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Molecular motion in solid bicyclo[2.2.2]octane and bicyclo[2.2.2]oct-2-ene studied by nuclear magnetic resonance

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Abstract. — Proton n.m.r. relaxation time measurements have been made on bicyclo[2.2.2]octane (BCO) and bicyclo[2.2.2]oct-2-ene (BCOE). Measurements for each sample were made throughout the plastic and brittle phases, down to 77 K. The results have been interpreted in terms of the various molecular motions occurring in the solid. Below the plastic-brittle phase transition point anisotropic molecular reorientation appears to occur. The activation enthalpy for this motion is 17.1 ± 1.2 kJ.mol⁻¹ in BCO and 17.3 ± 1.2 kJ.mol⁻¹ in BCOE. Above this phase transition a rapid endospherical reorientation is observed and relaxation time measurements yield an activation enthalpy of 7.7 ± 0.9 and 7.4 ± 0.6 kJ.mol⁻¹ in BCO and BCOE respectively. At higher temperatures molecular self-diffusion becomes the dominant controlling mechanism for T₁03C₁ and T₂. The activation enthalpy for this process is found to be 95.1 ± 2.1 and 66.8 ± 6.3 kJ.mol⁻¹ in BCO and BCOE respectively. Correlation times, τ, for translational and reorientational motion are evaluated. The results and mechanisms for reorientational and translational motion are discussed in relation to the respective crystal structures and thermodynamic properties of the materials. Results related to the molecular reorientation in phase I of BCO are in quantitative agreement with those of incoherent quasi-elastic neutron scattering. The unit cell of the plastic phase I of BCOE which has been investigated by X-ray powder diffraction is f.c.c., with a₀ = 0.908 ± 0.002 nm.

1. Introduction.

This work reports a detailed nuclear magnetic resonance relaxation time study of the molecular motion in the crystalline state of bicyclo[2.2.2]octane and bicyclo[2.2.2]oct-2-ene, hereafter referred to as BCO and BCOE respectively.

These compounds have already been studied in their crystalline state by a number of different techniques. Calorimetric studies of the heat capacities and transition behaviour [1] and vapour pressure determinations of sublimation enthalpies [2, 3] have been reported. The results of these are summarized in table I. Both compounds exhibit a « plastic » phase [4, 5] which extends over a wide temperature range. The melting entropies differ widely and there is one more phase transition reported for BCOE than for BCO [1]. This second (phase II-III) transition has a very small entropy and its occurrence might be related to the presence of impurities, as in diamantane [6].
The molecular structure of these two compounds is roughly globular (Fig. 1), they differ only in the existence of a double bond in BCOE. This lowers the molecular symmetry of BCOE to $C_{2v}$ [7] from pseudo $D_{3h}$ for BCO [8]. Crystal structures are known from X-ray diffraction studies on both BCO [9-11] and BCOE (this work). The main results are presented in table II. An isothermal compressibility study has also been reported for BCO [12].

Molecular motion in the solid state of BCO and BCOE has previously been investigated by a study of n.m.r. second moment [13] and for BCOE only, by spin-lattice relaxation time measurements [14]. Below approximately 100 K the experimental second moments agree with calculated values, assuming a rigid lattice. For both compounds a large decrease in the second moment is observed before reaching the phase II-I transition point. In BCOE there is evidence for the beginning of a plateau region, of about 7 $G^2$, corresponding to a reorientation of the molecule about its pseudo ternary axis [13]. No such plateau is observed for BCO, where the second moment drops directly to a much lower value. In the plastic phase of both materials the second moment remains constant up to about 300 K. Its value corresponds to rapid endospherical reorientation of the molecules. This interpretation was supported by results of a spin-lattice relaxation time study of BCOE which also allowed the activation enthalpies for the motions to be measured [14]. No n.m.r. measurements have previously been reported above room temperature. Here we measure and compare the molecular motions, both translational and reorientational, occurring in both the plastic and brittle phases of BCO and BCOE using proton n.m.r. relaxation time measurement.

2. Experimental methods.

2.1 Sample preparation. — BCO and BCOE were purchased from Wiley Organics (Columbus, Ohio, U.S.A.). Both crude products showed approximately 2 % single impurity levels as determined by vapour phase chromatography (VPC). In BCO the impurity was identified as BCOE, both by VPC and proton high-resolution n.m.r. The impurity present in BCOE was not identified. Both compounds were purified.

