

# Proton and Carbon-13 NMR Relaxation Studies on *t*-Butyl Thiol

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The proton and carbon-13 NMR linewidths and spin-lattice relaxation times have been measured for the liquid and solid phases of *t*-butyl thiol. The abrupt decrease in the proton and carbon-13 linewidths at the solid I → solid II transition temperature is attributed to molecular self-diffusion associated with a change of lattice structure. A molecular jump time of  $6.5 \times 10^{-7}$  s at the melting point for solid I has been obtained. An analysis of the proton and carbon-13 spin-lattice relaxation times for all phases of *t*-butyl thiol is reported. The proton and carbon-13  $T_1$  values show marked discontinuities at the melting point and the solid I → solid II transition temperature. However, whereas the proton data cannot distinguish between solids II and III, the carbon-13 linewidth and  $T_1$  values show pronounced discontinuities at the transition temperature. The latter observation is also reflected in a concomitant increase of about four orders of magnitude in the rotational correlation time at the II → III boundary. The rotational correlation time for solid I is 1.0 ps at the melting point. The dominant motions causing spin-lattice relaxation are overall molecular tumbling in the liquid, solid I and largely solid II phases and reorientation of the *t*-butyl group in solids III and IV.

*t*-Butyl thiol,  $(\text{CH}_3)_3\text{CSH}$ , is one of a series of approximately globular molecules which are known to form orientationally disordered (plastic) solid phases.<sup>1</sup> *t*-Butyl thiol is reported to undergo three isothermal solid-solid phase transitions at 152, 157 and 199 K, with entropy changes of 3.22, 0.50 and 0.58 R, respectively.<sup>2,3</sup> The four solid phases are designated I, II, III and IV in order of decreasing temperature. *t*-Butyl thiol melts at 274 K with a low entropy of fusion (1.09 R), a characteristic of plastic crystals.

An X-ray study<sup>4</sup> of phase I has revealed a random orientation of molecules on a face-centered cubic lattice with  $a = 0.880$  nm. The crystal structures of the lower-temperature phases have not, to our knowledge, been reported. However, Guthrie and McCullough<sup>3</sup> have proposed, on the basis of calculations of molecular disorder, that phases II and III of *t*-butyl thiol are body-centered cubic and hexagonal, respectively. Other evidence<sup>5</sup> indicates, however, that phase II may not be cubic.

NMR methods, in particular proton second moment and spin-lattice relaxation time measurements, have been used extensively to characterize and measure the rates of rotational and translational motions in the brittle and plastic phases of organic solids.<sup>1</sup> Earlier dielectric<sup>6,7</sup> as well as proton<sup>8</sup> and deuterium<sup>5</sup> NMR linewidth studies on *t*-butyl thiol and two of its deuterated analogues indicate that overall molecular reorientation occurs in solid I and probably solid II, whereas a combination of  $C_3$  internal methyl and  $C_3'$  *t*-butyl group rotations seem to take place in phase IV.

A powerful feature of the NMR technique is the possibility of monitoring and studying the resonances of different nuclei. Proton and carbon-13 NMR relaxation time measurements, for example, are complementary in the sense that they monitor the rotations of different internuclear vectors; taken together, results for the two nuclei may thus provide a better characterization of anisotropic motions. In this paper we therefore pres-

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ent the results of proton and carbon-13 linewidth and spin-lattice relaxation time measurements on *t*-butyl thiol in its liquid and solid phases.

## Experimental

*t*-Butyl thiol obtained from Fluka AG was purified by distillation. The freshly distilled liquid was transferred into 3 and 8 mm o.d. NMR tubes, degassed by four freeze-pump-thaw cycles and sealed under vacuum. The sealed NMR tubes were inserted into 5 and 10 mm o.d. NMR tubes containing a small amount of acetone- $d_6$  or deuteriochloroform which served as internal  $^2\text{H}$  lock-signal source. The former and latter samples were used for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements, respectively. At low temperatures, where both the  $^1\text{H}$  and  $^{13}\text{C}$  signals were very broad, we used  $^2\text{H}$  external lock in order to avoid overlap with the sharp signal from the lock substance.

