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Matched Spin Probes for the Study of the Overall Motion of Model Lubricants

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For ESR studies of molecular rotation in liquids, it is desirable to match the spin probe as closely as possible to the solvent molecules. In this work the solvents were model lubricants whose overall motion has been characterized from carbon-13 NMR relaxation measurements. Two compounds were studied, the approximately cylindrical molecule 5-(*n*-octyl)naphthalene (ON) (a model low-traction fluid) and the approximately spherical molecule dicyclohexy-3,4-furan dicarboxylate (DCFDC) (a model high-traction fluid). For these two compounds the matched spin probes 5-(*n*-octyl)-1,1,13,3-tetrakis(trideuteriomethyl)isoindolin-2-yloxyl (OTMIOD) and 4,5-bis(cyclohexyloxycarbonyl)-1,3,2-dithiazol-2-yl (BCCD), respectively, were prepared. ESR measurements were made on OTMIOD in ON and in toluene at two frequencies, namely 9 GHz (X band) and 94 GHz (W band), and the importance of making the high-frequency measurements was demonstrated for evaluation of the anisotropy parameters. The results are different for the two solvents, thus proving the necessity for matching the spin probe to the solvent. BCCD was shown to be tumbling isotropically in DCFDC. Activation energies were derived for the overall motions from the ESR and NMR measurements. These activation energies were compared with those for the viscosities of the solvents. The viscosities of both ON and DCFDC were measured over a wide temperature range using an ESR method. © 1997 by John Wiley & Sons, Ltd.

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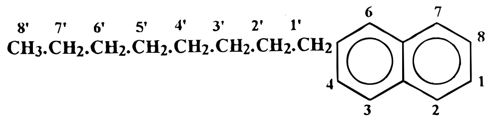
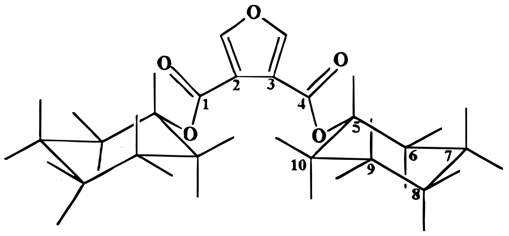
INTRODUCTION

For ESR studies of molecular rotation in liquids, it is important to match the spin probes used as closely as possible with respect to size, shape and reactivity. Such matching is essential if the probe is not to perturb the system, even though the probe may only be present at concentrations less than 1 mM. This has rarely been done—we have used the technique in a previous study[1] and others have used it for an investigation of the ordering of spin-labelled nematogen-like probes dissolved in nematic liquid crystals.[2] It is also rare to carry out comparative ESR and NMR studies, perhaps because of the challenge of synthesizing a spin probe analogue of a solvent molecule. Here we present magnetic resonance results from a study of two compounds, the approximately cylindrical molecule 5-(*n*-octyl)naphthalene (ON) (a model low-traction fluid) and the approximately spherical molecule dicyclo-3,4-furan dicarboxylate (DCFDC) (a model high-traction fluid).



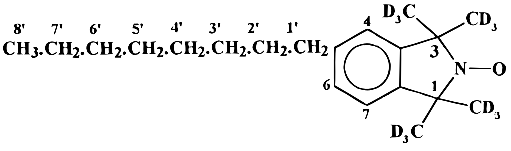
ON



DCFDC

For this work we prepared the matched spin probes 5-(*n*-octyl)-1,1,3,3-tetrakis(trideuteriomethyl)isoindolin-2-yloxyl (OTMIOD) and 4,5-bis(cyclohexyloxycarbonyl)-1,3,2-dithiazol-2-yl (BCCD), respectively.

Whereas OTMIOD is stable indefinitely, a sample of the radical BCCD exists for only a few days. For OTMIOD in ON and in toluene we made measurements at the W-band, in addition to X-band measurement, which enhances the accuracy of measurement of



OTMIOD

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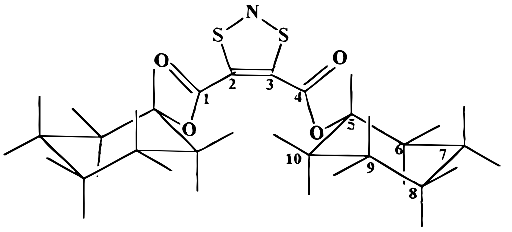


BCCD

the g-tensors and the frequency dispersion thus allowing determination of the elements of the rotation tensor, **R**.

EXPERIMENTAL

Materials

4,5-Bis(cyclohexyloxycarbonyl)-1,3,2-dithiazol-2-yl (BCCD). This free radical was prepared by adding dicyclohexyl but-2-ynedionate (kindly donated by Mr J. Leaver) to a mixture of S_4N_2 and S_4N_4 in dichloromethane.[3,4] The solution was filtered and then the solvent was evaporated off prior to adding the liquid under investigation.

5-(*n*-Octyl)-1,1,3,3-tetrakis(trideuteriomethyl)isoindolin-2-yloxyl (OTMIOD). The preparation of this free radical has been described previously.[5]

2-(*n*-Octyl)naphthalene (ON). The first stage involved the preparation of 2-naphthyl *n*-octyl ketone using a method based on that of Banister and Elsner.[6] Finely powdered anhydrous aluminium chloride (39 g, 0.45 mol) was added in 10 g portions to a stirred solution of naphthalene (67 g, 0.82 mol) and *n*-octanoyl chloride (67 g, 0.82 mol) in freshly distilled nitrobenzene (200 cm^3) cooled to −5 °C. To the reaction mixture at 0 °C was slowly added concentrated hydrochloric acid, also at 0 °C. The mixture was filtered and the filtrate formed two layers; the organic layer was separated and washed with water and then dried with sodium sulphate. Nitrobenzene was removed by distillation then the crude ketone was distilled (b.p. 219 °C/10 mmHg). The ketone was purified by crystallizing twice from ethanol and then it was reduced to ON by the Huang–Minlon method[7] as follows. The ketone (10 g) was added to a solution of sodium hydroxide (4 g) in diethylene glycol (70 cm^3), together with hydrazine hydrate (5 cm^3 of 95%). The mixture was refluxed for 3 h then the reaction mixture was heated at 220 °C for a further 12 h, during which time the upper layer of hydrazone changed from orange–red to almost colourless with a faint blue fluorescence. After cooling, the mixture was acidified with dilute hydrochloric acid and then extracted with toluene. The latter was distilled off and the ON was purified by vacuum distillation over sodium (b.p. 166 °C/3 mmHg).