![Diagram of molecules](image)

*Fig. 1. — Schematic diagram of the molecules of (a) bicyclo[2.2.2]oct-2-ene and (b) bicyclo[2.2.2]octane. $C_2$ is a two-fold and $C_3$ a three-fold symmetry axis.*

Table I. — Thermodynamic parameters from references [1-3].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature</th>
<th>Entropy</th>
<th>Latent heat of sublimation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(K)</td>
<td>(J.mol$^{-1}$.K$^{-1}$)</td>
<td>(kJ.mol$^{-1}$)</td>
</tr>
<tr>
<td>BCO</td>
<td>T.P. = 164.25</td>
<td>27.9</td>
<td>48.2 (298 K)</td>
</tr>
<tr>
<td></td>
<td>T.M. = 447.5</td>
<td>18.7</td>
<td>46.3 (323-363 K)</td>
</tr>
<tr>
<td>BCOE</td>
<td>T.P. (III-II) = 110.5</td>
<td>3.3</td>
<td>43.8 (298 K)</td>
</tr>
<tr>
<td></td>
<td>T.P. (II-I) = 176.5</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T.M. = 389.7</td>
<td>10.2</td>
<td></td>
</tr>
</tbody>
</table>

T.P. : Transition point.
T.M. : Melting point.
Table II. — Crystallographic properties of BCO and BCOE

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (K)</th>
<th>Crystal structure</th>
<th>Z</th>
<th>Lattice space group</th>
<th>Cell Dimensions (nm)</th>
<th>Density (g/cm³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(High temperature</td>
<td>293</td>
<td>f.c.c.</td>
<td>4</td>
<td>Fm3m</td>
<td>0.9105</td>
<td>0.964</td>
<td>[9]</td>
</tr>
<tr>
<td>phase)</td>
<td>265</td>
<td>f.c.c.</td>
<td>4</td>
<td>Fm3m</td>
<td>0.914</td>
<td>0.962</td>
<td>[10]</td>
</tr>
<tr>
<td>BCO</td>
<td>100</td>
<td>h.c.p.</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>(Low temperature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BCOE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(High temperature</td>
<td>Room temperature</td>
<td>f.c.c.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

by VPC on a 3m column (20% SE30 on silica) at 363 K. Previously detected impurities were then undetectable on a vapour phase chromatogram (10% SE30 and 10% Carbowax) indicating an impurity level, for detectable material, of less than 0.1%. The purified products were then transferred to n.m.r. tubes by vacuum sublimation over a molecular sieve, degassed, and sealed under vacuum.

2.2 RELAXATION TIME MEASUREMENTS. — Proton spin-lattice relaxation times, $T_1$, were measured at 14.3 MHz using a 90°-r-90° pulse sequence. A few measurements of $T_1$ were also made at 30 MHz. Proton spin-lattice relaxation times in the rotating frame, $T_{1p}$, were measured using a 90° pulse followed immediately by a pulse of adjustable time duration shifted in phase by 90° from the initial pulse. The intensity of the r.f. magnetic field, $B_1$, was determined from the lengths of $nn$ pulses ($n = 1$ to 4). The spin-spin relaxation times $T_2$, were measured using the $90°-r-180°$ spin-echo sequence.

All relaxation time measurements were made on polycrystalline samples and were estimated to be accurate to ± 10%. The temperature of the sample was controlled to approximately ± 1 K and measurements were made on both increasing and decreasing temperature cycles.

2.3 X-RAY DIFFRACTION STUDY. — The unit cell of BCOE in its plastic phase was determined at room temperature using a Debye-Scherrer powder camera utilising Cu Kα radiation. Measurements give nine lines which were fitted to a f.c.c. lattice with $a_0 = 0.908 ± 0.002$ nm.

3. n.m.r. results.

3.1 OVERVIEW. — The experimental results are given in figures 2 and 3 as plots of relaxation times versus reciprocal temperature. Measurements of $T_1$ and $T_{1p}$ extend from liquid nitrogen temperatures up to the respective melting points of BCO and BCOE. $T_2$ measurements are restricted to a limited temperature range below the melting points. Also shown on the figures are the second moment measurements due to Darmon and Brot [13]. Both $T_1$ and $T_{1p}$ measurements exhibit discontinuities at the phase II-I transition points. In BCO the transition was observed at 162.5 ± 1 K, in good agreement with calorimetry [1].
Super-cooling of the high temperature phase I, by approximately 6 K below the transition temperature, was observed. In BCOE the phase II-I transition point was found to be at 170 ± 2 K, which is approximately 6 K below the previously reported value. No discontinuity in the relaxation time measurements was observed close to the small calorimetric λ-point, centred on 110.5 K. Our $T_1$ measurements in BCOE are in general agreement with those already reported at 25 MHz by Brot et al. [14].

