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I. — $^{13}$C $T_1$ NMR study of the reorientational and ring-puckering motions of cyclopentene in the liquid state

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Résumé. — Le temps de relaxation spin-réseau $T_1$ et l’effet nucléaire Overhauser des trois carbones distincts du cyclopentène ont été mesurés en RMN du $^{13}$C entre 220 et 300 K, afin d’étudier la dynamique d’inversion de cette molécule en phase liquide.

Les données ont d’abord été analysées dans l’hypothèse d’une diffusion rotationnelle du cyclopentène considéré comme un rotateur asymétrique rigide. La rotation la plus lente se produirait alors autour du pseudoaxe C$_5$ avec des différences importantes entre les valeurs des trois constantes de diffusion rotationnelle. Ces conclusions semblent avoir peu de sens physique. De plus, elles sont en désaccord avec celles déduites d’études par infrarouge, Raman et diffusion des neutrons. Le mouvement d’inversion du cycle a donc été considéré ensuite comme un mécanisme efficace de relaxation du $^{13}$C. Bien que le nombre de paramètres nécessaire pour décrire les mouvements externes et internes excède le nombre d’informations expérimentales disponibles, on peut montrer que la molécule exécute environ $(5 \pm 4) \times 10^{12}$ sauts par seconde à 300 K entre ses deux conformations équivalentes, pliées selon un angle de 25 à 30°. L’énergie d’activation associée à ce processus semble assez faible puisque la fréquence de saut est encore de l’ordre de $(1 \pm 0.5) \times 10^{12}$ s$^{-1}$ à 220 K. D’autre part, la rotation d’ensemble de la molécule apparaît pratiquement isotrope en accord avec les conclusions des études optiques et neutroniques. On trouve $D_r = (0.22 \pm 0.02) \times 10^{12}$ s$^{-1}$ à 300 K et une énergie d’activation de 5,1 kJ.mole$^{-1}$.

Abstract. — The $^{13}$C NMR spin-lattice relaxation time $T_1$ and Nuclear Overhauser Effect (NOE) of the three distinct carbons of cyclopentene have been measured between 220 and 300 K in order to obtain some information about the ring-puckering motion in the liquid state.

The data are first analysed under the hypothesis that the rotational diffusion of cyclopentene resembles that of a rigid asymmetric top. The slower rotation is then calculated to occur around the pseudo-C$_5$ axis and large differences are found between the three rotational diffusion constants $D_{xx}, D_{yy}, D_{zz}$. These results seem to have little physical meaning. Furthermore they do not agree with those obtained by infrared, Raman and quasielastic neutron scattering. Therefore the ring-puckering motion has to be considered as an efficient $^{13}$C relaxation mechanism. Although parameters needed to describe both external and internal motions cannot all be determined from the information available one can qualitatively show that at 300 K the molecule executes about $(5 \pm 4) \times 10^{12}$ jumps s$^{-1}$ between its two equivalent bent conformations characterized by a puckering angle of 25 to 30°. The activation energy associated with this process seems to be low since the jump rate is still about $(1 \pm 0.5) \times 10^{12}$ s$^{-1}$ at 220 K. On the other hand, the whole molecule rotation is found to be nearly isotropic in agreement with the conclusions of the optical and neutron spectroscopies $D_r = (0.22 \pm 0.02) \times 10^{12}$ s$^{-1}$ at 300 K with an activation energy of 5.1 kJ.mole$^{-1}$.
1. Introduction.

Molecular dynamics studies performed in the last decade mainly concern rigid and rather symmetrical molecules [1-3]. Molecular systems undergoing fast conformational changes have been the object of a large number of detailed studies by infrared, Raman and microwave spectroscopies, but essentially in the gas phase [4-7].

An increasing and natural interest is now appearing towards the extension of the methods and theories of molecular dynamics to non-rigid molecules in condensed states. Although they are more complicated, these systems generally present more interesting features than the rigid ones, from a chemical and sometimes even biological point of view.