Dicyclohexyl-3,4-furan dicarboxylate (DCFDC). We have already reported the preparation of this compound.[8]

NMR carbon-13 relaxation measurements

The carbon-13 chemical shifts (ppm, referred to TMS) of 5-*n*-octylnaphthalene were found to be as follows:

Aromatic carbons		Chain carbons	
1	124.99	1′	36.45
2	127.96	2′	31.68
3	125.77	3′	29.97
4	127.66	4′/5′	29.78
6	126.46	4′/5′	29.87
7	127.80	6′	32.34
8	127.39	7′	23.11
		8′	14.45

Carbon-13 spin–lattice relaxation times, T_1, and nuclear Overhauser effect (NOE) measurements were made for the aromatic carbons at several radiofrequencies and over a wide range of temperatures. These parameters provide a useful means of studying molecular motion in liquids.[9–12] In this work, T_1 and NOE data were collected using a Bruker 300 MHz spectrometer at the University of Surrey and a Jeol Alpha 500 MHz at Jeol UK, Welwyn Garden City. Proton decoupling was achieved using a Waltz 16 pulse sequence. The 90° pulse lengths were 7.5–8.5 and 9.2–9.7 μs for the 300 and 500 MHz instruments, respectively. Neat ON and DCFDC were degassed and placed in flame-sealed 8 and 5 mm NMR tubes for the 300 and 500 MHz spectrometers, respectively. The 8 mm tubes were placed inside 10 mm NMR tubes and the annulus was filled with deuterated reference sample suitable for the temperature range. The sample temperature controllers were calibrated to give sample temperature measurements accurate to within ±1 °C. Only carbons with protons attached were investigated as the dominant relaxation mechanism is dipole–dipole. Inversion–recovery was used for the measurement of T_1. The number of scans was 24 and 8 for the 300 and 500 MHz spectrometers, respectively. An inverse-gated decoupling pulse sequence was used to remove the NOE from a carbon-13 spectrum, and this was then compared with a normal spectrum to obtain the NOE. The peak intensities of the completely decoupled spectra were divided by the peak intensities of the inverse-gated decoupled spectrum. The NOE factor, η, is this value minus one. Table 1 lists the T_1 and NOE values for the aromatic carbons attached to hydrogen of octylnaphthalene. These carbons were selected for study in preference to the chain carbons since they represent the rigid part of the molecule. The NMR data for DCFDC will be given elsewhere.[13]

ESR spectroscopy

X-band spectra were obtained at the University of Illinois with a Varian Century Series E-112 spectrometer fitted with a Varian Model 906790 temperature controller; the temperature was measured to a precision of ±0.5 °C with a copper–constantan thermocouple, placed near the sample, and an Omega Engineering Model 410A1A digital unit. The magnetic field was measured with a Varian Model 92980102P NMR tracking gaussmeter. X-band spectra were also obtained at the University of Surrey with a Jeol RE1X spectrometer equipped with a Jeol DVT-2 sample temperature controller. Both spectrometers employed the EPRWare software and hardware package (supplied by Scientific Software Services) for data collection.

The W-band (94 GHz) spectrometer was designed and constructed at the University of Illinois EPR Center and been described elsewhere.[14–16] The scan and the centre of the magnetic field were calibrated with a GMW Metrolab precision NMR teslameter (model PT2025). The microwave frequency was measured with an IEP Microwave Model 578 source-locking microwave counter. The temperature of the entire cavity

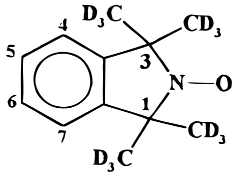
Table 1. Carbon-13 T_1 and NOE values for some aromatic carbons of neat 5-*n*-octylnaphthalene at various temperatures

Carbon						
	T_1 (s) values at 75.4 MHz					
	328 K	313 K	298 K	283 K	268 K	
1	1.38	0.91	0.57	0.34	0.21	
2	1.35	0.90	0.57	0.33	0.21	
3	1.20	0.77	0.50	0.29	0.19	
4	0.69	0.47	0.33	0.22	0.17	
6	1.35	0.90	0.58	0.34	0.21	
7	1.36	0.92	0.57	0.34	0.21	
8	1.12	0.75	0.47	0.28	0.18	
	T_1 (s) values at 125.7 MHz					
	323 K	313 K	303 K	293 K	283 K	273 K
1	1.22	0.86	0.68	0.52	0.40	0.29
2	1.21	0.89	0.68	0.52	0.41	0.34
3	0.94	0.82	0.58	0.46	0.38	0.29
4	0.62	0.52	0.42	0.34	0.25	0.24
6	1.20	1.00	0.71	0.54	0.41	0.30
7	1.12	0.92	0.68	0.50	0.38	0.32
8	1.02	0.76	0.60	0.46	0.32	0.27
	NOE values at 125.7 MHz					
	323 K	313 K	303 K	293 K	283 K	273 K
1	2.50	2.56	2.49	2.32	2.13	1.82
2	2.40	2.57	2.52	2.31	2.15	1.85
3	2.69	2.55	2.48	2.33	2.03	1.73
4	2.47	2.29	2.15	1.96	1.48	1.33
6	2.43	2.55	2.53	2.34	2.13	1.89
7	2.54	2.55	2.44	2.36	2.09	1.81
8	2.38	2.58	2.54	2.32	2.03	1.73

assembly was controlled by directing nitrogen gas from the Varian X-band controller into the bore of the superconducting magnet. The sample temperature was measured as at X-band but the thermocouple was located inside the resonator block.

