



ESR line shape studies of N(4n butyl benzilidine) 4amino 2,2,6,6tetramethyl piperidine 1oxide (BBTMPO) in toluene

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Citation: The Journal of Chemical Physics **84**, 577 (1986); doi: 10.1063/1.450603 View online: http://dx.doi.org/10.1063/1.450603 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/84/2?ver=pdfcov Published by the AIP Publishing

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ESR line shape studies of *N*-(4-*n* butyl benzilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO) in toluene

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(Received 13 August 1985; accepted 18 September 1985)

BBTMPO was synthesized by a condensation of 4-n butyl benzaldehyde and 4-amino 2,2,6,6tetramethyl piperidine N-oxide (4-tempamine). The shape of the resulting spin probe, estimated using the Dreiding models, is a spherocone of length 10.7 Å capped by hemispheres of radii 6.6 and 4.0 Å, respectively. The magnetic parameters of BBTMPO in toluene at 77 K were determined. Variable temperature ESR line shape studies in the temperature range of 142-211 K revealed that BBTMPO exhibited anisotropic rotational diffusion in toluene along the long axis of the spherocone and in the direction parallel to the N-O bond. Rotational diffusion along the long axis was found to be 3 ± 0.5 and 7 ± 0.5 times faster for frozen and liquid toluene, respectively, than the other two axes. The line shapes have been simulated by using the stochastic Liouville theory of slow-motional effects on ESR spectrum. The slow tumbling spectrum (158 K) in the model-sensitive region showed good agreement for a Brownian model. The plot of τ_R vs 1/T over the whole temperature range yield a good linear fit with two slopes, with the activation energy for reorientation process of 4.9 kcal/mol in the liquid state, and 9.9 kcal/mol in the solid state. The higher activation energy of rotational reorientation coupled with a lower anisotropy of molecular reorientation (N) in the solid state, indicates that the rotational degrees of freedom is more restricted in the frozen state than in the liquid state. Molecular reorientation for BBTMPO in toluene was analyzed in terms of the hydrodynamic free space model for molecular relaxation in liquids. The stickiness factor S was found to be 0.6 while the anisotropic interaction parameter κ which measures the coupling of rotation to translation was found to be 0.7. For perdeuterated 2,2,6,6-tetramethyl-4-piperidine N-oxide (PD-Tempone) in toluene the stickiness factor was calculated to be 0.3, and k was 0.4. The doubling in size and weight in going from PD-Tempone to **BBTMPO** increases the stickiness factor and κ from 0.3 to 0.6, and 0.4 to 0.7, respectively. The similarity in the structure of BBTMPO to that of liquid crystal methoxy benzilidine butyl aniline (MBBA) and its potential use as a spin probe for MBBA is discussed.

INTRODUCTION

Detailed ESR and ELDOR relaxation studies have been made on the nitroxide spin probe 2,2,6,6-tetramethyl piperidine N-oxide in liquid and frozen media.¹⁻⁴ The reorientational motion of this spin probe has been found to be isotropic in toluene and glycerol-water solvents.¹ Since Tempone has an isotropic overall shape this is not too surprising. In this paper we wish to study the effect of solute size on the reorientational motion of the probe by an analysis of the ESR line shapes using the slow-tumbling theory of Freed.⁵ One of the objectives of this work is to demonstrate the applicability of this theory to experimentally observable systems and to show its usefulness in understanding how ESR line shapes reflect molecular motions.

The solute chosen in this study is N-(4-*n*-butyl benzilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO). This compound was prepared by a condensation of 4-*n*-butyl benzaldehyde and 4-amino 2,2,6,6-tetramethyl piperidine N-oxide (4-tempanine). The structure of BBTMPO is shown in Fig. 1. The resemblance of the molecular structure of BBTMPO to N-(p-methoxy benzilidine)-pbutylaniline (MBBA), a liquid crystal, is very good, and they both have similar length. BBTMPO is about twice the length of Tempone and has a molecular weight (315.5) of about twice that of Tempone (170.3). BBTMPO is thus a suitable probe to study the effect of doubling the solute size and weight on ESR line shapes in neat liquids. It has a rodlike structure and it is rigid, and its rotational motion is expected to be anisotropic. It is about three times heavier and longer than the solvent molecules (toluene).