NMR has been one of the first techniques applied to the study of these systems. In particular, $^{13}$C spin-lattice relaxation time measurements have been shown to yield, via appropriate models, rather direct information about the motion of the CH vectors of the molecule [8-10]. The $^{13}$C spin-lattice relaxation is essentially of intramolecular origin and it is possible to isolate the purely dipolar interaction with the directly bonded protons by means of measurements of the Nuclear Overhauser Effect (NOE) [11].

A more difficult task is to differentiate the respective contribution of the internal and external motions to the observed relaxation. This problem, inherent to the nature of the molecule is encountered to a certain extent in any technique. The advantage of $^{13}$C $T_1$ NMR measurements is that they provide as many data as there are distinct CH vectors present in the molecule.

The first systems investigated were methylated molecules with a fast internal rotation of the methyl group [10]. In this case a rather obvious distinction occurs between the relaxation of the CH vectors in the rigid part of the molecule due to the overall molecule reorientation and the relaxation of a CH vector of the methyl group affected by both internal and external motions.

More recently, models have been developed for molecules presenting conformational flexibility. The dipolar relaxation time $T_1^D$ has for example been related by London [12, 13] to characteristic correlation times of overall isotropic reorientation and of exchange between two equivalent conformations. A similar treatment has been given by Baldo et al. [14] for a butterfly-like molecule having the CH vector in one of the librating planes. The latter work allows the more general case of an asymmetric top molecule to be treated.

A number of other works predict the expected influence of combined external and internal motions on the $^{13}$C $T_1$ values [15-17].

However, one can remark that apart from the specific case of methylated molecules the experimental illustration of these models is scarce. So, we have tried to select a system presenting well defined and rather simple motional and geometrical features in order to obtain clear evidence for the influence of the internal motion.

The cyclopentene molecule seems to be a good candidate. It undergoes a very well known ring-puckering motion in the gas phase [18] and there are good indications that the bent equilibrium structure persists in the liquid state [19-21] with a potential energy barrier between the two equivalent forms (Fig. 1) which is not very much increased from the gas state value of 232 cm$^{-1}$ [22].

On the other hand, orders of magnitude for the overall reorientation rate have been obtained by other techniques such as infrared and Raman spectroscopies [23] or quasielastic neutron scattering [22] and it is of fundamental interest to compare the results coming from these different sources.

Finally, the cyclopentene molecule has three distinct $^{13}$C sites and the angular amplitudes of the three corresponding CH vectors during the ring-puckering are rather different (Table I) in such a way that the molecule is very suitable for a $^{13}$C $T_1$ NMR study.

![Fig. 1. — Puckered equilibrium conformation of cyclopentene. The puckering angle $\alpha_0$ has the value 22.3° in the gas state [18]; G is the centre of mass.](image)

Table I. — Geometrical parameters of the cyclopentene molecule.

<table>
<thead>
<tr>
<th>Puckering angle $\alpha_0$ (degrees)</th>
<th>0</th>
<th>22.3</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moments of inertia $\times 10^{40}$ (g.cm$^2$)</td>
<td>$I_x = 116.65$</td>
<td>$I_x = 114.76$</td>
<td>$I_x = 116.9$</td>
</tr>
<tr>
<td></td>
<td>$I_y = 114.61$</td>
<td>$I_y = 115.80$</td>
<td>$I_y = 118.1$</td>
</tr>
<tr>
<td></td>
<td>$I_z = 215.34$</td>
<td>$I_z = 211.99$</td>
<td>$I_z = 209.3$</td>
</tr>
<tr>
<td>Change in angle of the CH vector after the ring-puckering (degrees)</td>
<td>$C_1$</td>
<td>16.1</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td>$C_2$</td>
<td>12.5</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>$C_3$</td>
<td>5.1</td>
<td>6.7</td>
</tr>
</tbody>
</table>
2. Theory.