Sample preparation

Approximately 1 mM solutions were prepared as follows (1) OTMIOD in toluene; (ii) OTMIOD in ON, (iii) BCCD in DCFDC; (iv) TMIOD in ON; and (v) TMIOD in DCFDC.



TMIOD

In order to fit the small W-band cavity, silica capillaries (0.7 mm i.d., 0.87 mm o.d., 10 cm length) were sealed at one end and then bent at 90° at about 25 mm from that end. Solutions were degassed in the capillaries by five freeze–pump–thaw cycles and then sealed with a blow-torch while keeping the sample frozen with liquid nitrogen. Samples for X-band examination were contained in 5 mm o.d. tubes at the end of which was fitted a greaseless tap to facilitate degassing.

Treatment of ESR data

Isotropic rotation. If a spin probe can be assumed to be rotating isotropically, the rotational correlation times can be calculated from the following set of equations:

$$w(m_I) = A + Bm_I + Cm_I^2 \tag{1}$$

where $w(m_I)$ is the linewidth for a given nitrogen-14 manifold; the values of B and C can be found from the experimental line heights, h, and linewidths (mT), w, using the equations[17]

$$B = 0.866w_{+1}[1 - (h_{+1}/h_{-1})^{1/2}] \tag{2}$$

$$C = 0.866w_0[(h_0/h_{+1})^{1/2} + (h_0/h_{-1})^{1/2} - 2] \tag{3}$$

then

$$\tau_c{}^B = 15B/(4b\Delta B_0) \tag{4}$$

and

$$\tau_c{}^C = 8C/(28.02 \times 10^6 b^2) \tag{5}$$

The constants b and Δ can be evaluated from the magnetic parameters given in Table 2 using the relationships

$$b = 4\pi[A_{zz} - (A_{xx} + A_{yy})/2]/3 \tag{6}$$

$$\Delta = (2\pi\beta_e)[g_{zz} - (g_{xx} + g_{yy})/2]/h \tag{7}$$

Anisotropic rotation. Rotational motion was studied in the fast-motional region of OTMIOD in toluene (205–273 K) and ON (273–352 K) using a band-shape fitting procedure to allow for anisotropic motion. For high digital resolution, 1.0 or 0.5 mT scan ranges and 1000 data points were used to record each of the nitrogen hyperfine components. Using a least-squares simulation program[18] we found that the spectra can be modelled well by a Voigt (Lorentzian and Gaussian correlation) function including the carbon-13 satellite lines. Figure 1 shows an example of such fitting for the $m_I = 0$ line of

Table 2. Isotropic and anisotropic *g*-factors and nitrogen hyperfine interactions (mT) for the spin probes OTMIOD and BCCD

Parameter	OTMIOD[a] W-band	OTMIOD[b] X-band	BCCD[c] X-band
g_{xx}	2.00911	2.0081	2.0143
g_{yy}	2.00624	2.0057	2.0049
g_{zz}	2.00230	2.0020	2.0025
$\langle g \rangle$	2.00588	2.0053	2.0072
g_{iso}	2.00587	2.0050	2.00709
A_{xx}	0.47	0.50	0.20
A_{yy}	0.45	0.44	0.19
A_{zz}	3.31	3.38	2.90
$\langle A \rangle$	1.41	1.44	1.10
a_{iso}	1.43	1.41	1.099

[a] In toluene and in ON. Errors are ±0.00003 for *g*-factors and ±0.02 mT for hyperfine interactions.

[b] Data taken from TMIOD in toluene.[5,19] Errors are ±0.0002 for anisotropic *g*-factors and ±0.02 mT for anisotropic hyperfine interactions.

[c] Data taken from 4,5-bis(methoxcarbonyl)-1,3,2-dithiazol-2-yl in chloroform.[25] Errors are ±0.0002 for anisotropic *g*-factors and ±0.02 mT for anisotropic hyperfine interactions.

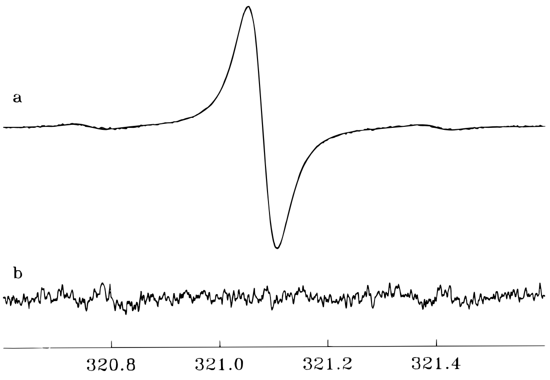


Figure 1. (a) Central line of the X-band experimental ESR spectrum at 210 K of OTMIOD in toluene with superimposed results of least-squares simulations. (b) Difference (residual) between experimental and simulated spectrum shown in tenfold amplification. Lorentzian linewidth $\Delta B^{\mathrm{L}}_{\mathrm{p-p}} = 0.0417 \pm 0.0002$ mT, inhomogeneous broadening modelled as a Gaussian envelope $\Delta B^{\mathrm{G}}_{\mathrm{p-p}} = 0.0188 \pm 0.0003$ mT, carbon-13 hyperfine constant $a^{\mathrm{C\text{-}13}}_{\mathrm{iso}} = 0.639 \pm 0.002$ mT.

the X-band spectrum of OTMIOD in toluene at 210 K. The low value of the residual shown in Fig. 1(b) demonstrates that the model describes the spectrum exceptionally well. Deviations near the carbon-13 satellites are small and are probably caused by nitrogen-15 satellites whose influence was not included in the model. The carbon-13 isotropic hyperfine splitting was found to be 0.639 ± 0.002 mT, which is in good agreement with the value of 0.640 ± 0.005 mT we found previously[19] by direct measurement.