### 3.2 BICYCLO[2.2.2]OCTANE.

#### 3.2.1 High temperature phase I.

*a) Reorientational motion.* — Above the transition point, up to about 300 K, the second moment was constant in value and corresponded to fast endo-spherical molecular reorientation [13]. This motion manifests itself in our $T_1$ data where, up to 380 K, we find (Fig. 2) that log ($T_1$) is independent of frequency and shows a linear dependence on $10^9/T$. $T_{1p}$ is also equal to $T_1$ up to 263 K. However, a much more detailed picture of that motion is now available. In an X-ray study of the plastic phase I of BCO, Sauvajol and Amoureux [11] have shown that the molecular and crystallographic $C_3$ axes are coincident. As required by space group symmetry, the orientational disorder among eight equilibrium positions corresponding to the four $C_3$ crystallographic axes may be achieved by assuming $90^\circ$ jumps of the molecules around the $C_4$ crystallographic axes. Moreover, the best reliability factor was obtained for a quasi isotropic orientational distribution function around the $C_3$ axis, indicative of a molecular motion around this axis. Recently, the results of two independent studies of the temperature dependence of incoherent quasi-elastic neutron scattering were published for phase I of BCO [15, 16]. Both were interpreted using a model in which the molecule executes $60^\circ$ jumps around its principal symmetry axis together with $90^\circ$ jumps around the $C_4$ crystallographic axes. Both studies were able to distinguish the correlation times for each of the two motions and concluded that the $60^\circ$ jumps are more frequent than the $90^\circ$ jumps, and have a lower activation enthalpy. The ratio $\tau_6/\tau_4$ at 250 K is 5.4 according to Bee et al. [16] and 9.0 according to Leadbetter et al. [15]. The activation enthalpies deduced from these two studies are in general agreement (Table III), but the correlation times given in [16] appear to be shorter. It is therefore interesting to check whether n.m.r. relaxation time measurements are in agreement with the motional features deduced by neutron scattering and to examine

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leadbetter et al. [15]</td>
<td>I.Q.N.S.</td>
<td>$\tau_6 = (9.1 \pm 3).10^{-13} \exp[(5.3 \pm 0.5) \text{kJ.mol}^{-1}/RT]$</td>
</tr>
<tr>
<td>Bee et al. [16]</td>
<td>I.Q.N.S.</td>
<td>$\tau_4 = (2.7 \pm 1.8).10^{-12} \exp[(7.6 \pm 1.5) \text{kJ.mol}^{-1}/RT]$</td>
</tr>
<tr>
<td>This study</td>
<td>n.m.r.</td>
<td>$\tau_6 = 1.743 \times 10^{-13} \exp[5.64 \text{kJ.mol}^{-1}/RT]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\tau_4 = 1.952 \times 10^{-13} \exp[8.90 \text{kJ.mol}^{-1}/RT]$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\tau_i = (1.3 \pm 0.6).10^{-13} \exp[(7.7 \pm 0.9) \text{kJ.mol}^{-1}/RT]$</td>
</tr>
</tbody>
</table>

I.Q.N.S. : incoherent quasielastic neutron scattering. Other terms are explained in the text.
whether they help to decide in favour of one of the two studies. From the n.m.r. measurements only one correlation time for this composite motion can be determined and in the absence of any relaxation time minimum, it is not possible to determine whether this correlation time is related to the slower of two motions having very different jump rates or to a mean value between two motions of comparable rate. Only a rough estimate of the correlation time \( \tau_c \) for overall molecular tumbling may be obtained, using the formula proposed by Resing [17] to account for \( T_1 \) due to a similar type of motion in adamantane

\[
1 \frac{1}{T_1} = \frac{2}{3} \gamma^2 M_2(\text{intra}) \left[ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right] + \frac{2}{3} \gamma^2 M_2(\text{inter}) \left[ \frac{\tau_c/2}{1 + \omega_0^2 \tau_c^2/4} + \frac{2 \tau_c}{1 + \omega_0^2 \tau_c^2} \right]. \tag{1}
\]

The second moment value calculated by Darmon [18] is \( M_2(\text{intra}) = 16.8 \times 10^{-8} \text{T}^2 \) and \( M_2(\text{inter}) = 6.9 \times 10^{-8} \text{T}^2 \). The rotational correlation time is then given by \( \tau_c = (1.3 \pm 0.6) \times 10^{-13} \text{s} \exp[(7.7 \pm 0.9) \text{kJ/mol}^{-1}/RT] \). Comparison with neutron scattering results in table III seems to indicate a better agreement with the results of Bee et al. and n.m.r. might here give the mean of the correlation times for the two processes whose rates are similar.

Alternatively, a more precise comparison can be obtained using the correlation times deduced from incoherent quasielastic neutron scattering (I.Q.N.S.) studies to calculate spin-lattice relaxation times \( T_1 \) with the help of a group theory formalism.

