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*Mendeleev Commun.*, 2008, **18**, 21–23
Mendeleev Communications

# Magnetic characteristics and orientation of a new nitroxide radical in an ordered matrix

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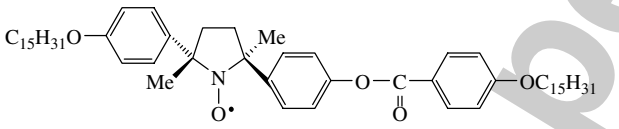
DOI: 10.1016/j.mencom.2008.01.009

**The magnetic characteristics of a liquid crystalline nitroxide radical 2,5-dimethyl-2-pentadecyloxyphenyl-5-[4-(4-pentadecyloxybenzenecarbonyloxy)phenyl]pyrrolidine-1-oxide in solution and in solids were studied by EPR spectroscopy; the EPR spectra of the radical were found to be highly sensitive to orientation and structural changes of the matrix.**

Organic liquid crystalline substances with a nitroxide unit in the core portion were synthesised.[1–3] These substances are important because of their perspective magnetic properties.[1–3] They can also be used as paramagnetic probes for EPR spectroscopic studies, especially for the dynamics of liquid crystals.

The aim of this work was to study the magnetic properties of the liquid crystal nitroxide radical 2,5-dimethyl-2-pentadecyloxyphenyl-5-[4-(4-pentadecyloxybenzenecarbonyloxy)phenyl]-pyrrolidine-1-oxide **1** by EPR spectroscopy and the ordering of this stable radical in an aligned liquid crystal matrix. The rigid structure of the core part and an elongated shape of radical **1** allowed us to expect that the radical is a sensitive paramagnetic probe for studying oriented materials.




**1**

Both 2*S*,5*S*-enriched and racemic **1**† were synthesised according to a published procedure.[1–3]

The UV-VIS spectra of both 2*S*,5*S*-enriched and racemic **1** are identical (Figure 1). They show the absorption band with $\lambda_{max}$ = 444 nm, $\varepsilon_{max}$ = 11.3±1.0 dm$^3$ mol$^{-1}$ cm$^{-1}$. This band corresponds to the absorption of the NO radical fragment.[6]

The EPR spectra† of the solutions of 2*S*,5*S*-enriched and racemic **1** in toluene, a mixture of toluene and methylcyclohexane (1:1) or methyltetrahydrofuran were recorded at 293 K. The spectra of both 2*S*,5*S*-enriched and racemate substances are identical to within experimental errors. The EPR spectrum of the radical in toluene is presented in Figure 2(*a*). Averaged magnetic parameters are $g$ = 2.0058±0.0001 and HFS constant $A$ = 1.35±0.02 mT.

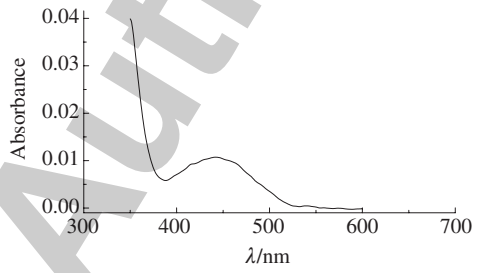



**Figure 1** UV-VIS spectrum of the radical in toluene at 298 K.

The spectrum in Figure 2(*a*) exhibits additional components [Figure 2(*b*)]. The components marked by solid arrows can be attributed to $^{13}$C hyperfine splitting; $A$ ~ 0.5 mT. An ascription of the components marked by dotted arrows is not so clear. The purity of the test substances was checked chromatographically, so these components could not be explained by an admixture of a biradical compound. It was proved that amplitudes of these components relative to the central component amplitude were temperature independent, so these components were not the result of dimerisation or association of radicals in solution. This splitting can be attributed to $^{13}$C in another location in the

† (2*S*,5*S*)-**1** (85.2% *ee*): $[\alpha]_D^{26}$ –66.88 ($c$ = 0.965, THF). Phase transition temperature [heating (°C), Cr 71.1 SmC* 91.0 Iso; cooling, Cr 46.8 SmC* 89.4 Iso]. EPR (THF) $g$ = 2.0058, $a_N$ = 1.35 mT. IR (KBr, $\nu$/cm$^{-1}$): 764, 840, 1071, 1166, 1253, 1313, 1375, 1472, 1507, 1608, 1735, 2922. Found (%): C, 78.54; H, 10.10; N, 1.59. Calc. for $C_{55}H_{84}NO_5$ (%): C, 78.71; H, 10.09; N, 1.67.