Since the spectra change gradually with temperature, they were fitted automatically: the best least-squares fit of each spectrum was used as a first approximation for fitting the next spectrum in the sequence.[16] The homogeneous (Lorentzian) linewidth, $\Delta B^{\mathrm{L}}_{\mathrm{p-p}}$, determined for each of the nitrogen hyperfine components, m_{I}, as shown in Fig. 1 was analysed in terms of the linewidth parameters A, B and C. At X-band frequencies only B and C are useful parameters for analysing the rotational dynamics of a radical.[20] The ratio C_9/B_9 imposes a linear restraint on the principal values of $\mathbf{R}_{\mathrm{i}}$ of the rotational tensor $\mathbf{R}$ through the following allowed value equation (AVE):

$$\rho_x = \alpha \rho_y + \beta \qquad (8)$$

where $\rho_i = \mathbf{R}_{\mathrm{i}}/\mathbf{R}_{\mathrm{z}}$, $i = x, y$ and the constants α and β are functions of C_9/B_9, principal values of the $\mathbf{A}$ and $\mathbf{g}$ tensors and the magnetic field.[20,21] In this paper, the x-axis is defined as lying along the N—O bond and the y-axis is in the plane of the aromatic ring. The treatment of the W-band data is similar but band-shape fitting was carried out on the whole spectrum (Fig. 2) and now only the parameters A and B of Eqn (8) are useful, hence the constants α and β of the AVE equation are based on A_{94} and B_{94}.

Viscosity measurements

ESR provides a ready means of measuring viscosities of neat liquids by determining the rotational correlation times, τ_c, of a suitable spin probe. The correlation times are related to the Gierer–Wirtz equation:

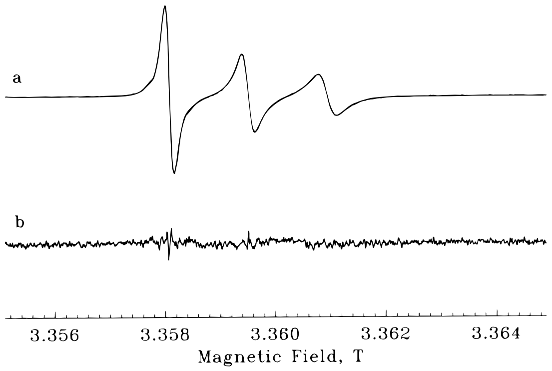


Figure 2. (a) Superimposed calculated and experimental W-band spectra of OTMIOD in ON at 322.4 K. (b) Tenfold amplification of the residual obtained by subtracting the two spectra.

$$\tau_c \approx 4\pi r^3 \eta f / 3kT \qquad (9)$$

where r is the radius of the spin probe, η is the viscosity and f is the microviscosity factor, usually taken to be 0.16 when the volume of the solute is comparable with that of the solvent molecules. A suitable spin probe is 1,1,3,3-tetrakis(deuteriomethyl)isoindolin-2-yloxyl (TMIOD).[22] For better precision, it is advisable to choose a probe that has no unresolved hyperfine interactions which is virtually true for TMIOD.[19] Using the HYPERCHEM[23] computer program and bond lengths and angles from an x-ray crystallographic study,[24] it was estimated that the van der Waals radii in the x, y and z directions are 0.471, 0.426 and 0.361 nm, respectively, hence the effective radius is 0.417 nm. The probe was found to tumble isotropically in water, which was chosen as a viscosity standard. The value of f was found to be 0.13 and this was used to obtain the viscosity data obtained for ON and DCFDC given in Table 3.

RESULTS AND DISCUSSION

Magnetic parameters

Accurate values of the anisotropic g-factors and nitrogen hyperfine interactions of the spin probes are required for measuring viscosities and for analysing rotational dynamics. These were obtained from solid-state X-band ESR spectra of the parent radicals of both

Table 3. Viscosities of ON and DCFDC

ON		DCFDC	
Temperature (K)	Viscosity (kg m^{-1} s^{-1})	Temperature (K)	Viscosity (kg m^{-1} s^{-1})
273.1	7.38×10^{-2}	313.3	1.69×10^{-2}
283.1	5.06×10^{-2}	323.2	1.03×10^{-2}
293.0	3.51×10^{-2}	333.1	0.667×10^{-2}
303.0	2.57×10^{-2}	343.0	0.448×10^{-2}
321.9	1.95×10^{-2}	353.0	0.305×10^{-2}
322.9	1.64×10^{-2}	362.9	0.245×10^{-2}
		382.8	0.173×10^{-2}

BCCD[25] and OTMIOD: for the parent radical of the latter some data were obtained from single-crystal X-band ESR observations.[24] Good data can also be gained from high-field ESR measurements such as we have made at the W-band (94 GHz) on OTMIOD in frozen toluene and in ON. The W-band spectra are illustrated in Fig. 3, from which it can be seen that the hyperfine splittings of the *x* and *y* manifolds are better resolved for toluene than for ON; however, both spectra yielded the same magnetic parameters. The parameters from all these experiments are summarized in Table 2. There is reasonable agreement between the values obtained at the X- and W-bands for OTMIOD; the latter set was used in our calculations since the higher dispersion is likely to give better values. Note that X-band data from TMIOD are listed in preference to those for OTMIOD because the latter did not give a good rigid-limit spectrum. All rigid-limit W-band spectra were corrected for a small microwave shift in a way similar to that described by Budil *et al.*[20] Spectral parameters were derived from the X-band rigid limit spectra by simulation using the QPOWA computer simulation program and those from the W-band spectra were extracted by simulations (optimized with a simplex procedure) of second-derivative spectra using the SIMPOW program.[26]