The rotational intra-molecular spin-lattice relaxation time depends only on the spectral densities of the auto-correlation functions of second-order spherical harmonics. For rigid molecules reorienting between equilibrium positions, these can be calculated using group theory [19-21]. For a powder sample in which the molecules perform reorientations around both fixed (crystallographic) axes and mobile (molecular) axes, the relaxation time for the intramolecular part of the dipolar interaction may be calculated using the spectral densities derived by Virlet and Quiroga [22] under the assumption that the two reorientations are uncorrelated. By applying their formulae to \( 0(\text{crystallographic}) \times C^0(\text{molecular}) \) reorientations, we obtain

\[
\frac{1}{T_1} (\text{intra}) = \frac{3}{5} \gamma^4 h^2 N^{-1} \sum_{i \neq j} \frac{1}{8} (3 \cos^2 \theta_{ij} - 1)^2 r_{ij}^6 H(\tau_{\text{T}}^{-1}, \omega_0, 2 \omega_0) + \sum_{i \neq j} \frac{1}{8} \sin^4 \theta_{ij} r_{ij}^6 \{ H(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, \omega_0, 2 \omega_0) + 2 H(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, \omega_0, 2 \omega_0) \}
+ \sum_{i \neq j} \frac{1}{2} \sin^2 \theta_{ij} \cos^2 \theta_{ij} r_{ij}^6 \{ 2 H(\tau_{\text{E}^{-1}}, \omega_0, 2 \omega_0) + H(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, \omega_0, 2 \omega_0) \}; \tag{2}
\]

\( \theta_{ij} \) is the angle between the internuclear vector \( r_{ij} \) and the molecular reorientational axis, and

\[
H(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, \omega_0, 2 \omega_0) = \sum_{m=1}^2 m^2 \xi(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, m \omega_0) \tag{3}
\]

with

\[
\xi(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}, m \omega_0) = \frac{\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}}}{(\tau_{\text{T}}^{-1} + \tau_{\text{E}^{-1}})^2 + m^2 \omega_0^2} \tag{4}
\]

\( N \) is the number of resonant spins (protons) in the molecule; \( \gamma \) and \( h \) have their usual meaning. As in [16] we shall assume that the molecule is jumping with equal probability to next neighbour positions only, that is 60° jumps around the molecular axis and 90° jumps around any [100] direction, with correlation times \( \tau_6 \) and \( \tau_4 \) respectively. Using this simplifying assumption, and according to [22] the correlation times for each irreducible representation of the groups which appear in formula (2) are related to \( \tau_4 \) and \( \tau_6 \)

\[
\frac{T_1^{-1}(\text{intra})}{T_1^{-1}(\text{intra})} = \frac{M_2(\text{intra})}{2 M_2(\text{inter})} \approx 20\%. \tag{6}
\]

This value is in agreement with experimental determinations of the intermolecular contribution [23, 24] in similar compounds.

In figure 4, our experimental \( T_1 \) are compared with \( T_1 \) calculated using the correlation times \( \tau_4 \) and \( \tau_6 \) calculated from the incoherent quasielastic
Fig. 4. — Reorientational motion in phase I of BCO as seen by n.m.r. and incoherent quasielastic neutron scattering. $\Delta T$; $\Delta$ experimental relaxation times $T_1$ at $B_0 = 0.705$ and 0.335 T respectively. The straight lines are calculated as explained in § 3.2.1, equations (2) and (5) and using data from: Bee et al. [16] —— straight line, Leadbetter et al. [15] —— dotted line.

neutron scattering studies [15, 16]. The agreement is within experimental uncertainty ($< 20 \%$) using the correlation times from Bee et al. This confirms that both the neutron scattering and n.m.r. experimental results may be quantitatively explained using exactly the same jump model and the same atomic coordinates. The discrepancy which appears on figure 4 with $T_1$ calculated from the work of Leadbetter et al. may come in part from a slightly different jump model and (or) a different set of atomic coordinates. Taking into account the additional different probabilities for 120° and 180° jumps as given in reference [15] increases the calculated $T_1$ values slightly, but a discrepancy still remains.

Finally, the reorientational molecular motion in the plastic phase of BCO seems rather similar to that observed in 1-azabicyclo[2.2.2]octane [ABCO]. In that compound, both quasi-elastic neutron scattering [25] and n.m.r. $^{14}$N and $^1$H relaxation time measurements [26] were able to distinguish between two reorientational motions and each concluded that $C_3$ reorientation was faster than the 90° jumps by factors 2.6 and 4.2 respectively at room temperature. However, in ABCO, the threefold molecular and crystallographic axes do not coincide [27] leading to 24 possible orientations for each molecule instead of 8 for BCO.

b) Translational motion. — $T_{1p}$ between 263 K and the melting point is obviously controlled by another motion. The temperature dependence is increased and a sharp minimum is observed (Fig. 2). This new motion also affects $T_1$ above 380 K when a sudden decrease is observed. Moreover, a previously unreported line narrowing is observed in this temperature region with a corresponding rapid increase in $T_2$ with increasing temperature. This behaviour, which is similar to that observed in many other plastic solids, is attributed to molecular self-diffusion.