(±)-**1**: Phase transition temperature [heating (°C), Cr 79.7 SmC 91.1 Iso; cooling, Cr 58.7 SmC 89.3 Iso].

UV-VIS spectra were recorded using a Shimadzu-2401 spectrometer.

EPR spectra were recorded using a Varian E-3 spectrometer. The samples were placed in quartz ampoules (inner diameter of 3 mm; height of 10 mm) and vacuum deaerated. The annealing of the samples was performed in a flow of nitrogen at a preset temperature. The accuracy of temperature control was ±2 °C.

The nematic liquid crystal (*n*-4-methoxybenzylidene-*n*-butylanilin, MBBA) was chosen as a matrix for ordering the radicals. Commercial MBBA was purified by vacuum distillation at 10$^{-3}$ Torr. The clearing point comes to 318 K; according to published data,[4,5] it is 316–321 K. The stable radical was dissolved in the liquid crystal at 298 K; the radical concentration was ~0.5×10$^{-3}$ mol dm$^{-3}$. The number of radical centres in solution was calculated by the double integration of EPR spectra. A crystal of $CuCl_2 \cdot 2H_2O$ with a known number of paramagnetic centres was used as a standard.

The liquid crystal was aligned by the magnetic field of the EPR spectrometer at 298 K. The liquid crystal director was aligned perpendicular to the axis of the ampoule. The aligned sample was cooled in the magnetic field to 77 K. The EPR spectra were recorded by consecutive turning of the ampoule around the axis with a step of 10° using a goniometer with an accuracy of ±1°. The angular dependence of the EPR spectra did not change at 77 K in the time scale of the experiment (*i.e.*, several hours), so the orientation of the matrix remained invariable within this time interval.

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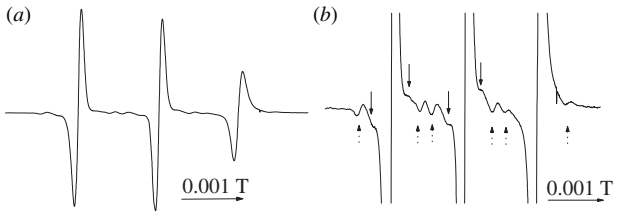


**Figure 2** EPR spectrum of (*a*) the radical in toluene at 298 K, (*b*) the above spectrum in detail. The components marked by solid and dotted arrows can be attributed to $^{13}C$ hyperfine splitting (see the text).

molecule. It should be $^{13}C$ in position with a rather large spin density ($A$ ~ 1.16 mT). The examples of similar $^{13}C$ hyperfine splitting constants in nitroxide radicals were given previously.[7,8]

The EPR spectra of the radical in methyltetrahydrofuran, toluene and MBBA were recorded at 77 K. The spectra of both 2*S*,5*S*-enriched and racemate substances in each matrix are identical to within experimental errors. The unresolved structure of left and central components of spectrum is observed in all media (Figure 3). The peculiarity of the left component vanishes at 118 K, but an unresolved structure of the central component remains; further heating does not give any effect. Possibly, this splitting is the result of anisotropic HFS on the protons of methyl groups.

The extent of spectrum distortion is the least in the case of MBBA. A computer simulation of this spectrum was used for the determination of anisotropic magnetic parameters of the radical. The spectrum was simulated and the parameters of interest were fitted so that the sum of the squares of differences between the simulated and experimental spectra was minimal.[9] The result of this simulation is in a good agreement with the experimental spectrum (Figure 4). From this simulation the anisotropic magnetic parameters were obtained: $g_x = 2.0083 \pm 0.0002$, $g_y = 2.0066 \pm 0.0002$, $g_z = 2.0021 \pm 0.0002$, $A_x = 0.26 \pm 0.05$ mT, $A_y = 0.44 \pm 0.03$ mT, $A_z = 3.14 \pm 0.04$ mT.

