azoxyanisole (PAA). On going from the isotropic to the nematic phase, a remarkable decrease of the  $^{14}N$  hyperfine splitting was observed, together with a significant shift of the spectrum to lower field. The methyl proton splitting, barely observable in the isotropic phase, becomes well resolved in the nematic phase, because of the increase of the proton coupling and line narrowing.

The  $g$  and the  $^{14}N$  hyperfine  $A_N$  tensors of nitroxide radicals have already been measured by EPR [7] and by ENDOR [8] using diluted solutions of the nitroxide in host single crystals. More recently, accurate values of the  $g$  tensor components were obtained by high field EPR [9]. The same tensor values can be assigned to **1**, since in nitroxides the unpaired electron is localized on the NO groups and its distribution does not change appreciably from one derivative to another.

The  $g$  and hyperfine tensor principal axes coincide and they lie along the nitrogen–oxygen bond, along the  $\pi$  orbital axis and in the direction which completes the orthogonal frame. Knowing the  $g$  and  $A_N$  tensors, the orientational order of **1** in the liquid crystal phase can

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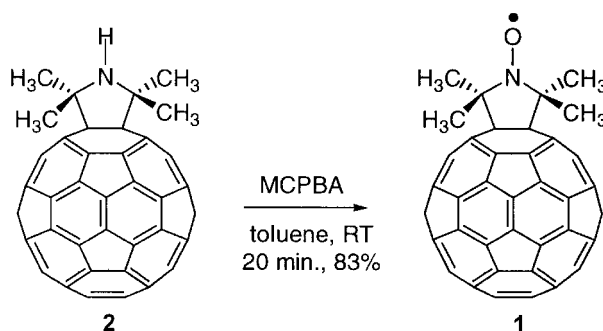
be inferred from the spectrum, whose characteristics depend on the orientation of these axes with respect to the liquid crystal director. Furthermore, the resolved hyperfine structure of the protons of the four methyl groups gives us an internal check since the proton splitting variation should be accounted for by the same orientational order parameters.

For the proton hyperfine anisotropy we rely on an accurate estimate, which can be obtained by simple calculations, based on the point dipole approximation. This is a good approximation, since the electron–proton distance in **1** is sufficiently large.

A high orientational order was obtained, which was rather unexpected for this molecule because of its close to spherical shape. The experimental results are compared with theoretical predictions obtained with the so-called ‘surface tensor’ method [10, 11] which is based on the parameterization of the short range solvent–solute interactions in terms of surface contact interactions between the solute and the nematic solvent. In this way the anisotropy of the interactions depends on the molecular surface of the solute. Such a model has been proven capable of providing good estimates of the orientational order of molecules in liquid crystal phases [10–12].

## 2. Experimental

The Fulleropyrrolidine **1** was prepared in 83% yield by *m*-chloroperbenzoic acid (MCPBA) oxidation of the pyrrolidine derivative **2** at room temperature. Derivative **2** was synthesized by a slight modification of the methodology reported by Schick *et al.* [13], starting from  $\alpha$ -aminoisobutyric acid, acetone and C<sub>60</sub> in the presence of anhydrous sodium sulphate. The purity of compounds **1** and **2** (>98%) was checked by HPLC on a silica stationary phase (column Phenomenex Luna 5  $\mu$ , 250  $\times$  4.6 mm; toluene (**1**,  $t_R$  = 8.9 min.), toluene/ethyl acetate 9/1 (**2**,  $t_R$  = 9.3 min.); flow 1 ml min<sup>-1</sup>,  $\lambda$  = 340 nm).



MCPBA: *m*-chloroperbenzoic acid

Figure 1. Structures of compounds **1** and **2**.

A detailed method for the synthesis of [60]Fulleropyrrolidine-2,2,5,5-tetramethyl-1-oxyl (**1**) is now given. To a solution of derivative **2** (11.2 mg, 14  $\mu$ mol) in toluene (20 ml) MCPBA (13.6 mg, 80  $\mu$ mol) in toluene (4 ml) was added under a nitrogen atmosphere. After 20 min at room temperature (TLC, toluene/ethyl acetate 9/1,  $R_f$  (**1**) = 0.86; toluene,  $R_f$  (**1**) = 0.53) the solution was washed with 5% aqueous NaHCO<sub>3</sub> (3  $\times$  15 ml). The organic phase, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, was concentrated under reduced pressure and the residue loaded onto a column for flash chromatography (SiO<sub>2</sub>, 2  $\times$  12 cm). Elution with toluene gave **1** (9.5 mg) in 83% yield. IR (KBr): 3430, 2980, 2928, 1369, 1630, 1462, 1432, 1376, 1369, 1215, 1184, 1030, 574, 546, 528 cm<sup>-1</sup>. UV-Vis (cyclohexane)  $\lambda_{max}$  215, 254, 313, 432 nm. MALDI-MS (C<sub>66</sub>H<sub>12</sub>NO)  $m/z$ : 834 [M<sup>+</sup>].