X-band (9 GHz) measurements on *n*-octylnaphthalene

Plots of C_9 *vs.* B_9 for OTMIOD in ON and in toluene are shown in Fig. 4; two good straight lines are obtained, the slope C_9/B_9 being 0.80 and 0.84, respectively. Most of the data points for these plots were obtained with the ratio of the viscosity to absolute temperature being less than 10^{-5} kg m^{-1} s^{-1} K^{-1}, hence contributions from non-secular spectral densities may become non-negligible. Thus the C_9/B_9 values may best be considered as starting values for calculating anisotropy parameters as will be discussed below.

W-band (94 GHz) measurements on OTMIOD in toluene and in *n*-octylnaphthalene

Spectra were recorded in the temperature ranges 230–294 and 292–343 K for toluene and ON, respectively: these ranges correspond to the fast motion regime. A typical W-band spectrum of OTMIOD in this regime is shown in Fig. 2. Figure 2(a) is composed of two curves, the experimental and the least-squares simulated spectra. The spectra are virtually indistinguishable, as can be seen from the tenfold amplified residual shown in Fig. 2(b); the small deviations are probably caused by magnetic field or microwave frequency instabilities. The slight asymmetry seen in Fig. 2 arises from an admixture of a dispersion often present in high-field ESR spectra obtained with single-channel detection. To compensate for this, an adjustable phase shift was included in the fitting procedure.[16] The carbon-13 satellite lines also had to be included in order to obtain an accurate fit. Deuterium substitution of all the methyl protons in OTMIOD significantly decreases the effects of hyperfine interactions, although uncertainties in the remaining inhomogeneous broadening could still affect the analysis of the data.[14] In our fitting model for the X- and the W-band spectra the remaining inhomogeneous broadenings were modelled as a Gaussian function. From X-band measurements, the width of the Gaussian envelope is 0.0188 ± 0.0002 mT and from W-band measurements 0.0247 ± 0.0004 mT. The larger W-band width of the Gaussian envelope may be attributed to inhomogeneities in the magnetic field (specified as 1 ppm or 0.0034 mT) and in phase and frequency instabilities of the microwave oscillator. Figures 5 and 6 show linewidth parameters measured at the W-band for ON and toluene, respectively. It can be seen that for ON the data conform well to straight-line plots. For toluene, where the data extend to high temperatures, this is also true for B_{94} and C_{94} but for A_{94} a deviation from linearity is seen at $\log(\eta/T) \leqslant 5.5$. This deviation may be explained by spin exchange. At 94 GHz contributions from non-secular terms to the spectral parameters for a typical nitroxide radical can be neglected for $\tau_R \geqslant 20$ ps (or $B \geqslant 0.01$ mT)[16] and this condition is satisfied for all the temperatures used. The fact that non-secular densities can be neglected is additionally illustrated by the linear dependences of B_{94} and C_{94}

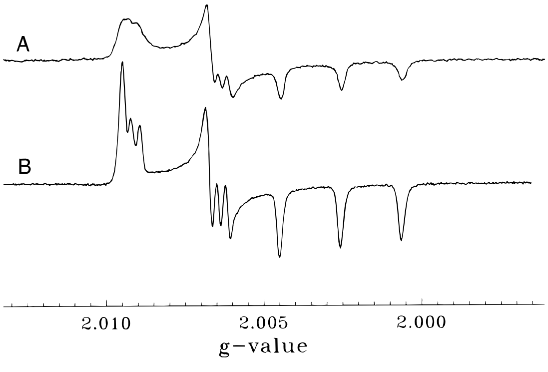


Figure 3. Rigid-limit first-derivative 95 GHz ESR spectra at 140 K of OTMIOD in (A) ON and (B) toluene.

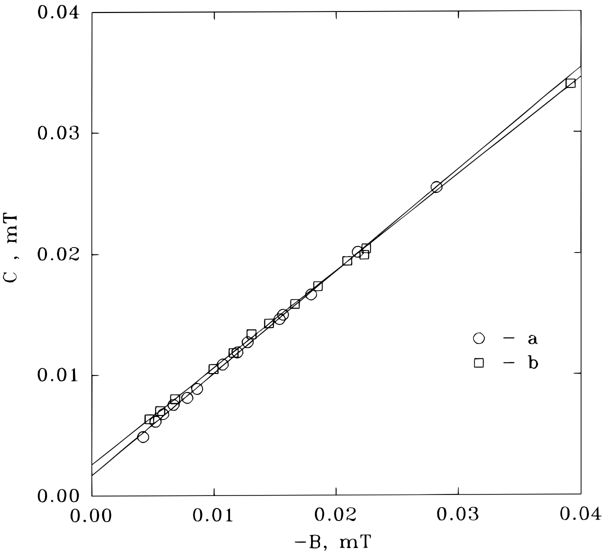


Figure 4. Plot of C_9 against B_9 for OTMIOD in (a) ON and (b) toluene.