EXPERIMENTAL

Synthesis of the spin-probe BBTMPO

Preparation of 4-n butyl benzaldehyde

11.82 g (50 mM) of 4-*n* butyl benzaldehyde diethyl acetal (Fluka suppliers) were added in one portion to a well stirred mixture of concentrated hydrochloric acid (5 ml), tetrahydrofuran (15 ml) and distilled water (50 ml). The resulting solution was stirred for 2 days at room temperature and heated to 70 °C for 2 h. Title compound was isolated by ethereal extraction $(3 \times 50 \text{ ml})$. The pooled organic extracts were washed with 10% sodium bicarbonate (30 ml), brine



FIG. 1. The structure of BBTMPO. Using the Dreiding models the molecule can be approximated as a prolate spheroid with a = 8 Å and b = 3.3 Å.

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0021-9606/86/020577-07\$02.10

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(30 ml) and dried over sodium sulfate, and concentrated *in vacuo*. Vacuum distillation yielded 7.12 g (88%) of purified aldehyde as a colorless liquid:

bp: 123-4 °C (10 mm) lit: 70 °C (1 mm),

IR (neat): 3040 (w), 2940 1717 (CHO), 1610 (C=C), 850, 830,

NMR (neat): 0.86 (t, 3H, J = 5), 1.41 (m, 4H), 2.56 (t, 2H, J = 7)

7.23-7.77 (AA 'XX', 4H, J), 9.97 (s, 1H).

N-(4-n butyl benzylldene) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BBTMPO).

In a 25 ml round bottom flask connected to a Dean Stark trap were placed 1 g (5.84 mM) of 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (Molecular Probes suppliers) and 1.06 g (6.54 mM) of 4-n butyl benzaldehyde in 15 ml of benzene. After one hour of reflux the resulting dark red solution was concentrated *in vacuo* to yield 1.89 g of crude material as an orange solid (mp: 63-67 °C). A 1.00 g portion of this material was purified by filtration on a 15*1 cm column filled with neutral alumina with 100 ml of hexane as an eluant. Concentration of the filtrate yields 0.72 g of the title compound as light brown needles (mp: 80-81.5 °C) of sufficient purity (74% from tempamine). The analytical sample was obtained by several recrystallizations from hexane (mp: 81.5-82 °C):

IR (KBr): 3010 (w), 2970, 2928, 2850 (br), 1640 (C=N), 1606

(C=C), 1450, 1235, 1170 (N-O), 830.

The elemental composition and the result of the elemental analysis for BBTMPO $(C_{20}H_{31}N_2O)$ is as follows:

C% 76.14	H% 9.90	N% (8.87)	(Theoretical)
C% 76.03	H% 9.90	N% (8.83)	(Experimental).

Line shape measurements

The ESR spectra were taken over a range of temperatures from 142 to 211 K and at liquid nitrogen temperature (77 K) with a Varian E-109 spectrometer interfaced with an E-953 data acquisition system at the X-band frequency (9.1 GHz) and a modulation frequency of 100 kHz. Both microwave power and modulation were verified experimentally to be at least ten times below the onset of broadening. The spectra were centered in a magnetic field of 3248 G and had a scan range of 100 G. Magnetic field sweep was calibrated with a Varian E-500-2 self-tracking NMR Gaussmeter. Microwave frequencies were measured with a Hewlett-Packard 5342A microwave frequency counter. Spectra were all signal averaged three times to increase the signal-to-noise ratio. Recorded spectra were digitized to 4096 points and stored on cassette tapes for later analysis. The temperature was controlled by a Varian E-257 variable temperature unit to within ± 0.5 °C. The absolute temperature was checked at the geometric center of the cavity with a copper-constantan thermocouple and found to be accurate to ± 1 °C. The temperature gradient over the active region of the cavity, relative to temperature at the center, was ± 0.5 °C. Scan speed and

time constant were also carefully chosen so as not to introduce any artifact from scanning.