The  $^1\text{H}$  and  $^{13}\text{C}$  spectra were measured at 90.02 and 22.63 MHz on a Bruker CXP 100 spectrometer. Strong proton irradiation ( $\leq 20$  kHz) was used when measuring the  $^{13}\text{C}$  NMR spectra in order to remove scalar coupling and broadening due to  $^1\text{H}$ - $^{13}\text{C}$  heteronuclear dipolar coupling. The sample temperature was regulated and stabilized to within  $\pm 0.5$  K in the high-temperature range (above  $\sim 293$  K) and to within  $\pm 1$  K in the low-temperature range (below  $\sim 293$  K) by means of a Bruker B-ST100/700c temperature control unit.

The  $T_1$  times were measured by inversion-recovery  $(180^\circ - \tau - 90^\circ - T)_n$ , with  $T \geq 5T_1$  except for the quaternary carbon for which fast inversion-recovery ( $T \ll 5T_1$ ) was used.<sup>9</sup>  $T_2$  was measured by a modified Meiboom-Gill spin-echo technique. Short and long  $\tau$ -values in the range  $\sim 0$  to  $1.5 T_1$  (plus the equilibrium value) were alternated in order to minimize systematic errors due to spectrometer performance problems. The number of accumulations varied from 28 to 360, depending on the linewidth and signal-to-noise ratio. Typical  $90^\circ$  pulse widths were about 3 and 12  $\mu\text{s}$  for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively.

Exponential weighting was applied to the 8 K  $^{13}\text{C}$  free induction decays. A non-linear three-parameter fitting of peak heights, using at least 10 experimental points (including the equilibrium intensity), was used for calculating the  $T_1$  and  $T_2$  values. The standard deviations of the  $T_1$  values were of the order of 4–6 %.

## Results and discussion

The half-linewidths,  $\Delta\nu_{1/2}$ , of the  $^1\text{H}$  and  $^{13}\text{C}$  signals were measured for the liquid and solid phases of *t*-butyl thiol. Some hysteresis in the heating/cooling data was observed, suggesting that the samples are very slow to reach equilibrium.

At temperatures just below the melting point it was possible to observe signals due to both a liquid and a solid (plastic) component in the  $^{13}\text{C}$  spectrum. The  $^{13}\text{C}$  methyl signal for solid I appeared 0.41 ppm downfield of the corresponding signal for the liquid phase. Similar downfield shifts of the  $^{13}\text{C}$  signal at the melting point have been observed for pivalic acid, *t*-butyl chloride and hexamethylethane (0.33, 0.40 and 0.57 ppm, respectively).<sup>10,11</sup> The observed downfield shifts for these plastic crystals are largely attributed to environmental changes occurring at the melting point.

For solids I and II the  $^1\text{H}$  signals were broad ( $\Delta\nu_{1/2} \sim 1\text{--}14$  kHz), in contrast to the relatively sharp  $^{13}\text{C}$  signals ( $\Delta\nu_{1/2} \sim 3\text{--}500$  Hz). A striking feature of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra is the marked decrease in the linewidths at the solid I  $\rightarrow$  solid II transition temperature. Only a few cases of line-narrowing on cooling have, to our knowledge, been reported previously for organic crystals.<sup>8,12,13</sup> It is noteworthy, however, that for pivalic acid<sup>12</sup> and *t*-butyl chloride<sup>13</sup> a decrease in the methyl proton linewidth has been observed at the upper thermal transition temperature, and in *t*-butyl bromide<sup>13</sup> at the lower. The abrupt line-narrowing at the solid I  $\rightarrow$  solid II transition temperature for *t*-butyl thiol can probably be explained in terms of enhanced molecular self-diffusion associated with a change of lattice from face-centered cubic in solid I to body-centered cubic in solid II.<sup>8</sup> Further support for this assumption is provided by the observation that the translational jump frequencies of plastic crystals at the melting point are characteristically a factor of five greater for body-centered cubic than for face-centered cubic solids and are independent of the degree of orientational disorder.<sup>14</sup> A discontinuous change in the carbon-13 linewidth was also observed at the solid II  $\rightarrow$  solid III transition temperature. However, it was not possible to distinguish between phases III and IV on the basis of the linewidth data.