Recently, a new method has been developed for the determination of orientation distribution function of anisotropic paramagnetic species based on a numerical analysis of the angular dependence of EPR spectra.[10]

It was established that the angular dependencies of EPR spectra of both 2*S*,5*S*-enriched and racemic **1** in the same oriented samples are equal. Thus, these compounds do not differ in their ability to orient in aligned MBBA.

Figure 5(*a*) shows the EPR spectra of **1** in aligned MBBA recorded at 0° and 90° between the director of the liquid crystal and the magnetic field vector. The value of $h$ marked in Figure 5(*a*) is very sensitive to the orientation alignment of the radical. Figure 5(*b*) shows the dependence of $h$ on magnetic field strength. It is obvious that at 0.3–0.5 T, the orientation of the paramagnetic probe is practically equal. In our experiments, the liquid crystal was aligned at 0.4 T.

The eighteen EPR spectra that correspond to different positions of the ordered sample in the magnetic field were recorded

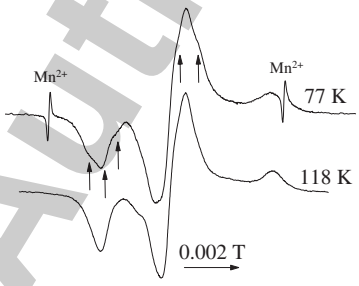


**Figure 3** EPR spectra of the radical in glassed toluene at 77 and 118 K.

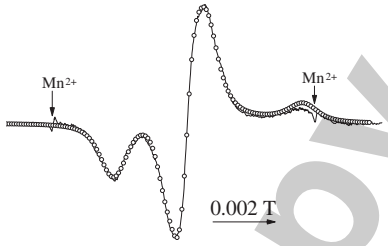


**Figure 4** EPR spectrum of the radical in MBBA at 77 K (line) and the simulation result of this spectrum (circles).

in our experiments [Figure 6(*a*)]. According to a method,[10] all of the experimental spectra were simulated jointly with orientation function that was expressed in terms of spherical harmonics as follows:

$$\rho(\beta,\gamma) = \sum_{j=0}^{\infty} \left\{ 0.5 a_{j0} P_j(\cos\beta) + \sum_{k=1}^{j} P_j^k(\cos\beta)[a_{jk}\cos(k\gamma) + b_{jk}\sin(k\gamma)] \right\}, \quad (1)$$

where $P_j$ are Legendre polynomials, $P_j^k$ are associated Legendre functions; angles $\beta$ and $\gamma$ characterise the position of the symmetry axis of the sample (director of liquid crystal) in the reference fame connected with a paramagnetic particle.

The expansion coefficients were determined through the minimization of discrepancies between simulated and experimental spectra. A global minimum was obtained using the non-linear least-squares method. The spectra were simulated using the spin Hamiltonian, which includes the second-order terms with regard to the energy of nuclear Zeeman interaction and contribution of forbidden transitions. The convolution of Gaussian and Lorentzian functions was used for the representation of an individual line shape.

The result of mutual simulation of the experimental spectra is shown in Figure 6(*b*). Some deviation of simulated spectra from experimental ones possibly results from additional proton HFS that was not taken into account in the course of calculations. Since the main directions of $g$ and HFS tensors of the studied species coincide, the magnetic properties of the radical were described as orthorhombic. In this case, only the coefficients $a_{jk}$ with even $j$ and $k$ are different from zero. The second, forth, sixth and eighth order terms of equation (1) were taken into consideration. It was checked that the addition of higher