Samples in the concentration range of $(3 \pm 2) \times 10^{-4}$ M were degassed on a Pope vacuum line and toluene purchased from Merck was used without further purification. The sample tubes were 3 mm i.d. by 4 mm o.d. Pyrex tubing. The sample tube was adapted to 9 mm o.d. at the open end in order to fit into the quick disconnect fitting (Seal structure, Sargent-Welch part No. S-76639-A, size 24/40) on the vacuum line manifold. The sample tube was immersed in liquid nitrogen and the valve opened to the vacuum system. After several freeze-pump-thaw cycles, the sample tube was sealed by using a torch. The vacuum measured by a digital vacuum gauge manufactured by Granville-Philips was 10 mT. The concentration of the nitroxide in toluene was checked experimentally and found to be absent of broadening due to exchange.

RESULTS AND DISCUSSION

The most important requirement in analyzing slowtumbling spectrum is to have accurate values of magnetic tensors A and g determined from the rigid limit spectrum. These magnetic parameters are needed for the simulation of the variable temperature spectra. The rigid limit spectrum of BBTMPO in toluene at 77 K is shown in Fig. 2(a). The rigid limit simulation of BBTMPO in toluene in Fig. 2(b) was performed using the general methods of Lefebre and Maruani⁶ adapted to nitroxides by Polnaszek.⁷ The simulation employs Simpson's numerical integration over θ in 85 intervals and over φ in 40 intervals. The central region of the rigid limit spectrum of BBTMPO in toluene is not as well resolved compared to that of the deuterated nitroxide spin probe because of inhomogeneous broadening by the 12 protons. The parameters A_z and g_z correspond to the midpoint of the two extrema which is $2A_z$, while g_z corresponds to the midpoint of the extrema. g_x , g_y , A_x , and A_y and the linewidth are varied to fit the experimental spectrum until the line shape of the central portion is simulated. The Lorentzian line shape gave the best overall fit. The reason that the center of the spectrum has a Lorentzian shape is perhaps a result of some



FIG. 2. (a) Rigid-limit ESR spectrum of BBTMPO in toluene at 77 K. (b) Simulated rigid limit spectrum of (a). The magnetic parameters used for the simulations were $g_x = 2.0097$, $g_y = 2.0060$, $g_z = 2.0023$, $A_x = 7.0$ G, $A_y = 5.3$ G, and $A_z = 34.20$ G.

TABLE I. Magnetic parameters of BBTMPO in toluene.

g _x	<i>g</i> _y	g,	(g)	A _x	A,	A,	α	ß
2.0097	2.0060	2.0023	2.0060	7.0 G	5.3 G	34.20 G	4.9 G	0.2 G

residual motion at 77 K and therefore the condition for the validity of a rigid limit $|H_1(t)\tau_R/\hbar| > 1$ is not as strong for the center of the spectrum $(A \sim 5 \text{ G})$ as it is for the outer part of the spectrum $(A \sim 33 \text{ G})$. This may be the cause of orientationally dependent linewidth needed to fit the spectrum. The form for the orientationally dependent intrinsic linewidth is assumed to be

$$T_2^{-1} = \alpha + \beta \cos^2(\theta),$$

where θ is the polar angle relative to the z axis of the nitroxide. These α and β values are listed in Table I. α and β values were 4.9 and 0.2 G, respectively. The intrinsic linewidth for the parallel (z) orientation can be determined from fitting the low-field peak. Figure 2(b) is the simulated rigid limit spectrum of BBTMPO in toluene using the magnetic parameters which gave the best fit. These magnetic parameters are listed in Table I.

The ESR spectra of BBTMPO in toluene were recorded as a function of temperature from 142 to 211 K. Figure 3 shows the ESR spectra of BBTMPO in the liquid state above the freezing point to toluene (163 K), and Fig. 4 shows the ESR spectra of BBTMPO in the solid state. The ESR spectra in Fig. 3 reveal that these spectra are very different from those encountered in solutions at X band in the motionally narrowing region. For example, in a nonviscous solvent nearly all nitroxides exhibit three equally spaced sharp hyperfine lines of nearly equal height. The sharp lines are caused by rapid isotropic tumbling motion which averages away all anisotropic effects in the g tensor and the electron-



FIG. 3. Experimental ESR spectrum of BBTMPO in toluene in the temperature range of 162.8–211 K.