The values of $B_1$ used satisfy the condition $B_1 > B_{loc}$. Thus a weak collision theory of nuclear magnetic spin relaxation may be used to analyse the relaxation time data. Self-diffusion in molecular crystals is thought to proceed by a vacancy mechanism [28]. We use the spectral density functions calculated by Wolf [29] for a discrete monovacancy diffusion mechanism on an f.c.c. lattice to analyse the relaxation time data. These calculations predict that a minimum in $T_{1p}$ will be observed when $\omega_0 \tau_d = 0.45$. The value of $T_{1p}$ at the minimum is given by

$$\frac{1}{T_{1p}} = 0.236 \gamma^2 M_2 \omega_1. \quad (7)$$

From the measured $T_{1p}$ minima, of 2.14 ± 0.33 ms ($B_1 = 9.2 \times 10^{-4}$ T) and 0.76 ± 0.14 ms ($B_1 = 3.3 \times 10^{-4}$ T), a value for $M_2$ of 0.0068 ± 0.0013 mT$^2$ is obtained. This is 30% less than the value obtained experimentally by Darmon and Brot [13] and calculated from the lattice parameter for an endospherical reorientational motion. A similar discrepancy arises if the uncorrelated random walk analysis due to Torrey [30] is employed.
Values for the diffusional correlation time, \( \tau_d \), were deduced from the \( T_1 \), \( T_2 \) and \( T_{1p} \) results, and appear in figure 6. Values of \( \tau_d \) deduced from \( T_1 \), \( T_2 \) and \( T_{1p} \) data are consistent. A slight departure from an Arrhenius behaviour is observed for larger \( \tau_d \) values, between \( 10^{-2} \) s and \( 10^{-1} \) s, but these correspond to long \( T_{1p} \) values which were more difficult to measure and from which a reorientational contribution was subtracted. Since these points are less reliable they were ignored when fitting the data to give \( \tau_d(s) = (2.4 \pm 0.7) \times 10^{-18} \exp[(95.1 \pm 2.1) \text{kJ} \times \text{mol}^{-1}/RT] \).

3.2.2 Low temperature phase II. — In the low temperature phase, from below the transition point down to approximately 120 K, the log (\( T_1 \)) versus \( 10^3/T \) plot is linear and shows an \( \omega_0^2 \) dependence. \((\omega_0 = \gamma B_0 \) is the Larmor frequency, in a static magnetic field \( B_0 \), for a nucleus with gyromagnetic ratio \( \gamma \).)

The dominant spin-lattice relaxation mechanism in this region is thought to be due to a reorientational motion whose correlation time, \( \tau_r \), is greater than \( \omega_0^2 \approx 10^{-8} \) s. The occurrence of the phase transition prevents the \( T_1 \) minimum being observed at higher temperatures, but a \( T_{1p} \) minimum of 141 ± 15 ps, at 138 K, for a \( B_1 \) of 10.2 \times 10^{-4} \text{T} is observed. The observation of only one reduction in the second moment in that region [13], coupled with the fact that the gradient of the linear regions of the log (\( T_1 \)) and log (\( T_{1p} \)) plots are equal, within the limits of experimental error, suggests that one motion controls both \( T_1 \) and \( T_{1p} \). The linear regions yield activation enthalpies of 14.9 \text{kJ.mol}^{-1} and 17.1 \text{kJ.mol}^{-1} from the \( T_1 \) (at 14.3 MHz) and \( T_{1p} \) results respectively.

The modulation of the second moment caused by this motion may be estimated using the equation [31]

\[
\frac{1}{T_{1p}} = K \left[ \frac{3 \tau_r}{1 + 4 \omega_0^2 \tau_r^2} + \frac{5 \tau_r}{1 + \omega_0^2 \tau_r^2} + \frac{2 \tau_r}{1 + 4 \omega_0^2 \tau_r^2} \right]
\]

(8)

where \( \omega_0 = \gamma B_0 \) and \( \omega_1 = \gamma B_1 \) and \( K \) is dependent on the type of motion. In a first approximation, for molecular reorientation in a powder sample, \( K = 2 \gamma^3 M_{2mod}/3 \) where \( M_{2mod} \) is that part of the apparent second moment of the resonance line that is modulated by the motion [32]. To account for an anisotropic motion one would need to distinguish between the inter- and intramolecular contributions to the second moment and to calculate the specific spectral density functions for the motion. In the region of the \( T_{1p} \) minimum equation (8) reduces to

\[
\frac{1}{T_{1p}} = \gamma^2 M_{2mod} \left[ \frac{\tau_r}{1 + 4 \omega_1^2 \tau_r^2} \right]
\]

(9)

which predicts a minimum in \( T_{1p} \) when \( \omega_1 \tau_r = 0.5 \). From equation (9) we obtain \( M_{2mod} \approx 11 \times 10^{-8} \text{T}^2 \), which is far less than the observed reduction in second moment of \( 23 \times 10^{-8} \text{T}^2 \) between 100 K and 170 K [13]. Such a discrepancy is often observed in low temperature phases of molecular solids [33, 34]. Substituting the value for \( M_{2mod} \) (~11 \times 10^{-8} \text{T}^2) back into equation (9) and assuming an Arrhenius temperature dependence for \( \tau_r \) of the form

\[
\tau_r = \tau_0 \exp(\Delta H^*/RT),
\]

(10)

leads to \( \tau_r = (7.0 \pm 4.0) \times 10^{-13} \text{s} \exp[(17.1 \pm 1.2) \text{kJ} \times \text{mol}^{-1}/RT] \).