The measured linewidths,  $\Delta\nu_{1/2}$ , were used to calculate the spin-spin relaxation time,  $T_2$ , using

the relationship applicable to a Lorentzian line narrowed by a unique motional process, viz.:

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \quad (1)$$

Semi-log plots of the  $T_2$  values obtained versus the inverse temperature are shown in Figs. 1 and 2. The agreement with the directly measured  $T_2$  values is very good (Fig. 2). Owing to rapid overall molecular reorientation in solids I and II, all the intramolecular, and part of the intermolecular,  $^1\text{H}$ - $^1\text{H}$ ,  $^1\text{H}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar interactions are averaged out. We therefore believe that the considerable line-narrowing observed in the proton and carbon-13 spectra for solid I and for the high-temperature region of solid II, is due to averaging of the residual intermolecular dipolar interactions by translational self-diffusion of the molecules in the crystal lattice. By using linear regression on the  $T_2$  proton data, activation energies of 31.5 and 33.6 kJ mol $^{-1}$  have been obtained

for solids I and II, respectively, in good agreement with previously reported values for *t*-butyl compounds.<sup>8,15,16</sup> A similar treatment of the carbon-13  $T_2$  data yields activation energies in the range 26–27 kJ mol $^{-1}$ .

An expression for  $T_2$  may be obtained using Torrey's isotropic random-walk model with average molecular jump time  $\tau$ .<sup>1,17</sup> Since  $\tau^{-1}$  for the plastic phase is much less than the resonance frequency the expression for  $T_2$  simplifies to

$$\frac{1}{T_2} = 0.922 \gamma^2 M_{2r} \tau \quad (2)$$

where  $\gamma$  is the magnetogyric ratio and  $M_{2r}$  is the intermolecular second moment for like spins for the absorption line prior to diffusional narrowing. The proton second moments at supercooled temperatures for solids I and II of *t*-butyl thiol are reported to be  $9 \times 10^{-9} T^2$  and  $1.15 \times 10^{-8} T^2$ , respectively.<sup>8</sup> These values are good estimates of  $M_{2r}$  since self-diffusion is expected to be negligible in the supercooled phases. Using eqn. (2) it is calculated that  $\tau = 6.5 \times 10^{-7}$  s and  $1.1 \times 10^{-4}$  s in solid I at 274 K ( $T_m$ ) and 199 K ( $T_i$ ), respectively. The former value is close to the average value ( $6.2 \times 10^{-7}$  s) reported for a series of fcc solids at their melting points.<sup>14</sup> At 199 K in solid II for *t*-butyl thiol we calculate  $\tau = 4.9 \times 10^{-5}$  s, which is about half the value found for solid I at the same temperature.

The  $^1\text{H}$  and  $^{13}\text{C}$  spin-lattice relaxation times for *t*-butyl thiol have been measured for the liquid and solid phases. Semi-log plots of  $T_1$  versus the inverse temperature are shown in Figs. 1 and 2. The decrease in the  $^{13}\text{C}$   $T_1$  values with increasing temperature in the high-temperature region for the liquid phase (and also for the quaternary carbon of solid I) probably reflects an increasing contribution from the spin-rotation mechanism. The  $T_1$  values for the thiol proton appear to approach a maximum with increasing temperature of the liquid phase, owing to the onset of self-diffusion modulated intermolecular spin-lattice relaxation. The  $^1\text{H}$  and  $^{13}\text{C}$   $T_1$  relaxation times for *t*-butyl thiol are otherwise governed by intramolecular dipole-dipole interactions modulated by molecular reorientation. It is, however, reasonable to believe that the intermolecular dipolar interactions make a small contribution to the observed  $^1\text{H}$   $T_1$  times for the liquid phase and, in the