FIG. 4. Experimental ESR spectra of BBTMPO in frozen toluene in the temperature range of 162.8–142 K.

nuclear hyperfine (A) tensor. If the rotational motion is slowed by increasing the solvent viscosity, averaging is incomplete. The result is unequal broadening of the three derivative peaks and the spectrum becomes asymmetric. For PD-Tempone in toluene, the g and A components are such that in X-band measurements the center-field line is slightly shorter than the low-field line, while the high-field line is always significantly shorter than the other two lines. As temperature is decreased (or viscosity is increasing), the lowfield line becomes progressively shorter than the center-field line while the intensity of the high-field line decreases even further. The point to be made here is that as the viscosity increases, the intensity of the low-field line becomes less than that of the central line. The ESR spectra in Fig. 3, which were taken above the freezing point of toluene, showed the unusual feature that the low-field line was sharper than the center-field line and clearly indicated anisotropic rotational diffusion of BBTMPO in toluene. Such behavior has already been observed^{8,9} but detailed theoretical interpretations were not given.

The spectra in Fig. 5 were simulated by using three different axes (x', y', z') of rotation holding the anisotropy (N)of the rotation at 7. We define N as the ratio R_{\parallel}/R_{\perp} , where R_{\parallel} is the rotational diffusion constant along the z' symmetry axis, R_{\perp} is the rotational diffusion constant along the x' and y' axes, and the rotation is assumed to be axially symmetric. Figure 5 shows the effect of anisotropic rotational diffusion (N = 7) along the x', y', and z' axes on the intensity of the three derivative lines. The feature that emerges from this simulation is that only for z' = X the intensity of the lowfield line is the highest among the three lines and the intensities of the three lines decreases from low field to high field. For z' = Y the intensity of the low-field line is less than that of the center-field line, while for z' = Z axis, the intensity of the low-field line. The N

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FIG. 5. Effect of the axes of rotation on the intensity of ESR lines at N = 7.

value of 7 was obtained after a careful simulation of the experimental spectrum by using different anisotropy (N) of the rotation. The rotationally invariant linewidth, which allows correction for the inhomogeneous broadening by unresolved hyperfine structure, in all the three simulations is 1.1 G. This is a reasonable estimate for linewidths of ~1.7 G observed experimentally for the center-field line.⁹

The ESR spectra in Fig. 4 were taken at temperatures below the freezing point of toluene. These spectra are representative of the slow-motional region. Correct treatment of such data requires the simulation of ESR spectra in the slow tumbling region. For this purpose the stochastic Liouville theory for slow-motional effects on ESR spectra for S = 1/2and I = 1 for nitroxides⁴ must be used to simulate magnetic resonance line shapes when the motional narrowing theories^{11,12} break down. For isotropic solvents this occurs when the line starts to become asymmetric and/or the splitting constants begin to deviate from a constant value.

The slow tumbling theory⁵ has been successful in the theoretical analysis of the ESR line shapes in the slow or intermediate rotational regions. In these regions the radical is tumbling too slowly for the earlier relaxation theories to apply, yet is not tumbling slowly enough for the spectrum to have approached its rigid limit. If we define $H_1(t)$ as the rotational-dependent perturbation in the spin Hamiltonian and τ_R as the rotational correlation time, then slow tumbling in magnetic resonance means the inequality $|H_1(t)\tau_R/\hbar| < 1$ is no longer fulfilled. Freed, Bruno, and Polnaszek¹³ have developed a general approach used to simulate magnetic resonance line shapes for any process that involved Markoffian stochastic modulation of $H_1(t)$. This method can describe ESR line shapes over the whole range of τ_R from the motional narrowing region through the rigid limit.

In Fig. 6 the ESR spectra were simulated by varying the τ_R values, taking N = 7 and using the magnetic parameters in Table I. The criterion for the simulation is a match of the intensities of the three lines with the experimental spectra and the width of the center-field line. The corresponding τ_R values for each spectrum were also given in Fig. 6. Analysis of the slow motional spectra showed very good agreement between calculated and observed spectra regardless of which reorientational models were used. This means that in the



FIG. 6. Simulated spectra for Fig. 3 using N = 7 (except for the last spectrum in which N was 4).

temperature range of 163–211 K, the ESR line shapes of BBTMPO in toluene are not model sensitive. In all the simulations, N was 7 except for the last spectrum [Fig. 6(e)] in which N was 4. We found that this spectrum, which corresponds to BBTMPO in frozen state, could not be simulated by using N = 7, because it would lower the intensity of the low-field line by too much. As noted by Goldman *et al.*,¹⁴ the primary effect of varying the value of N is to change the relative amplitude of the low-field line, the N = 4 determined from our simulation did give a very good match of the relative amplitude of the low-field line.