The liquid crystal 4-4'-azoxyanisole (PAA) was used as a solvent. For this nematogenic solvent the temperature of the crystalline–nematic phase transition is 391 K, while the nematic–isotropic phase transition temperature is 408.5 K. Other solvents, such as E7, were also considered and gave similar results. However, less resolved spectra were obtained.

Derivative **1** was finely blended with PAA powder (c. 10<sup>-4</sup> M) and dissolved by heating (c. 390 K) in a 4 mm o.d. quartz tube under nitrogen flow, in order to deoxygenate the sample. EPR measurements were carried out with a computer-controlled Bruker ER 200D X-band spectrometer, equipped with a nitrogen flow cryostat and using a standard TE<sub>102</sub> rectangular cavity.

## 3. Results and discussion

The EPR spectrum of the nitroxide free radical **1** in the presence of a static magnetic field **B** is accounted for by the following spin Hamiltonian, including the electronic Zeeman and hyperfine terms:

$$H = \beta_e g B_Z S_Z + a_N I_{Nz} S_Z + \sum_1^{12} a_H I_{Hz} S_Z \quad (1)$$

where  $\beta_e$  is the Bohr magneton,  $a_N$  and  $a_H$  are the isotropic part of the nitrogen and proton hyperfine tensors, respectively, and the high field approximation  $a \ll g\beta_e B_Z$  is assumed. The isotropic proton hyperfine couplings are considered to be equal because of the rapid rotation of the methyl groups around the C–C bonds. When the free radical is dissolved in the nematic phase of a liquid crystal solvent having the director aligned with the magnetic field, the Hamiltonian becomes:

$$\begin{aligned} H = & gB_Z S_Z + (2/3)(\text{tr } \mathbf{S} \cdot \mathbf{g})B_Z S_Z + a_N I_{Nz} S_Z \\ & + (2/3)(\text{tr } \mathbf{S} \cdot \mathbf{T}_N)I_{Nz} S_Z + \sum_1^{12} a_H I_{Hz} S_Z \\ & + (2/3)(\text{tr } \mathbf{S} \cdot \mathbf{T}_H)I_{Hz} S_Z \end{aligned} \quad (2)$$

where  $\mathbf{S}$  is the Saupe matrix, which describes the orientation of the molecular axes with respect to the liquid crystal director, and  $\mathbf{T} = \mathbf{A} - a \mathbf{I}$  is the anisotropic part of the hyperfine interaction tensor  $\mathbf{A}$ .

From equations (1) and (2), the shift of the  $g$  factor and hyperfine splitting on passing from the isotropic to the nematic phase, is given by:

$$g_{\text{nem}} = g + (2/3)(\text{tr } \mathbf{S} \mathbf{g}) \quad (3a)$$

$$a_{\text{nem}} = a + (2/3)(\text{tr } \mathbf{S} \mathbf{T}) \quad (3b)$$

allowing for the determination of the ordering matrix  $\mathbf{S}$  if the  $\mathbf{g}$  and  $\mathbf{T}$  tensors are known.

The EPR spectra of compound **1** in the isotropic and the nematic phases of PAA have been recorded in the temperature range 420–380 K. Passing from the isotropic to the nematic phase of the solvent, a shift to a lower field is observed together with a large reduction of the nitrogen hyperfine coupling constant. On decreasing the temperature in the nematic phase, a further decrease of the  $a_N$  and an increase in the  $g$  factor are observed. In figures 2(a) and 2(b) the spectra at  $T = 420$  K (isotropic phase) and  $T = 380$  K (nematic phase) are shown. The latter temperature is chosen because of the best resolution and the maximum shift of the  $a_N$  and  $g$  values. Moreover, in the nematic phase the methyl proton hyperfine splitting is well resolved as shown in figure 3(b), where the low field  $^{14}\text{N}$  hyperfine components in the two phases are shown in detail, together with their computer simulation.