We report here the basic formalism which relates the $^{13}$C $T_1$ relaxation time to some relevant parameters of the external and internal dynamics of the molecule using the following approximations:

1) Only the dipolar interaction of the $^{13}$C with the neighboring protons is considered. In the case where other mechanisms contribute to the measured $T_1$, the relaxation time of purely dipolar origin $T_D^0$ is extracted after a separate measurement of the NOE factor $\eta$ according to the following expression:

$$ T_1 = \eta \frac{2 \gamma_C}{\gamma_H} T_D^0 $$

where $\gamma_C$ and $\gamma_H$ are respectively the gyromagnetic ratios of $^{13}$C and of $^1$H. $\eta$ takes a maximum value close to 2 when $T_1$ is purely dipolar.

2) $T_D^0$ is related to the spectral density $J_{CH}(\omega)$. Several important simplifications can be made to the form of $J_{CH}(\omega)$. First of all, as we are considering relatively fast motions, the hypothesis of extreme narrowing can be made. Then, by working under proton decoupling conditions and neglecting the cross-correlation terms, one is left simply with $J_{CH}(0)$ the autocorrelation spectral density of the CH vector.

Finally, since the $n$ protons directly bonded to the considered carbon contribute much more than the other protons of the molecule to the $^{13}$C relaxation, $T_D^0$ is given by the following simple expression:

$$ T_D^0 = \frac{1}{T_1^D} = n \frac{10}{3} J_{CH}(0) $$

or in terms of the correlation time $\tau_c$

$$ T_D^0 = n \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r_{CH}^6} \tau_c $$

where $r_{CH}$ is the CH bond length respectively taken as 1.085 and 1.095 Å for carbons 3 and 1, 2.

3) The molecule is supposed to perform two kinds of independent motion: overall reorientation treated on the basis of a diffusive model for an asymmetric top molecule [24], and ring-puckering internal motion occurring by instantaneous jumps between two equivalent conformations.

The autocorrelation spectral density of the CH vector $J_{CH}(0)$ is related to the correlation function $C_{qq}(t)$ by

$$ J_{CH}(0) = -\frac{3}{10} \pi \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r_{CH}^6} \int_0^{+\infty} C_{qq}(t) \, dt $$

where

$$ C_{qq}(t) = \left< Y_{2q}^* (\Omega(t)) \, Y_{2q} (\Omega(0)) \right> $$

The $Y_{2q}$ are spherical harmonics of the second order whereas $\Omega_q(t)$ and $\Omega_q(0)$ represent the polar angles of the CH relaxation vector at time $t$ and zero respectively in the laboratory frame XYZ. The brackets indicate the ensemble average and the star complex conjugation.

To describe the simultaneous uncorrelated motion of reorientation and ring-puckering, it is convenient to define a reference frame $xyz$ bound to G the only invariant point in the molecule (Fig. 1). If $\Omega(0)$ represents the polar angles of the CH vector in the $xyz$ frame, $g(0)$ the Euler angles relating the $XYZ$ and $xyz$ frames and $D_{qm}^{(2)}(g(0))$ the Wigner matrix elements of second order, we have the relation:

$$ Y_{2q} (\Omega(t)) = \sum_{m=-2}^{2} D_{qm}^{(2)} (g(0)) \, Y_{2m} (\Omega(0)) $$

which allows the correlation function (5) to be rewritten:

$$ C_{qq'}(t) = \sum_{m,m'=-2}^{2} \left< D_{qm}^{(2)} (g(t)) \, D_{qm'}^{(2)}(g(0)) \right> \left< Y_{2m}^{*} (\Omega(t)) \, Y_{2m'} (\Omega(0)) \right> $$

where the Wigner matrix elements characterize the overall reorientational motion in the laboratory frame whereas the time dependent spherical harmonics are governed by the ring-puckering motion in the $xyz$ frame.