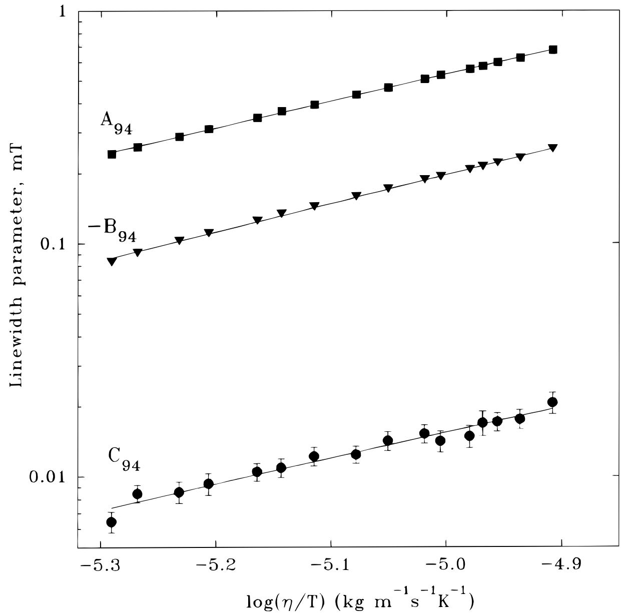


Figure 5. Plot of W-band linewidth parameters against log(*η*/*T*) for OTMIOD in ON.

linewidth parameters in the logarithmic plots shown in Figs 5 and 6. The slopes are essentially the same for the linewidth plots in both these figures which is evidence for the absence of internal motion effects.[20]

The slopes A_{94}/B_{94} of the plots (Fig. 7) are different for the two solvents, being 2.424 for toluene and 2.490 for octylnaphthalene. The intercepts on the A_{94} axis, A', are 0.0317 and 0.0327 mT, respectively: they arise from frequency-independent contributions to the linewidth. These values of A' are typical of those for nitroxyl spin probes. For example, in another study[16] it was found that $A' = 0.025$ mT for 3-doxyl-17*β*-hydroxy-5*α*-androstane in *o*-xylene.

There are two forms of the allowed-value Eqn (8) corresponding to the low- and high-field measurements, namely

$$\alpha_{\mathrm{CB}}\,\rho_x = \beta_{\mathrm{CB}}\,\rho_y + \gamma_{\mathrm{CB}} \tag{10}$$

$$\alpha_{\mathrm{AB}}\,\rho_x = \beta_{\mathrm{AB}}\,\rho_y + \gamma_{\mathrm{AB}} \tag{11}$$

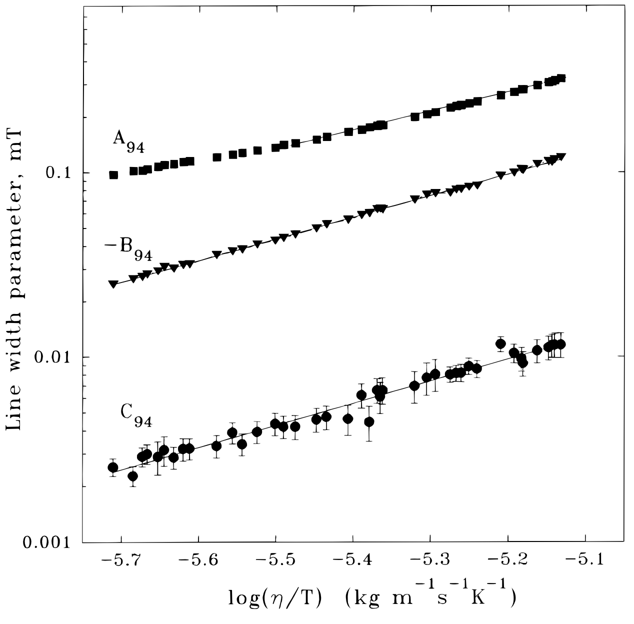


Figure 6. Plot of W-band linewidth parameters against log(*η*/*T*) for OTMIOD in toluene.

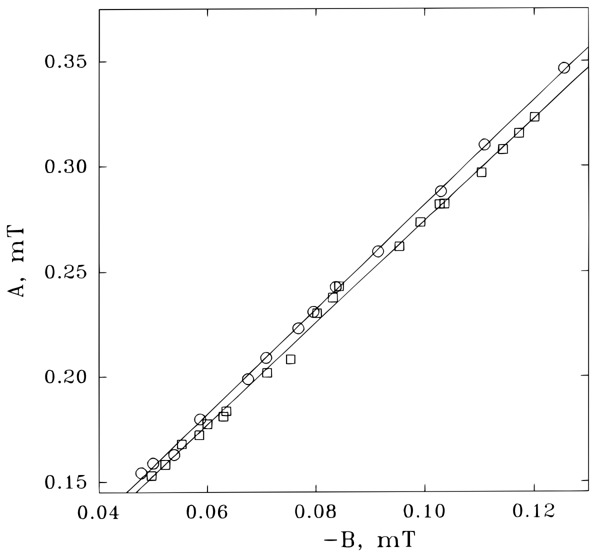


Figure 7. Plot of A_{94} against B_{94} for OTMIOD. Circles represent the ON data and squares the toluene data.

Plots of these functions are shown in Fig. 8. For OTMIOD in toluene the intersections of the two lines occur at $\rho_x = 5.4 \pm 0.3$, $\rho_y = 2.5 \pm 0.2$ and for OTMIOD in octylnaphthalene at $\rho_x = 6.7 \pm 0.3$, $\rho_y = 2.5 \pm 0.2$. The ellipses drawn at the intersections indicate the uncertainties in the measurements. These parameters show that in each solvent OTMIOD rotates fastest about the axis aligned with the N—O bond of the radical, while the slow rate of rotation is about the axis perpendicular to the aromatic ring. The data also show that R_x is greater for ON that for toluene while R_y and R_z are about the same. Once ρ_x and ρ_y are known, then the optimum values of τ_c can be found as a function of temperature. The anisotropy was found to be independent of temperature.