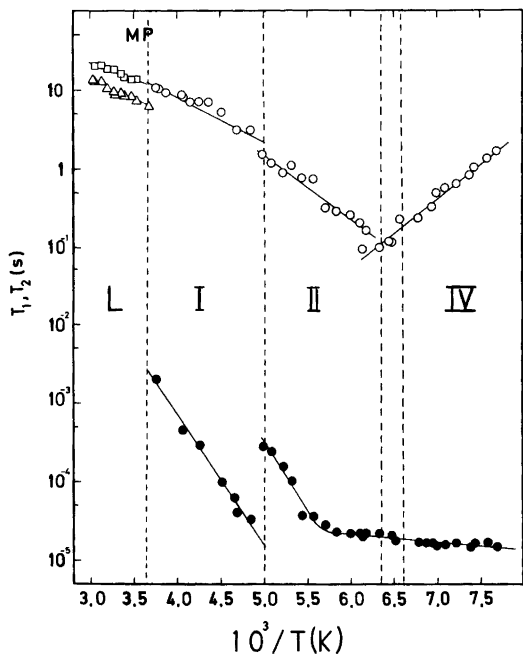


Fig. 1. Proton  $T_1$  (open symbols) and  $T_2$  (filled symbols) relaxation times for *t*-butyl thiol versus reciprocal temperature.  $\Delta$ , methyl protons;  $\square$ , thiol protons;  $\circ$  and  $\bullet$ , methyl and thiol protons.

high-temperature region, for phase I (*vide infra*). A deuteron lineshape study of  $(\text{CD}_3)_3\text{CSH}$  has shown that the  $C'_3$  rotation is significantly faster than the  $C_3$  rotation in solid IV, and that the molecule undergoes a phase change before the  $C_3$  rotation becomes rapid enough to average the quadrupolar interaction ( $\sim 10^{-6}$  s).<sup>5</sup> We have therefore calculated the  $^1\text{H}$  and  $^{13}\text{C}$  spin-lattice relaxation times for *t*-butyl thiol by assuming that the molecules undergo isotropic overall tumbling and/or internal  $C'_3$  reorientations with correlation times  $\tau_r$  and  $\tau_i$ , respectively. Since the molecular structure of *t*-butyl thiol is not known, we have assumed that the *t*-butyl group has ideal tetrahedral C-C-C and C-C-H angles and  $C_{3v}$  symmetry, so that all hydrogen atoms are staggered with respect to the carbon atoms. The  $C'_3$  rotations will then occur between three equilibrium positions separated by  $120^\circ$ . It then follows that the two H-H vectors of the methyl group will make angles  $\theta = 90^\circ$  or  $(180 - 109.5)^\circ/2$  with the  $C'_3$  rotation axis. Similarly, in the absence of  $C'_3$  rotation, two of the three C-H vectors of each methyl group make an angle  $\theta = 70.5^\circ$  with the  $C'_3$  axis, whereas the remaining C-H vector is parallel to this axis.

By using the treatment developed by Stejskal and Gutowsky,<sup>18</sup> and by Woessner,<sup>19</sup> it is now readily shown that the intramolecular dipole-dipole proton spin-lattice relaxation time for the *t*-butyl group is given by

$$\frac{1}{T_1(\text{H})} = (A+B)[g(\omega_{\text{H}}, \tau_r) + 3g(\omega_{\text{H}}, \tau_c)] \quad (3)$$

where

$$g(\omega_{\text{H}}, \tau) = \frac{\tau}{1 + \omega_{\text{H}}^2 \tau^2} + \frac{4\tau}{1 + 4\omega_{\text{H}}^2 \tau^2}, \quad (4)$$

$$\tau_c = (1/\tau_r + 1/\tau_i)^{-1}, \quad A = \frac{3}{20} \gamma_{\text{H}}^4 \hbar^2 r_{\text{HH}}^{-6}$$

and

$$B = \frac{9}{10} \gamma_{\text{H}}^4 \hbar^2 r'_{\text{HH}}{}^{-6}.$$

$r_{\text{HH}}$  is the internuclear H-H separation of a  $\text{CH}_3$  group and  $r'_{\text{HH}}$  is the distance between the centres