FIG. 7. Comparison of experimental spectrum at 157.9 K of BBTMPO in toluene with simulated spectra in the model-sensitive region.

Figure 7 shows a comparison of the experimental spectrum at 157.9 K with three simulated spectra using Brownian, moderate jump, and strong jump models. This is the model-sensitive region where $\tau_R \simeq 1 \times 10^{-8}$ s. The simulation was obtained by adjusting τ_R holding N = 3. It can be seen from Fig. 7(b) that the Brownian model gave the best overall fit. We note with passing interest that for small nitroxides such as PD-Tempone, it has been shown¹ that in the slow motional region, a moderate jump diffusion model gives very good agreement between the experimental spectrum (of PD-Tempone in toluene) and the simulated spectrum, while the comparison is quite unsatisfactory for the Brownian and strong jump models.

Figure 8 showed the theoretical simulation of the ESR spectra in Fig. 4 with N = 3 and the Brownian model. The magnetic parameters used in the simulations were those listed in Table I. For simulations where $\tau_R < 5 \times 10^{-9}$ s, we generally used an L value of 10, and K value of 4. Using the equations in the slow tumbling program, we obtained N DIM = 87, J DIM = 28, NSY = 20, and NSY2 = 63. For τ_R longer than 5×10^{-9} s, we increased the value of L and K to 22 and 8, respectively. We then obtained N DIM = 297, J DIM = 40, NSY = 38, and NSY2 = 234. With higher L and K values, we can simulate line shapes for $\tau_R = 6.25 \times 10^{-7}$ s.

The parameters mentioned above are defined as follows. N DIM is the dimension of the main program and is calculated by using the formula $NDIM = 3 + [6 \times L \times (L + 6)/8] - [3 \times (L - K TERM) \times (L - K TERM + 2)/4],$ J DIM = $(3 \times K TERM) + 16$ when L > K TERMand J DIM = $(3 \times K TERM) + 10$ when L = K TERM. NSY is calculated by using the formula NSY = $5 + (3 \times L MAX/2)$, and NSY2 is calculated by using the formula NSY2 = $3 + [3 \times L MAX \times (L MAX + 6)/8]$. L is the terminating L value in the expansion and it is an



FIG. 8. Simulated spectra for Fig 4 using the Brownian model. The N values were all 3 except for the last spectrum in which N was 4.

even number. K TERM is the terminating value of K for the asymmetric expansion terms due to differences in the X and Y principal axes of the A and g tensors. Values of K TERM must be even and less than or equal to the L value. L MAX is the maximum L value to be used for any plot, and it must be equal or less than L.

The values of τ_R so obtained are plotted as a function of η/T for the spectra taken at the higher temperatures in Fig. 9. It can be seen that τ_R is linear in η/T . The slope of τ_R vs η/T is 1.70(5)×10⁻⁶ s K P.⁻¹. For spherical top or linear molecule this correlation time can be expressed as

$$\tau_R = (4/3)(\pi r_0^3/k_B)(\eta/T) \cdot \kappa, \tag{1}$$

where k_B is the Boltzmann constant, T the absolute temperature in K, η the coefficient of shear viscosity of the solvent, r_0^3 a molecular volume which is constant for BBTMPO, and κ an experimentally determined dimensionless coupling parameter called the anisotropic interaction parameter.^{16–18}

The molecular volume of BBTMPO has been estimated using Dreiding models to be 333 Å³ with the assumptions that the Tempone ring has a chair conformation with both nitroxy and imino groups in the equatorial position, and the imine double bond has an "anti" configuration as shown in Fig. 1. (These assumptions are currently tested by an x-ray crystallographic analysis.) From the slope of τ_R vs η/T , this gives $\kappa = 1.70(5) \times 10^{-6} \times 1.381 \times 10^{-16}/[333 \times (10^{-8})^3]$ = 0.707. κ for Tempone in toluene¹ and jojoba oil¹⁵ are 0.41 and 1.8×10^{-2} , respectively.