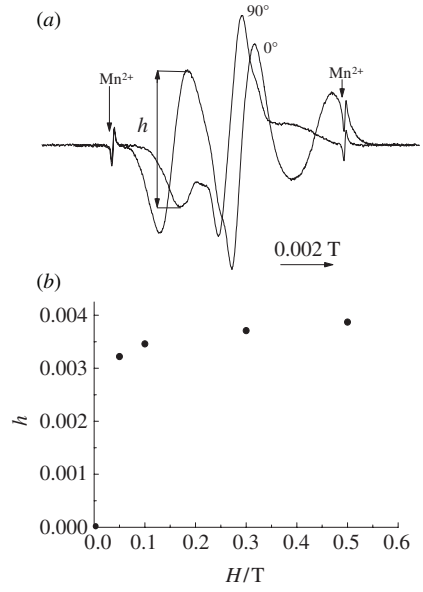


**Figure 5** (*a*) EPR spectra of radical in aligned MBBA recorded at 0° and 90° between the director of the liquid crystal and the magnetic field vector; (*b*) the dependence of $h$ on magnetic field strength; $h$ is normalised over the number of paramagnetic particles.

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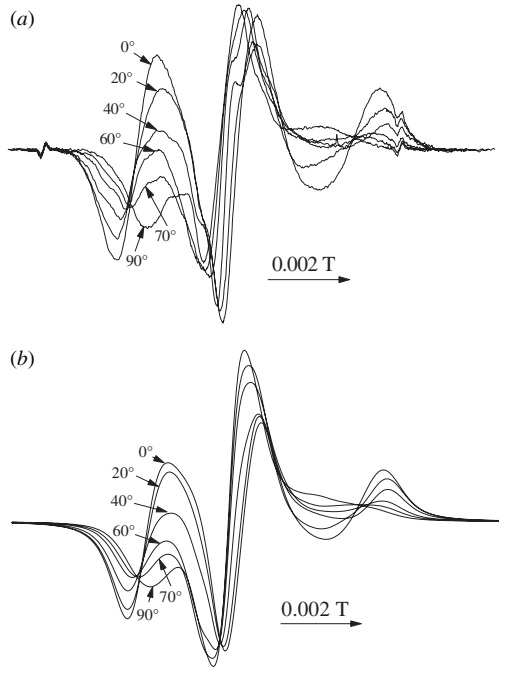


**Figure 6** (*a*) Experimental EPR spectra of the radical in aligned MBBA, recorded at different angles between the director of the liquid crystal and the magnetic field vector; (*b*) the result of a mutual simulation of these spectra.

**Table 1** The expansion coefficients of the orientation distribution function of the radical in aligned MBBA.

| $a_{20}$ | $a_{40}$ | $a_{60}$ | $a_{80}$ | $a_{22}$ | $a_{42}$ |
|---|---|---|---|---|---|
| 1.82 | –0.39 | –0.65 | –0.53 | 0.09 | 0.04 |

order terms does not lead to a decrease of discrepancies between modeled and experimental spectra. The coefficients are presented in Table 1. The coefficient $a_{00}$ reflects the number of species; for a normalised orientation function, $a_{00} = 1$. The coefficients $a_{44}$, $a_{6k}$ and $a_{8k}$ with $k \neq 0$ were found to be insignificant.

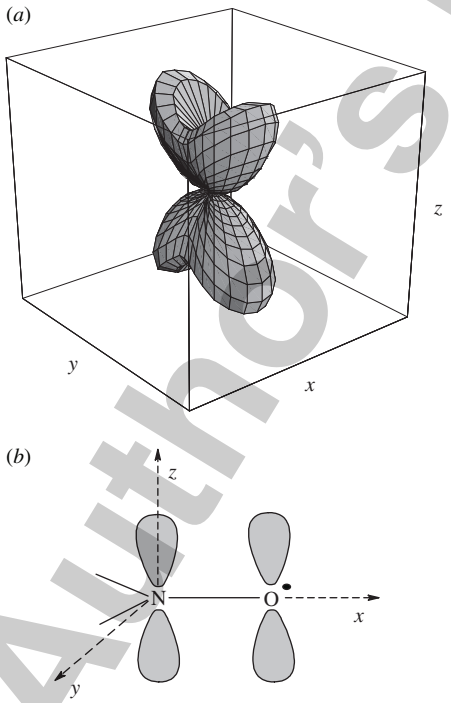


**Figure 7** (*a*) Orientation distribution function of the radical in aligned MBBA; (*b*) directions of the main axes of *g*-tensor in molecules of nitroxide radicals.