The spectra show an interesting effect with a prominent linewidth linear dependence on the  $^{14}\text{N}$  nuclear spin quantum number  $m_I$ . This effect could be used for obtaining information on the anisotropic rotational

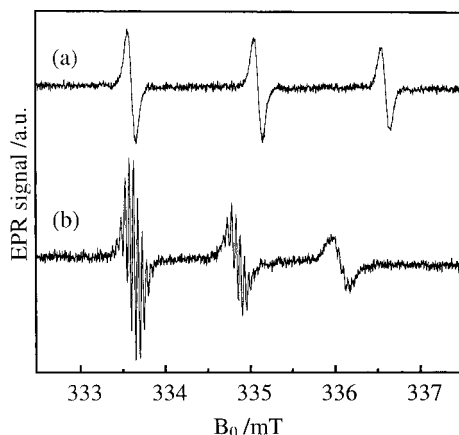


Figure 2. EPR spectra of **1** recorded (a) in the isotropic phase (420 K) and (b) in the nematic phase (380 K) of the liquid crystal solvent PAA. Note that spectrum (b) is shifted to lower field compared with spectrum (a) and shows a lower nitrogen hyperfine coupling constant, as well as a better resolved proton hyperfine structure.

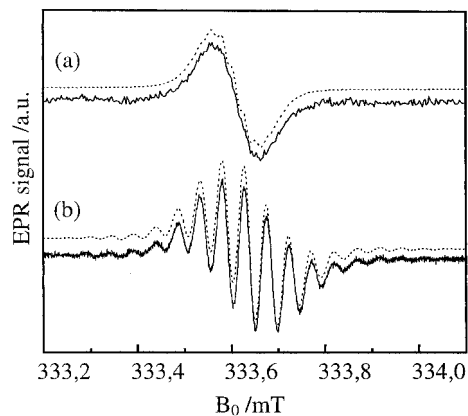


Figure 3. Low field line of the EPR spectra of **1** in (a) the isotropic and (b) the nematic phase of PAA together with their computer simulation (dotted lines). The hyperfine proton coupling constant is reduced by 0.022 mT on passing from the isotropic to the nematic phase.

molecular diffusion, as well as on the relative orientation between the anisotropic hyperfine and  $\mathbf{g}$  tensor, and the rotational diffusion tensor [14, 15].

The  $\mathbf{g}$  and  $\mathbf{A}_N$  tensor principal values obtained from literature data [8] are reported in table 1, while the measured  $g$  value and splitting constants in the two phases of the solvent are given in table 2. The principal axes of  $\mathbf{g}$  and  $\mathbf{T}_N$  are shown in figure 4.

Table 1. Principal values of the  $\mathbf{g}$  and  $\mathbf{A}_N$  tensors for nitroxide derivative **1**. The  $\mathbf{g}$  and hyperfine tensor principal axes coincide, and they lie along the nitrogen–oxygen bond, along the  $\pi$  orbital axis and in the direction which completes the orthogonal frame (see figure 4).

	$g$	$A_N/\text{mT}$
XX	2.0094	0.565
YY	2.0066	0.593
ZZ	2.0026	3.321
Isotropic value	2.0062	1.493

Table 2. Experimental values of  $g$  factor and hyperfine splitting constants measured for the isotropic and the nematic phases of the solvent PAA. The third line reports the shift of the measured values on passing from the nematic to the isotropic phase.

	$g$	$a_N/\text{mT}$	$a_H/\text{mT}$
Nematic phase	2.0073	1.201	−0.046
Isotropic phase	2.0062	1.493	−0.024
Shift	0.0011	−0.292	−0.022

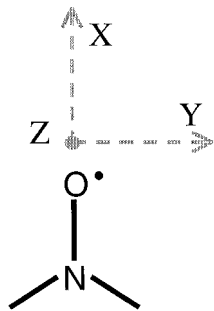


Figure 4. Principal axes of the  $A_N$  and  $g$  tensors of the nitroxide moiety. The Z axis correspond to the  $p_z$  orbital direction of the nitrogen atom.