The data reveal that OTMIOD tumbles anisotropically in both toluene and octylnaphthalene, giving three values of τ_c in the three directions *x*, *y* and *z*, where the *x*-axis lies in the direction of the N—O bond of

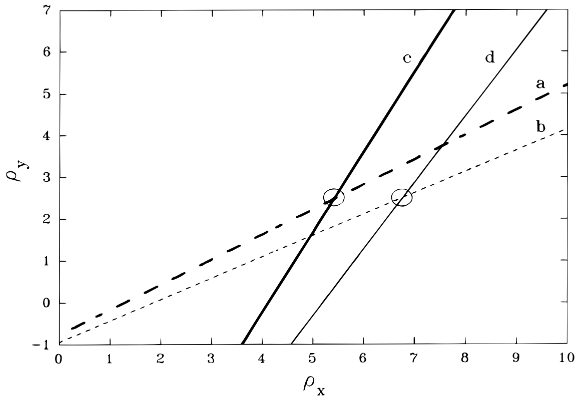


Figure 8. Anisotropy parameters for OTMIOD: linear constraints imposed by X-band measurements in (a) toluene and (b) ON and by W-band measurements in (c) toluene and (d) ON.

OTMIOD and the y-axis is at right-angles to it and in the plane of the molecule. In our analysis we assumed that the magnetic and molecular axes are coincident: this can be justified because Earle *et al.*[27] have shown that a deviation from coincidence of as much as 15° does not affect the results. From a single-crystal ESR study we have shown that the axes of the g and A tensors are coincident.[24] The values of the three correlation times at 298 K are 14 ± 1, 31 ± 2 and 76 ± 6 ps for toluene and 99 ± 7, 266 ± 15 and 669 ± 42 ps for ON, giving values for τ_R, the rotational time of the probe of 27 and 195 ps, respectively. The activation energies for the three directions were within experimental of each other and were found to be 13.4 ± 0.5 and 27 ± 1 kJ mol^{-1} for toluene and ON, respectively. The activation energies are in fair agreement with those associated with the viscosities of toluene and ON, which are 8.7 ± 0.5 kJ mol^{-1} and 23 ± 1 kJ mol^{-1}, respectively.

NMR carbon-13 relaxation measurements on *n*-octylnaphthalene

For a rigid molecule, the T_1 and NOE values of a carbon-13 nucleus relaxing through dipole interactions with N bound proton are given by[28]

$$T_1^{-1} = (N/10)(2\pi R)^2[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C) \tag{12}$$

$$\mathrm{NOE} = 1 + \left(\frac{\gamma_H}{\gamma_C}\right)\left\{\frac{[6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)]}{[6J(\omega_H + \omega_C) + 3J(\omega_C) + J(\omega_H - \omega_C)]}\right\} \tag{13}$$

where R is the dipolar coupling constant $(\mu_0/4\pi)r^{-3}\gamma_C\gamma_H(h/2\pi)$, γ is the magnetogyric ratio of a given nucleus and $J(\omega)$ are the spectral densities:

$$J(\omega) = 2\tau_c/[1 + (\omega\tau_c)^2] \tag{14}$$

In semi-rigid molecules, the reduced Lorentzian spectral density,

$$J(\omega) = S^2\{2\tau_c/[1 + (\omega\tau_c)^2]\} \tag{15}$$

has been used,[9] where the generalized order parameter, S^2, is a measure of the spatial restriction of internal motions. The carbon-13 T_1 and NOE data obtained at 75.4 and 125.7 MHz, listed in Table 1, were fitted using Eqns (12), (13) and (15) as reported previously.[9] It was apparent that the experimental NOE values were consistently lower than the calculated values. This discrepancy arises from a significant contribution to the relaxation from chemical shift anisotropy. This contribution is given by[29]

$$(T_{1\,\mathrm{CSA}})^{-1} = R_{1\,\mathrm{CSA}} = (\gamma^2 B_0^2/15)(\Delta\sigma)^2(1 + \eta^2/3)J(\omega_c) \tag{16}$$

where $\Delta\sigma = \sigma_{zz} - (\sigma_{xx} + \sigma_{yy})/2$ and the anisotropy parameter $\eta = 3(\sigma_{xx} - \sigma_{yy})/2\Delta\sigma$, and $|\sigma_{zz}| \geqslant |\sigma_{yy}| \geqslant |\sigma_{xx}|$. Thus the reduced spectral density given in Eqn (15) becomes

$$R_{1\,\mathrm{CSA}} = (\omega_c{}^2/15)(\Delta\sigma_{\mathrm{eff}})^2 S^2 J(\omega_c) \tag{17}$$

where $(\Delta\sigma_{\mathrm{eff}})^2 = \Delta\sigma^2(1 + \eta^2/3)$. Putting $\mathrm{NOE} = 1 + x$, Eqn (13) becomes

$$\mathrm{NOE} = 1 + x[R_{1\,\mathrm{DD}}/(R_{1\,\mathrm{DD}} + R_{1\,\mathrm{CSA}})] \tag{18}$$

An Arrhenius temperature dependence was assumed for τ_c and parameterized in terms of the correlation time at 298 K, τ_c (298) and an activation energy, E_a.[9]

The relaxation data for carbons 2, 3, 4, 6, 7 and 8 are not distinguishable within experimental error but they are very different from carbon 1. Thus the data for the former carbons were fitted simultaneously and separately from carbon 1. The results are shown in Table 4. It can be seen that all the parameters except τ_c (298) are within experimental error. The $\Delta\sigma_{\mathrm{eff}}$ values compare favourably with literature values for other protonated aromatic carbons (see Table 5).