The same model may be used to calculate \( T_1 \) [31], which is then given by

\[
\frac{1}{T_1} = K \left[ \frac{\tau_r}{1 + \omega_0^2 \tau_r^2} + \frac{4 \tau_r}{1 + 4 \omega_0^2 \tau_r^2} \right].
\]

(11)

Below the \( T_{1p} \) minimum, where \( \omega_0 \tau_r \gg \omega_1 \tau_r \gg 1 \), the ratio \( T_1/T_{1p} \) may be derived from equation (9) and (11) to be

\[
\frac{T_1}{T_{1p}} = \frac{3}{16} \left( \frac{B_0^2}{B_1^2} \right).
\]

(12)
Substituting the values for $B_o$ (0.335 T) and $B_1$ (10.2 x 10$^{-4}$ T) into equation (12) gives a theoretical ratio of 2.0 x 10$^4$. The experimental ratio at 120 K is only 3.4 x 10$^3$, which is approximately one-sixth of the calculated value.

An X-ray diffraction study has shown that BCO phase II is hexagonal [10] although it is also possible to index the observed reflections with an orthorhombic cell [15]. Bruesch [10] suggests that this structure arises from a slight contraction along one body diagonal of the cube and that the molecules are situated at, or very close to, their original positions in the plastic phase. The molecules in phase II are all orientated parallel with their 3-fold axis along $C_{hex}$. The large discontinuities in both $T_1$ and $T_{1p}$ plots (Fig. 2) when passing through the II-I transition and a small but clear discontinuous change in the length of the free induction decay indicate a sudden change in molecular motion at the transition point. This discontinuity is apparent on figure 5 which shows the reorientational correlation times in BCO and BCOE as a function of 10$^3$/T.

A 3-fold reorientation of the very similar BCOE molecule reduces the apparent second moment by only 12 x 10$^{-8}$ T$^2$ in accordance with theoretical calculation [13]. To account for the much larger reduction in BCO, it seems reasonable to assume that, in phase II of BCO, molecules are executing more than a 3- or 6-fold reorientation around their principal axis. We postulate that, in addition, the molecules also execute a 2-fold reorientation around their $C_2$ molecular symmetry axes. The two motions about mutually perpendicular axes should produce sufficient modulation of the dipolar interactions to account for the observed reduction in second moment. A precise calculation would be difficult and no obvious possibility of checking it exists since the occurrence of the phase transition prevents observation of the ultimate second moment plateau. These two motions may have different correlation times, as is the case for the two motions occurring in phase I. This could account for the much smaller value of the modulated second moment calculated from the $T_{1p}$ minimum which might be explained as due to $T_{1p}$ being sensitive to the $C_3$ reorientation only. The modulated second moment deduced from the $T_{1p}$ minimum is in good agreement with such an hypothesis. It is worth noting that incoherent quasielastic neutron scattering studies [15, 16] failed to characterize molecular motion in phase II, showing the limitation of this method in the study of motions whose correlation times are greater than about 10$^{-9}$ s [35].

Below 117 K, the $T_1$ measurements seem to be independent of frequency and their temperature dependence decreases. $T_{1p}$ also exhibits a weaker temperature dependence below 91 K and relaxation would appear to be dominated by a non-reorientational relaxation process. A very similar behaviour for $T_1$ has already been noticed in MoF$_6$ below 170 K [36], and it was suggested by Rigny and Virlet that the relaxation might be due to a librational motion of the molecules. If such an interpretation is to be considered, one would expect a similar behaviour (no frequency dependence of $T_1$) in all compounds whose rigid molecule contains no small atomic groups reorienting at low temperature. Unfortunately, we are aware of very few $T_1$ measurements at several frequencies in low temperature phases of such compounds. We note that no such behaviour is found in BCOE (this paper, § 3.3.2). Jackson [34] observed a reorientational relaxation behaviour in norbornadiene without any evidence of librational relaxation even for much longer $T_1$. Relaxation by paramagnetic impurities has been invoked in naphthalene [37] and biphenyl [38], but the relaxation times were much longer (~ 10$^4$ s) and the frequency dependence was not studied. It therefore appears that a detailed relaxation study at low temperature in such rigid organic molecules is still required before definite conclusions can be drawn.