Concerning the proton tensor, this was calculated for each proton in the point dipole approximation using:

$$T_H = g_N \beta_N g_e \beta_e [(3ij - r^2 \delta_{ij})/r^5] \quad (4)$$

where  $i, j = x, y, z$ , and assuming the electron to be placed one half on the N atom and the other half on the O atom [16]. Because of the rapid rotation, the proton tensor is assumed as the average of the tensors of the three protons of the same methyl group.

For a planar geometry of the pyrrolidine-1-oxyl ring, the  $T_H$  tensor of the protons of one methyl group in the  $x, y, z$  axes system of figure 4 is:

$$T_H = \begin{pmatrix} -0.043 & -0.035 & -0.032 \\ -0.035 & 0.046 & 0.078 \\ -0.032 & 0.078 & -0.003 \end{pmatrix} \quad (5)$$

The others are obtained by reflection with respect to the XY and ZX symmetry planes.

Using equations (3), from the literature values of  $g$  and  $T_N$  the order matrix  $S$  at  $T = 380$  K is calculated to be:

$$S = \begin{pmatrix} 0.38 & & \\ & -0.22 & \\ & & -0.16 \end{pmatrix} \quad (6)$$

It should be noted that this matrix refers to the ordering of the principal axes of the  $g$  and  $A_N$  tensors. As the temperature increases in the nematic phase, the orientational order diminishes as expected. The lowest  $S$  matrix elements calculated at 405 K, close to the isotropic–nematic phase transition temperature, are  $S_{XX} = +0.23$ ,  $S_{YY} = -0.13$ ,  $S_{ZZ} = -0.10$ .

From the electron–proton dipolar interaction tensor (5) and from (6) the shift of the proton splitting values on passing from the nematic to the isotropic phase could

be calculated using an equation similar to (3a) and (3b). A value of  $\Delta a_H = 0.014$  mT is obtained, which does not agree with the experimental result.

A theoretical estimate of the  $S$  matrix was obtained by using the ‘surface tensor’ model [10, 11], which relates the orientational order anisotropy in the nematic phase to the anisotropy of the molecular surface. This is done by assuming that each element of the molecular surface experiences a mean field, which tends to align it to the director, according to the expression:

$$dU = k_B T \varepsilon P_2(\mathbf{n}, \mathbf{s}), \quad (7)$$

where  $P_2$  is the second Legendre polynomial,  $\mathbf{n}, \mathbf{s}$  are unit vectors, respectively parallel to the director and normal to the surface element, and  $\varepsilon$  is a positive parameter, which gives the orienting strength of the medium. The overall potential suffered by the solute is then obtained by integrating equation (7) over the whole molecular surface. The latter is defined as the contour drawn by a sphere rolling on the assembly of van der Waals beads centred at the atomic positions [17, 18]. From the orienting potential, the Saupe matrix  $S$  of the solute can be calculated. In the present case the molecular surface has been defined starting from an optimized geometry, assuming standard van der Waals radii and a rolling sphere radius  $R = 3 \text{ \AA}$  [11]. The problem of the choice of the rolling sphere radius has already been analysed [11], and values in the range 2.5–5 Å were devised as the most appropriate for typical nematic solvents, made up of rather mobile groups which roughly have such dimensions. As a matter of fact, the order parameters are only slightly affected by the value of the radius  $R$  within this range; on the contrary, they would significantly decrease in the case of smaller rolling spheres, which would not be able to produce an effective smoothing of the outer surface of the van der Waals assembly, and on the other hand appear to be rather unrealistic. With  $\varepsilon = 0.048 \text{ \AA}^2$ , a reasonable value for PAA at a reduced temperature in the range  $T/T_{NI} \sim 0.90$ – $0.95$ , the following matrix is obtained:

$$S_{\text{Calc}} = \begin{pmatrix} 0.47 & & \\ & -0.21 & \\ & & -0.26 \end{pmatrix} \quad (8)$$

The matrix is expressed in the principal axes of ordering, shown in figure 5(a), which coincide with symmetry axes of the molecule in the case of a coplanar arrangement of the nitroxide group and of the pyrrolidine ring. Actually the ordering matrix is almost unaffected by the orientation of the nitroxide radical due to the smallness of its dimensions in comparison with the massive fullerene moiety. The calculated Saupe matrix indicates a sizeable orientational order of the solute (for the sake