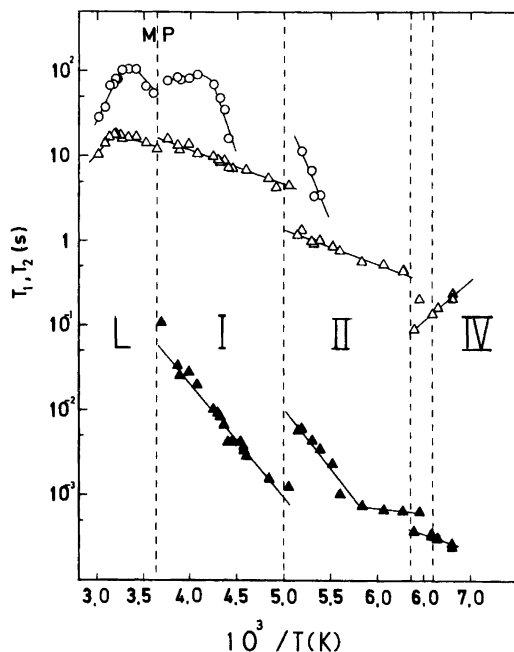


Fig. 2. Carbon-13  $T_1$  (open symbols) and  $T_2$  (filled symbols) relaxation times for *t*-butyl thiol versus reciprocal temperature.  $\circ$ , quaternary carbons;  $\triangle$ , methyl carbons;  $\blacktriangle$  and  $\bullet$ ,  $T_2$  from linewidth and spin-echo measurements of methyl carbons.

of the equilateral triangles formed by each methyl group. In obtaining eqn. (3) we have approximated the dipolar interactions between different  $\text{CH}_3$  groups within the same molecule by assuming that the protons in each  $\text{CH}_3$  group are located at the center of the triangle.

A corresponding expression for the  $^{13}\text{C}$  spin-lattice relaxation time produced by intramolecular dipole-dipole interactions modulated by isotropic reorientations and  $C'_3$  rotations has been obtained, *viz.*

$$\frac{1}{T_1(^{13}\text{C})} = (11C+D)f(\omega_{\text{H}}, \omega_{\text{C}}, \tau_r) + (16C+3D)f(\omega_{\text{H}}, \omega_{\text{C}}, \tau_c) \quad (5)$$

where

$$f(\omega_{\text{H}}, \omega_{\text{C}}, \tau) = \frac{\tau}{1 + (\omega_{\text{H}} - \omega_{\text{C}})^2 \tau^2} + \frac{3\tau}{1 + \omega_{\text{C}}^2 \tau^2} + \frac{6\tau}{1 + (\omega_{\text{H}} + \omega_{\text{C}})^2 \tau^2} \quad (6)$$

and

$$C = \frac{1}{90} \gamma_H^2 \gamma_C^2 \hbar^2 r_{CH}^{-6} \quad \text{and} \quad D = \frac{3}{20} \gamma_H^2 \gamma_C^2 \hbar^2 r'_{CH}{}^{-6}.$$

$r_{CH}$  is the C-H bond length of a methyl group and  $r'_{CH}$  is the distance between a methyl carbon and the center of the equilateral triangle formed by the three hydrogen atoms of one of the other methyl groups. The latter vector makes an angle of  $92.4^\circ$  with the  $C_3$  rotation axis.

In the solid phases III and IV of *t*-butyl thiol,  $\tau_r$  is very large; hence  $\tau_c = \tau_r$  and eqns. (3) and (5) then reduce to

$$\frac{1}{T_1(\text{H})} = 3(A+B) g(\omega_H, \tau_r) \quad (7)$$

and

$$\frac{1}{T_1(^{13}\text{C})} = (16C+3D) f(\omega_H, \omega_C, \tau_r). \quad (8)$$

The observation that  $T_1(\text{H})$  and  $T_1(^{13}\text{C})$  increase with increasing temperature in solids I and II implies that the rotational correlation time is less than the reciprocal resonance frequency