The data above can be analyzed in terms of hydrodynamic free space model for molecular relaxation in liquids¹⁹, a theory based on the existence of free spaces in the hydrodynamic continuum in which the molecule can rotate. The most probable shape for BBTMPO is a spherocone consisting of length 10.7 Å capped by hemispheres of radii b = 6.6Å and b' = 4.0 Å at the base and the top, respectively. The ratio of b'/b is 0.61. The estimated f_{stick} and f_{slip} assuming l/b = 2.5 - b'/b are 1.55 and 0.33, respectively. From the relationship

$$f_{\rm slip} = f_{\rm stick} C_{\rm slip}^{\rm hyd}, \tag{2}$$

 $C_{\rm slip}^{\rm hyd} = 0.33/1.55 = 0.213,$



FIG. 9. Plot of τ_R vs η/T in the temperature range of 162.8–192.5 K.

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where f_{stick} and f_{slip} are dimensionless rotational friction coefficients¹⁸ under stick and slip boundary conditions, respectively. $C_{\text{slip}}^{\text{hyd}}$ is a result of hydrodynamic calculation in which a large spheroidal object rotates in a continuous, homogeneous fluid. The stickiness factor²¹ can be calculated from the relationship

$$S = \frac{\kappa - C_{\text{slip}}^{\text{hyd}}}{1 - C_{\text{slip}}^{\text{hyd}}} = \frac{0.707 - 0.213}{1 - 0.213} = 0.628.$$
 (3)

The stickiness factor S is independent of molecular geometry and is zero in the slip and 1 in the stick limit, 0 < S < 1.

The stickiness factor can also be calculated by assuming that BBTMPO is a prolate spheroid in which a = 8 Å and b = 3.3 Å, $a^{\perp} = b/a$. Under stick boundary conditions, the dimensionless rotational friction coefficient calculated according to Perrin's²⁰ formula is $f_{\text{stick}}^{\perp} = 1.83$ and the corresponding values of f_{slip}^{\perp} calculated from

$$f_{\rm slip}^{1} = f_{\rm stick}^{1} \left[1 - (f_{\rm stick}^{1})^{-2/3} \right]$$
(4)

is 0.606. $C_{\text{slip}}^{\text{hyd}} = f_{\text{slip}}^1 / f_{\text{stick}}^1 = 0.331 \text{ and } S = 0.562 \approx 0.6.$

Tempone is a prolate axially symmetric ellipsoid¹ with $a_{\parallel} = a_x = 4.2$ Å and $a_{\perp} = 2.85$ Å. This gives $f_{\text{stick}}^1 = 1.18$ calculated from Perrin's formula and $f_{\text{slip}}^1 = 0.123$ calculated from Eq. 4. $C_{\text{slip}} = f_{\text{slip}}^1/f_{\text{stick}}^1 = 0.104$. The stickiness factor calculated from Eq. 3 is S = 0.344.

The anisotropy for rotation N, defined earlier as $N = R_{\parallel}/R_{\perp}$, is related to the geometric structure factor by means of the Stokes-Einstein equation¹

$$R_i = k_B T / (8\pi \eta a_{\parallel}^3 \sigma_i), \quad i = \parallel \text{ or } 1,$$
 (5)

$$N = R_{\parallel}/R_{\perp} = \sigma_{\perp}/\sigma_{\parallel}, \tag{6}$$

where

$$\sigma_{\parallel} = \frac{2}{3} \lambda^{2} (1 - \lambda^{2}) \left[1 - (1 - \lambda^{2}) \lambda^{-1} \right]^{-1} \times \ln \frac{1 + \lambda}{[1 - \lambda^{2}]^{1/2}} - 1,$$
(7)

$$T_{1} = \frac{2}{3}\lambda^{2}(2-\lambda^{2})\left[(1+\lambda^{2})\lambda^{-1} \times \ln\frac{1+\lambda}{[1-\lambda^{2}]^{1/2}} - 1\right]^{-1},$$
(8)

with

0

$$\lambda = (a_{\parallel}^2 - a_{\perp}^2)^{1/2} / a_{\parallel} \text{ and } 0 < \lambda \le 1.$$
(9)