From Table 4 it can be seen that carbon 1 has the longest correlation time of 277 ps whereas the other six carbons have a single value of 140 ps. The simplest interpretation of this is that there is faster rotation about an axis parallel to the C—H vector of carbon 1. The C—H vectors for the other carbons then subtend an angle of 60° to this axis. Using the Woessner equations[32] values of $\tau_\parallel$ and $\tau_\perp$ of 64 ± 8 and 277 ± 22 ps, respectively, were found, giving a value for the rotational correlation time, τ_R, of ON of 133 ± 13 ps. Thus, while $\tau_\perp$ (277 ps) agrees with the value of τ_y (266 ps) found for the spin probe, it is much smaller than the probe value of τ_z (669 ps), and $\tau_\parallel$ (64 ps) is shorter than τ_x (99 ps) found for the probe. Additionally, τ_R (195 ± 14 ps) for the latter is longer than the corresponding value for octylnaphthalene; this probably arises from the fact that the head group of OTMIOD is larger than that of ON. The activation energies from the ESR and NMR data are in good agreement, being 27 ± 1 and 30 ± 2 kJ mol^{-1}, respectively, but they are higher than the value of 23 ± 1 kJ mol^{-1} found from the viscosity data.

Table 4. Parameters derived from the T_1 and NOE data for some aromatic carbons of 5-*n*-octylnaphthalene

Parameter	Carbon 1	Carbons 2, 3, 4, 6, 7, 8
S^2	0.66 ± 0.03	0.68 ± 0.02
$\Delta\sigma_{\mathrm{eff}}$ (ppm)	183 ± 15	201 ± 16
τ_c (298) (ps)	277 ± 22	140 ± 7
E_a (kJ mol^{-1})	30.2 ± 2.1	30.6 ± 1.1

Table 5. $\Delta\sigma_{\mathrm{eff}}$ values for protonated carbons in aromatic hydrocarbons

Molecule	$\Delta\sigma_{\mathrm{eff}}$	Ref.
Benzene	189	30
Toluene	197	30
p-Xylene	178	30
Naphthalene	177, 189	31

Table 6. B and C parameters and rotational correlation times τ_c^B and τ_c^C for BCCD in DCFDC

Temperature (K)	B (mT)	C (mT)	τ_c^B (ps)	τ_c^C (ps)	C/B
373.1	−0.0978	0.102	157	220	−1.04
362.8	−0.114	0.122	183	265	−1.07
352.9	−0.144	0.153	231	332	−1.06
343.1	−0.180	0.189	289	410	−1.05
333.2	−0.244	0.263	392	569	−1.08
323.2	−0.293	0.318	471	682	−1.08
313.4	−0.389	0.393	625	851	−1.01

X-band (9 GHz) measurements on BCCD in DCFDC

ESR measurements were made on the spin probe BCCD in DCFDC. These showed that the radical is tumbling isotropically, hence it was unnecessary to obtain high-field data. Table 6 lists the values of B, C, τ_c^B and τ_c^C [using Eqns (2)–(7)] obtained at various temperatures. It can be seen that isotropic tumbling is indicated by the fact that C_9/B_9 is close to unity. From these data we found that the activation energy for tumbling is 23 ± 3 kJ mol^{-1} and the rotational correlation time at 298 K is estimated (by extrapolation) to be 2800 ± 500 ps.

The NMR relaxation data for DCFDC require a more elaborate interpretation than those for ON, which will be described elsewhere.[13] However, a summary of the main findings can be given here. The lowest temperature used in the experiments was 317.2 K but the value of τ_c at 298 K can be obtained by extrapolation and is found to be 3190 ps, in good agreement with the ESR value; the activation energy for the tumbling motion is 38 ± 7 kJ mol^{-1}, which is to be compared with the value of 39 ± 1 kJ mol^{-1} found for the activation energy associated with the viscosity of DCFDC. Again, the activation energies are in good agreement, However, the activation energy found from the ESR measurements is lower. The results we found in this study can be compared with those we found earlier[1] for measurements made with the BCCD spin probe in 2,4-dicyclohexyl-2-methylpentane (DCMP), which is not as close in structure to BCCD as is DCFDC. BCCD tumbles anisotropically in DCMP, the C_9/B_9 ratio being about -1.5.

CONCLUSION

The activation energies and rotational correlation times obtained in this study are listed in Table 7. The following conclusions can be drawn.

Table 7. Activation energies, E_a, for the overall rotational correlation times, τ_c, and viscosities and τ_c values at 298 K

	E_a (kJ mol^{-1})	τ_c (ps)
OTMIOD in ON (ESR)	27 ± 1	99 (x), 266 (y), 669 (z)[a]
ON (NMR)	30 ± 2	64 (∥), 277 (⊥)[b]
ON viscosity	23 ± 1	—
OTMIOD in toluene (ESR)	13.4 ± 0.5	14 (x), 31 (y), 76 (z)[a]
Toluene viscosity	8.7 ± 0.5	—
BCCD in DCFDC (ESR)	23 ± 3	2800
DCFDC (NMR)	38 ± 7	3190
DCFDC viscosity	39 ± 1	—

[a] These are τ_c values for the three rotational axes.
[b] These are the τ_c values for rotation about parallel (∥) and perpendicular (⊥) axes parallel to the C—H vector of carbon 1.

(i) There is reasonable agreement between the activation energies found for *n*-octylnaphthalene.
(ii) The activation energy for DCFDC found from the spin probe measurements is at variance with the values obtained from the NMR and viscosity data. Similarly, the spin probe OTMIOD in toluene does not give an activation energy in agreement with the viscosity value, thus demonstrating the need for matching of the spin probe with the solvent.
(iii) There is fair agreement between the rotational correlation times at 298 K for the systems studied by two different magnetic resonance techniques: the value of τ_c (298) found by NMR for ON agrees within experimental error with the ESR value.

The use of ESR at two frequencies (X- and W-band) allowed the calculation of the components of the rotational diffusion tensor for a fully anisotropic rotor. The sophisticated spectral data fitting procedures used, including allowance for inhomogeneous broadening and admixture of dispersion mode, maximize the precision of the data reported.

From the results obtained it can be seen that the matched spin probe approach using ESR provides a measure of the three anisotropic τ_c values, but these values are not available by NMR for the molecules studied here.

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