3.3 **Bicyclo[2.2.2]oct-2-ene.**

3.3.1 **High temperature phase I.** — Above the phase II-I transition point, up to about 300 K, the second moment is constant [13] and its value, 0.85 x 10$^{-8}$ T$^2$ is consistent with rapid endospherical molecular reorientation. For the same temperature range, up to 310 K, log ($T_1$) depends linearly on 10$^3$/T (Fig. 3) and is determined by this reorientation. Our $T_1$ values, which are not expected to be frequency dependent in the region where $\omega_0\tau_r \ll 1$ are only in rough agreement (within 30 %) with those of reference [14]. The temperature dependence of the reorientational correlation time is obtained using equation (1). The second moment values calculated by Darmon and Brot [13], $M_2$(intra) = 12.2 x 10$^{-8}$ T$^2$ and $M_2$(inter) = 6.9 x 10$^{-8}$ T$^2$ were used in equation (1) to calculate the temperature dependence of $\tau_r$ which is $\tau_r = (1.4 + 0.9).10^{-13}$ s.exp[(7.4 ± 0.6) kJ.mol$^{-1}$/RT].

The introduction of a double bond drastically changes the symmetry of the molecule, since the ternary axis disappears and only one $C_3$ axis remains instead of three. However, there is little change in the shape of the molecule, and a « pseudo » ternary axis may still be distinguished (see Fig. 1). Very little information is available on the crystallographic changes brought about by the introduction of a double bond. Our X-ray study only shows that phase I is very similar to phase I in BCO (Table II). Using $\alpha_0 = 0.908$ nm, we calculate the second moment value corresponding to fast isotropic reorientation [32] to be 0.81 x 10$^{-8}$ T$^2$ in good agreement with the experimental value 0.85 ± 0.05 x 10$^{-8}$ T$^2$ of Darmon and Brot [13]. Comparison of the reorientational correlation times in BCO and BCOE which appear in figure 5 shows a striking similarity for the plastic phases, and we postulate that the motions are probably identical. It has been noted in a previous study of
several plastic crystals [34] that the \( \tau \) value at the melting point, obtained by linear extrapolation from \( T_1 \) data at lower temperatures, lies in the range \( 3 \times 10^{-13} \) s to \( 2 \times 10^{-12} \) s. The values obtained in this study are \( 1.0 \times 10^{-12} \) s and \( 1.4 \times 10^{-12} \) s for BCO and BCOE respectively and would seem to conform to this trend.

As in the case of BCO, the observation of \( T_{1p} \) minima coupled with a previously unreported line narrowing observed as a rapid increase in \( T_2 \) between 345 K and the melting point, indicates that modulation of the dipolar interactions by molecular self-diffusion occurs in phase I. Values for the diffusional correlation times were obtained in the manner detailed in section 3.2.1. The value of \( M_2 \), deduced from the \( T_{1p} \) minima is \( 0.77 \pm 0.12 \times 10^{-8} \) T\(^2\). This value is 10% less than the value observed by Brot and Brot [13], which is far better agreement than in BCO. The temperature dependence of \( \tau_b \) is given by \( \tau_b(\beta) = (2.8 \pm 1.9) \times 10^{-16} \exp[(66.8 \pm 6.3) \text{kJ.mol}^{-1}/RT] \). The correlation times for self-diffusion, \( \tau_b \), appear in figure 6 plotted versus reciprocal temperature.

For a single vacancy mechanism, it is expected that the activation enthalpy for self-diffusion \( \Delta H^*_b \) should be roughly twice \( L_0 \), the latent heat of sublimation [40]. Although such a relation is only an estimate, it is usually satisfied for plastic crystals with relatively high entropies of melting (i.e. \( \Delta S_m > 17 \text{ J.K}^{-1}.\text{mol}^{-1} \)). Plastic crystals with lower entropies of melting (\( \Delta S_m < 17 \text{ J.K}^{-1}.\text{mol}^{-1} \)) show a progressive decrease in the ratio \( \Delta H^*_b/L_0 \) [41, 42].

Since the melting entropies of BCO and BCOE (Table I) are very different, comparison of their activation enthalpies for self-diffusion is instructive. The \( \Delta H^*_b/L_0 \) ratio in BCO is 1.98 using the value of \( L_0 \) from reference [2] and 2.05 using the value from reference [3]. This value is as expected considering the high melting entropy. BCOE may be classified among the compounds with a low melting entropy and the \( \Delta H^*_b/L_0 \) ratio which is found equal to 1.53 fits the general trend for such a compound. Considering the close similarity, noted already, between the reorientational parameters in the plastic phases of the two compounds, it would seem that self-diffusion is the only motion reflecting the difference between melting entropies.

It has been noted that there is a marked similarity in the mean molecular jump times, as determined by n.m.r. in a wide range of molecular plastic solids at their respective melting points. Tables of such values can be found in references [28, 32, 34] where it can be seen that a mean value is \( 4.5 \times 10^{-7} \) s for the f.c.c. structure. The values for BCO and BCOE are \( 3.0 \times 10^{-7} \) s and \( 2.5 \times 10^{-7} \) s respectively, in good agreement.