BBTMPO is a spheroidal particle with semiaxes $a_{\parallel} > a_{\perp}$ where $a_{\parallel} = a_{\nu} = 16$ Å, and $a_{\perp} = 6.6$ Å. One obtains $\sigma_{\parallel} = 1.32 \times 10^{-1}$ and $\sigma_{\perp} = 3.11 \times 10^{-1}$. One obtains N = 2.4 from Eq. (6) which is consistent, within experimental error, with our observation that $N = 3 \pm 0.5$ for BBTMPO in frozen toluene. In the liquid state, N is 7 ± 0.5 . The decrease in N is a result of freezing out of the rotational degrees of freedom in the solid state. Similar effect has been observed for peroxylamine disulfonate (PADS) radical in frozen water and glycerol solvent in which N is 2.9 ± 1 and 4.7 ± 1 , respectively.²²

The dependence of τ_R on 1/T over the whole temperature range studied shown in Fig. 10, yields a good linear fit with two slopes, with the activation energy for reorientation process of 4.9 kcal/mol in the liquid state, and 9.9 kcal/mol in the solid state. The higher activation energy of rotational



FIG. 10. Plot of $\ln \tau_R$ vs 1/T in the liquid and frozen states.

reorientation coupled with a lower N value in the solid state, indicates that the rotational motion is more restricted in the frozen state than in the liquid state.

The molecular structure and shape of BBTMPO is closely related to the liquid crystal MBBA. The structure of MBBA is:



MBBA

BBTMPO can be used to investigate the effect of molecular shape in the "slowly relaxing local structure" (SRLS) model.²³ In the SRLS model, each spin probes sees a net local potential which remains essentially constant during the time scale, τ_R , required for the spin probe to reorient. Then, over a longer time scale, the local reorienting potential relaxes. Since the molecular structure of BBTMPO closely resembles that of MBBA, it may be a more sensitive probe for the SRLS mechanism. In the future, we plan to study the SRLS mechanism using BBTMPO as spin probe.

CONCLUSION

BBTMPO was synthesized via a condensation of 4-n butyl benzaldehyde and 4-amino 2,2,6,6-tetramethyl piperidine *N*-oxide (4-tempamine). The shape of the resulting spin probe has been estimated using the Dreiding models to be a spherocone consisting of length 10.7 Å capped by hemispheres of radii b = 6.6 Å and b' = 4.0 Å at the base and the top, respectively. The rigid limit spectrum of BBTMPO in toluene was recorded at 77 K and the magnetic parameters were determined using the method of Lefebre and Maruani adapted to nitroxides by Polnaszek.

ESR spectra were recorded in the temperature range of 142–211 K. These spectra were simulated by using the stochastic Liouville method. It was found that the ESR spectra could be fitted by using the model of axially symmetric rotational diffusion with the symmetry axis along the long axis of the spheroid and in the direction parallel to the N–O bond. Brownian rotational diffusion was observed in the model sensitive region at $\tau_R \simeq 1 \times 10^{-8}$ s. This model is consistent with a system in which the solute (BBTMPO) is larger than the solvent (toluene). Rotational diffusion about the N–O bond axis was found to be 3 ± 0.5 and 7 ± 0.5 times faster for frozen and liquid toluene, respectively, than about the other axes over a wide range of τ_R values. A lower anisotropy of rotation (N = 3) coupled with a higher activation energy for reorientation ($E_a = 9.9$ kcal/mol) was observed for BBTMPO in toluene in the frozen state. The higher activation energy of rotational reorientation coupled with a lower N value in the solid state, indicates that the rotational degrees of freedom is more restricted in the frozen state than in the liquid state.

Molecular reorientation for BBTMPO in toluene was analyzed in terms of a stickiness factor (S) and found to be 0.6. The anisotropic interaction parameter κ which measures the coupling of rotation to translation was found to be 0.7. For PD-Tempone in toluene the stickiness factor was calculated to be 0.3, and κ is 0.4. The doubling in the size and weight in going from PD-Tempone to BBTMPO increases the stickiness factor and κ from 0.3 to 0.6, and 0.4 to 0.7, respectively.

ACKNOWLEDGMENT

This work was supported by the Research Committee of the University of Petroleum and Minerals as Research Project No. CY/ESR/30.

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