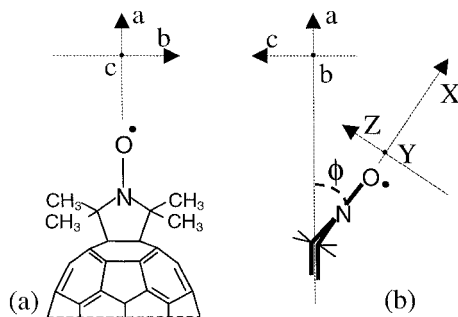


Figure 5. Comparison between (a) the molecular axes of the fullerene nitroxide derivative **1** and (b) the principal axes of the  $A_N$  and  $g$  tensors of the nitroxide group. Note that the two axis systems are not coincident due to a bent structure of the pyrrolidine ring.

of comparison we can mention that  $S_{aa} = 0.37$  is predicted under the same conditions for *p*-dichlorobenzene), with a small biaxiality in the plane perpendicular to the main ordering axis (*a*). Such a biaxiality ( $S_{bb} - S_{cc} > 0$ ) corresponds to a slightly higher propensity to align the *b* rather than the *c* axis to the director, in agreement with what can be expected from inspection of the molecular shape.

The origin of the orientational order is certainly the presence of the pyrrolidine ring, which breaks the icosahedral symmetry of [60]fullerene, giving it a more rod-like appearance. In order to gain more insight into the origin of the orientational order of [60]fulleropyrrolidine-2,2,5,5-tetramethyl-1-oxyl, we have calculated the Saupe matrix, under the same conditions leading to the values reported in equation (8), for the structures obtained from the original one (i) by eliminating the whole 2,2,5,5-tetramethylpyrrolidine-1-oxyl group and (ii) by replacing the methyl groups with hydrogens. In the former case the values  $S_{xx} = 0.02$ ,  $S_{yy} = 0$ ,  $S_{zz} = -0.02$  were obtained, showing that the effect of the slight perturbation of the [60]fullerene symmetry induced by the fused ring at the 6,6-junction is indeed vanishingly small. On the contrary, a significant degree of ordering was predicted for the structure (ii),  $S_{xx} = 0.36$ ,  $S_{yy} = -0.15$ ,  $S_{zz} = -0.21$ ; such a result confirms that the five membered ring substituent is responsible for the orientation of the solute, but also indicates the non-negligible contribution deriving from the methyl substituents.

From the comparison of the Saupe matrix derived from the measured splittings, equation (6), and that calculated with the surface interaction model, equation (8), an inversion of the deviation from axial symmetry appears ( $S_{yy} - S_{zz} < 0$  in (6)). This discrepancy could be eliminated if the principal axes of the nitrogen hyperfine and  $g$  tensors *X*, *Y*, *Z* do not coincide with the molecular axes *a*, *b*, *c* due to a deviation from planarity of the pyrrolidine ring as shown in figure 5 (b).

There are two equivalent conformations corresponding to the bent structure, possibly interconverting by a conformational exchange. If the exchange rate is slow, as expected for an interconversion barrier of about  $20 \text{ kJ mol}^{-1}$  (typical of a chair-twisted conformational jump in cyclohexane), the equivalent bent structures are by far the most probable conformations of the system. With respect to the calculation of the Saupe matrix the two conformations give identical results.

The non-planarity of the pyrrolidine ring is not at variance with the magnetic equivalence of the methyl groups, provided that the exchange between the two tilted conformations is fast enough to average the hyperfine coupling constant difference. Since the latter is very small (in the order of  $10^5 - 10^6 \text{ s}^{-1}$ ) even a slow exchange process is effectively able to average the hyperfine interaction of the methyl protons.

It should be noted that while the calculations based on the theoretical model are quite insensitive to small geometric modification, the results based on experimental findings are strongly affected by any discrepancy between molecular and nitroxide frame, as can be expected from the fact that the former are determined by the whole molecule, while the latter depend only on the nitroxide group.

An angle  $\phi = 22^\circ$  reproduces the theoretical Saupe matrix (8) giving:

$$\mathfrak{S} = \begin{pmatrix} 0.48 & & \\ & -0.22 & \\ & & -0.26 \end{pmatrix} \quad (9)$$

Using this latter matrix one obtains the proton hyperfine splitting variation  $\Delta a_H = 0.020 \text{ mT}$  in good agreement with the measured variation reported in table 2. A bent structure is not unexpected because it allows for the release of the energy due to the eclipsed conformation of the four methyl group in the planar structure.

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