3.3.2 Low temperature phase II and III. — From below the phase II-I transition point down to approximately 133 K the \( \log(T_{1f}) \) versus \( 10^3/T \) plot is linear and \( \omega_0^2 \) dependent (Fig. 3). The dominant relaxation mechanism in this region is thought to be due, as in the case of BCO, to a molecular reorientational motion.

The occurrence of the phase transition again prevents the \( T_1 \) minimum being observed at higher temperatures, but a \( T_{1p} \) minimum of 230 ± 10 \( \mu \)s for a \( B_1 \) field of 1.01 mT is observed. Below the \( T_{1p} \) minimum the log \( (T_{1p}) \) versus \( 10^3/T \) plot is linear down to approximately 105 K. The gradients of the linear regions of the \( T_1 \) and \( T_{1p} \) plots are equal, within the limits of experimental error, and yield activation enthalpies of 17.5 and 17.3 kJ.mol\(^{-1} \) respectively. Our \( T_1 \) measurements are in agreement with those of Brot et al. [14] at 25 MHz if one takes into account an \( \omega_0^2 \) dependence of \( T_1 \) in the linear region down to 150K. The activation enthalpy obtained by these authors is however 20% higher.

The relaxation times are again analysed in terms of equations (8) and (11). From the depth of the \( T_{1p} \) minimum a value for \( M_{2mod} \) of \( 6.6 \pm 0.9 \times 10^{-8} \) T\(^2\) is obtained, which is far less than the second moment reduction of \( 12.2 \times 10^{-8} \) T\(^2\) observed by Brot and Brot [13]. Substituting the value \( 6.6 \times 10^{-8} \) T\(^2\) for \( M_{2mod} \) into equation (9) gives \( \tau_b = (4.2 \pm 2.5) \times 10^{-12} \) s exp\[17.3 \pm 1.2 \text{ kJ.mol}^{-1}/RT\].

At 142 K the ratio \( T_{1f}/T_{1p} \) was measured to be \( 1.2 \times 10^3 \) which is approximately a factor of 18 lower than the value of \( 2.1 \times 10^4 \) predicted by equation (12) for \( B_1 = 10.1 \times 10^{-4} \text{ T} \) and \( B_0 = 0.335 \text{ T} \). These discrepancies are similar to those observed in BCO although the magnitude of the discrepancy in the \( T_{1f}/T_{1p} \) ratio is somewhat larger. Similar discrepancies have, however, been observed in several plastic crystals in their brittle phase [34].

The motion occurring in phase II and apparent from the reduction in the second moment between 135 K and the II-I transition was interpreted [13] as a reorientation around the pseudo 3-fold axis. However, the corresponding second moment plateau is not really reached, due to the abrupt occurrence of the phase transition. One might expect that the value of the second moment modulated by this motion, which may be deduced from the \( T_{1p} \) minimum, would help to identify the motion. Unfortunately, in the absence of a knowledge of the crystal structure in phase II, a detailed calculation using the proper distribution function for the anisotropic motion hasn’t been performed. As quoted above the \( M_{2mod} \) value deduced assuming an isotropic motion does not agree with the observed second moment reduction. However, the calculated value of \( M_{2mod} = 6.6 \times 10^{-8} \) T\(^2\) in BCOE is much less than the corresponding value of \( 11 \times 10^{-8} \) T\(^2\) in BCO in accord with the experimental second moment results. Thus, in BCOE phase II, the motion appears more restricted than in the corresponding phase of BCO, and a 3-fold reorientation, as in 1-azabicyclo[2.2.2]octane [13] seems the most probable.
Below 133 K down to 120 K, the $T_1$ results seem to exhibit a plateau region, as previously noticed [14]. The value for $T_1$ is frequency dependent, but the plateau is not reflected in $T_{1p}$ in that temperature range. Below 120 K down to 80 K the log ($T_1$) versus $10^3/T$ plot is again linear, but with a shallower gradient than that observed at higher temperatures. In this region an activation enthalpy of $5.8 \pm 1.0$ kJ.mol$^{-1}$ is obtained for the relaxation process and the behaviour of $T_1$ is in agreement with the results already obtained by Brot et al. [14]. These authors suggest the existence of a slow reorientation by $180^\circ$ around the $C_2$ axis of the molecule. This hypothesis is not in contradiction to our relaxation time data but seems more difficult to reconcile with the second moment data of [13]. The small calorimetric $\lambda$-point centred on 110.5 K does not seem to cause any discontinuity in the $T_1$ or $T_{1p}$ results, nor in the second moment measurements of Darmon and Brot [13]. The $T_{1p}$ results also exhibit a weaker temperature dependence at low temperatures but the change in slope (Fig. 3) occurs at 100 K. As already discussed in § 3.2.2, the low temperature behaviour of $T_1$ seems rather different from that in BCO.

References