The orientation distribution function of paramagnetic probe in aligned MBBA, constructed in accordance with the obtained expansion, is represented in Figure 7(*a*). This function demonstrates the orientation of the sample axis of anisotropy in the radical reference frame. The three principal *g*-tensor axes were chosen as the axes of coordinates; their directions in the molecules of nitroxide radicals are shown in Figure 7(*b*). In Figure 7, one can see that X axes of the probe molecules are oriented predominantly perpendicular to the director of the liquid crystal. Taking into account the structure of the radical, one can conclude that the probe molecules are directed along the aligned molecules of MBBA. The Y and Z axes of the majority of radicals form angles of ~55° and ~35° relative to the director of liquid crystal.

The temperature dependence of the orientation distribution function has been studied over a range from 77 to 273 K. Aligned samples were annealed at various temperatures during 1 h. EPR spectra were recorded at 77 K after annealing the samples. At 77–223 K, the angular dependence of the EPR spectra remained invariable; hence, the orientation distribution of radical **1** did not change. After annealing the sample at temperatures above 223 K, the EPR spectrum becomes a wide structureless component similar to the spectrum[1] of neat radical **1**. This spectrum does not show the angular dependence. Obviously, the crystallization of supercooled nematic MBBA occurs at temperatures above 223 K. As a result of this process, admixed radical molecules form a separate phase in which strong dipole–dipole interaction takes place.

Earlier, we observed the gradual change of orientation order of the stable radical TEMPOL during the annealing of the aligned liquid crystal 4-*n*-amyl-4′-cyanobiphenyl.[10] The changes in this case reflected both the change of the structure of the matrix and the heat movement of the paramagnetic molecules at the annealing of the sample, and it was impossible to determine the contribution of each process. The result of this work demonstrates that the change of the orientation distribution of radical **1** reflects the structure change of the matrix only. Probably, the elongated paramagnetic molecules of **1** are built in the liquid crystal more successfully than the circle-like molecules of TEMPOL. Consequently, this class of liquid crystalline nitroxide radicals can be used as paramagnetic probes for studying the dynamics of liquid crystals.

This work was supported by the Russian Foundation for Basic Research (project no. 06-03-32231).

## References

1 N. Ikuma, R. Tamura, S. Shimono, N. Kawame, O. Tamada, N. Sakai, J. Yamauchi and Y. Yamamoto, *Angew. Chem., Int. Ed. Engl*., 2004, **43**, 3677.
2 N. Ikuma, R. Tamura, S. Shimono, Y. Uchida, K. Masaki, J. Yamauchi, Y. Aoki and H. Nohira, *Adv. Mater*., 2006, **18**, 477.
3 N. Ikuma, R. Tamura, K. Masaki, Y. Uchida, S. Shimono, J. Yamauchi, Y. Aoki and H. Nohira, *Ferroelectrics*, 2006, **343**, 119.
4 C. van der Struijf, H. K. Nienhuys, D. Harryvan, G. Kotte and Y. K. Levine, *J. Magn. Reson.*, 1998, **130**, 253.
5 K. R. Sarma, *Liquid Crystal Displays*, CRC Press LLC, Boca Raton, FL, 2000.
6 J. W. F. Keana, J. R. Dinerstain and F. Baitis, *J. Org. Chem*., 1971, **36**, 209.
7 C. Chatgillaloglu and K. U. Ingold, *J. Phys. Chem*., 1982, **86**, 4372.
8 E. G. Janzen, U. M. Oehler, D. L. Haire and Y. Kotake, *J. Am. Chem. Soc*., 1986, **108**, 6858.
9 A. Kh. Vorobiev, V. S. Gurman and T. A. Klimenko, *Phys. Chem. Chem. Phys*., 2000, **2**, 379.
10 A. Kh. Vorobiev and N. A. Chumakova, *J. Magn. Reson*., 2005, **175**, 146.

*Received: 10th July 2007; Com. 07/2979*

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