( $\sim 10^{-9}$  s), i.e. the extreme narrowing condition prevails. It then follows from eqns. (3) and (5) that

$$\frac{1}{T_1(\text{H})} = 20(A+B) \tau_{\text{eff}}^{\text{HH}} \quad (9)$$

and

$$\frac{1}{T_1(^{13}\text{C})} = 270C \tau_{\text{eff}}^{\text{CH}} + 40D \tau_{\text{eff}}^{\text{HH}} \quad (10)$$

where

$$\tau_{\text{eff}}^{\text{HH}} = (\tau_r + 3\tau_c)/4 \quad \text{and} \quad \tau_{\text{eff}}^{\text{CH}} = (11\tau_r + 16\tau_c)/27.$$

Numerical values for  $A, B, C$  and  $D$  have been calculated by taking the C-H and C-C distances to be 0.109 and 0.154 nm, respectively. This gives  $r_{\text{HH}} = 0.178$  nm,  $r'_{\text{HH}} = 0.310$  nm and  $r'_{\text{CH}} = 0.282$  nm, from which we find  $A = 2.69 \times 10^9 \text{ s}^{-2}$ ,  $B = 2.89 \times 10^8 \text{ s}^{-2}$ ,  $C = 2.39 \times 10^8 \text{ s}^{-2}$  and  $D = 1.08 \times 10^7 \text{ s}^{-2}$ . Using these values it follows from eqns. (9) and (10) that, under the extreme narrowing condition, the intramolecular  $\text{CH}_3\text{-CH}_3$  dipolar interactions contribute only about 10% and 1% to the  $^1\text{H}$  and  $^{13}\text{C}$   $T_1$  relaxation times, re-

Table 1. Least-squares fit parameters of the Arrhenius equation  $\tau = \tau_0 \exp(E_a/RT)$  obtained from the  $\text{CH}_3$   $T_1$  data in Figs. 1 and 2.

	Correlation coefficient $r$	Activation energy $E_a$ (kJ/mol)	pre-exponential factor $\tau_0(\text{s}) \times 10^{14}$	$\tau(\text{ps})$ at the thermal transition points <sup>a</sup>	
<b>Liquid:</b>					
$T_1(\text{H})$	0.92	9.9	2.7	2.1	
$T_1(^{13}\text{C})$	0.79	7.1	5.7	1.3	
<b>Solid I:</b>					
$T_1(\text{H})$	0.93	9.6	1.4	1.0	4.8
$T_1(^{13}\text{C})$	0.98	7.8	3.3	1.0	3.7
<b>Solid II:</b>					
$T_1(\text{H})$	0.96	15	0.083	8.8	110
$T_1(^{13}\text{C})$	0.96	7.6	13	13	44
<b>Solid III/IV:</b>					
$T_1(\text{H})$	0.98	16	27	$6.8 \times 10^4$	
$T_1(^{13}\text{C})$	0.98	18	5.3	$7.8 \times 10^4$	

<sup>a</sup>Left column, upper transition point; right column, lower transition point.

spectively. In the following calculations we have therefore neglected the last term in eqn. (10).

As a consequence of the assumed tetrahedral geometry of the *t*-butyl group the modulation of the intra-CH<sub>3</sub> dipolar H-H interactions will be the same for both C<sub>3</sub>' and C<sub>3</sub> motions since the same expression is obtained for  $\tau_{\text{eff}}^{\text{HH}}$  whether  $\theta = 90^\circ$  or  $(180 - 109.5)^\circ/2$ .<sup>20</sup> In the latter case, however, the intramolecular CH<sub>3</sub>-CH<sub>3</sub> interactions in eqn. (3) (*B* term) will be modulated only by  $\tau_r$ , since the H-H' vector is not affected by the C<sub>3</sub> rotation. The corresponding expressions for  $T_1(^{13}\text{C})$  are obtained by taking into account that all three <sup>13</sup>C-H spin pairs of a methyl group are modulated by the internal C<sub>3</sub> rotation, whereas the CH<sub>3</sub>-CH<sub>3</sub> interactions are not affected by this motion. In eqn. (8) it is thus only necessary to multiply the *C* term by 3/2 and delete the *D* term. Under the condition of extreme narrowing,  $T_1(^{13}\text{C})$  is still given by eqn. (10) if  $\tau_{\text{eff}}^{\text{CH}}$  is redefined as  $(\tau_r + \tau_c)/9$ .

From the experimental  $T_1$  data presented in Figs. 1 and 2 we have calculated effective correlation times using eqns. (7)–(10). Activation energies and pre-exponential factors for the appropriate motions have been obtained from the Arrhenius equation as shown in Table 1. Generally, the parameters obtained from the <sup>1</sup>H and <sup>13</sup>C relaxation time data may differ since different effective correlation times are involved. Thus, it is seen that the <sup>1</sup>H measurements give consistently higher activation energies than the corresponding <sup>13</sup>C and <sup>2</sup>H measurements,<sup>5</sup> which are in better agreement. A small contribution from intermolecular interactions in the former case may also give rise to an apparent increase in the activation energy.

The methyl proton and carbon-13  $T_1$  values display marked discontinuities at the melting point, whereas the activation energies for the two phases are equal within experimental error. Effective correlation times at the melting point of about 2.1 and 1.3 ps for the liquid and 1.0 ps for solid I have been calculated from the  $T_1(\text{H})$  and  $T_1(^{13}\text{C})$  values, respectively (Table 1). These values are in good agreement with those reported for *t*-butyl thiol-*d*<sub>9</sub> at the melting point (1.5 and 1.3 ps for liquid and solid I, respectively).<sup>5</sup> The similar correlation times and activation energies obtained for the different spin-vectors of *t*-butyl thiol and its deuterated analogue are consistent with isotropic overall molecular tumbling in the

liquid and solid I phases. Correlation times have not been measured for many plastic organic crystals; however, the present data and other results<sup>1,5,11</sup> indicate that a value of about 1–2 ps for phase I at the melting point seems to be a characteristic property of non-associated globular compounds.

The marked discontinuities in the  $T_1(\text{H})$  and  $T_1(^{13}\text{C})$  values at the solid I → solid II transition temperature are followed by a considerable increase in the corresponding effective correlation times. However, whereas the activation energies obtained from the  $T_1(^{13}\text{C})$  data for the two phases are identical within experimental error, the  $T_1(\text{H})$  data give a marked increase in the  $E_a$  value for solid II. We believe that the latter observation reflects an increasing effect of anisotropic motion and intermolecular contributions in solid II relative to solid I, although overall molecular reorientation is still the dominant motion causing spin-lattice relaxation in both phases. The observation of quadrupolar splittings for the solid II phase of deuterated *t*-butyl thiol<sup>5</sup> is also consistent with marked anisotropic motion.

Only the <sup>13</sup>C NMR data show a marked discontinuity at the solid II → solid III transition temperature. The dominant motion causing <sup>1</sup>H and <sup>13</sup>C relaxation in solids III and IV is, undoubtedly, reorientation of the *t*-butyl group, since the rate of rotation of the methyl group is too low ( $\sim 10^6 \text{ s}^{-1}$  or less)<sup>5</sup> to contribute. Further support for this assumption is provided by the similar activation energies obtained for the C<sub>3</sub> reorientation in *t*-butyl thiol (16–18 kJ mol<sup>-1</sup>), *t*-butyl chloride (15 kJ mol<sup>-1</sup>),<sup>21,22</sup> *t*-butyl nitrate (15 kJ mol<sup>-1</sup>)<sup>23</sup> and *t*-butyl cyanide (16–17 kJ mol<sup>-1</sup>).<sup>24,25</sup>

Since the <sup>1</sup>H and <sup>13</sup>C  $T_1$  values increase with decreasing temperature for solids III and IV of *t*-butyl thiol, the motion causing relaxation must be slower than the reciprocal resonance frequency ( $\sim 10^{-9} \text{ s}$ ). Indeed, an increase of about four orders of magnitude is observed for the correlation time at the II → III boundary. The correlation time obtained at 157 K ( $7\text{--}8 \times 10^{-8} \text{ s}$ ) is, however, considerably less than the value reported for (CD<sub>3</sub>)<sub>3</sub>CSH at 158 K ( $1.1 \times 10^{-6} \text{ s}$ ).<sup>5</sup> This discrepancy can probably be ascribed in part to retardation of the *t*-butyl group as a result of the deuteration.

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