To describe the ring-puckering motion, a new frame $x' y' z'$ can be chosen in which the CH vector has fixed polar angles $\Omega'$. A relation similar to (6) but applied now to the $xyz$ and $x' y' z'$ frames, allows the correlation function to be put into the form:

$$ C_{qq'}(t) = \sum_{n,n',m,m'=-2}^{2} \left< D_{q'm'}^{(2)} (g(0)) \, D_{mn}^{(2)}(g(t)) \right> \left< D_{nm}^{(2)} (g'(t)) \, D_{nm'}^{(2)}(g'(0)) \right> \left< Y_{2n}^{*} (\Omega') \, Y_{2n'} (\Omega') \right> $$

where the separation of the ensemble averages follows from the hypothesis of non-coupling between the external and internal motions.
Assuming that the overall reorientation is of the diffusive type and that the xyz axes diagonalize the rotational diffusion tensor, equation (8) becomes

\[ C_{q-q}(t) = C_{q0}(t) = \sum_{m,m',n,n'}^{2} \left( \sum_{i,-2}^{2} \frac{1}{D_{m,n}} \right) \rho_{m,n}(i) \rho_{m',n'}(i) e^{-\omega_{i}t} \Phi_{m,n}(q'(t)) \Phi_{m',n'}(q(0)) \Phi_{m,n}^{*}(q'(t)) \Phi_{m',n'}^{*}(q(0)) \]  

(9)

where the coefficients \(a_{m}(i)\) and \(\omega_{i}\) which involve the three rotational diffusion constants \(D_{xx}, D_{yy}, D_{zz}\) are given in table II.

The \(x' y' z'\) frame can be chosen such that the CH vector lies on the \(z'\) axis. The only non-zero spherical harmonic is then:

\[ Y_{20}(q') = Y_{20}(0,0) = \frac{\sqrt{5}}{2\sqrt{\pi}} \]

and the correlation function (8) simplifies to:

\[ C_{q0}(t) = \frac{1}{4\pi^{2}} \sum_{m,m'}^{2} (-1)^{m} \sum_{i,-2}^{2} a_{m}(i) a_{m'}(i) e^{-\omega_{i}t} \Phi_{m,n}(q'(t)) \Phi_{m',n'}(q(0)) \Phi_{m,n}^{*}(q'(t)) \Phi_{m',n'}^{*}(q(0)) \]  

(10)

We are left with the averaging of the part of equation (10) relative to the ring-puckering. At this stage it is necessary to introduce an explicit model for the conformational change. As in most previous work [12-16], we suppose that the relaxation vector CH performs instantaneous jumps between two equivalent positions. If the residence time at each site is called \(t_{e}\), the following expression is obtained

\[ \langle D_{m,n}^{(2)}(q'(t)) D_{m,n}^{(2)}(q(0)) \rangle = \sum_{i,j=1}^{2} P(\alpha_{i}, \beta_{i}) P(\alpha_{j}, \beta_{j}) D_{m,n}^{(2)}(\alpha_{i}, \beta_{i}) D_{m,n}^{(2)}(\alpha_{j}, \beta_{j}) \]  

(11)

\( P(\alpha_{i}, \beta_{i}) \) is the a priori probability for the CH vector in site \(i\) to have polar angles \(\alpha_{i} = \phi\) and \(\beta_{i} = \theta\) in the \(xyz\) frame. If the \(i\) and \(j\) sites are equivalent \(P(\alpha_{i}, \beta_{i}) = P(\alpha_{j}, \beta_{j}) = 1/2\). Moreover, in the jump model the conditional probabilities between two sites are:

\[ P(\alpha_{i}, \beta_{i}/\alpha_{j}, \beta_{j}, t) = 1/2 + 1/2 \exp(-2/t_{e}) \]  

(12)

and

\[ P(\alpha_{i}, \beta_{i}/\alpha_{j}, \beta_{j}, t) = 1/2 - 1/2 \exp(-2/t_{e}) \]  

(13)

By using the previous expressions, the correlation time defined according to equations (2) and (3) by:

\[ \tau_{c} = J_{CH}(0) \frac{10}{3} \frac{r_{CH}^{6}}{\hbar^{2}} \]  

(14)

can now be calculated as:

\[ \tau_{c} = \sum_{i=1}^{2} \sum_{m,n}^{2} (-1)^{m} a_{m}(i) a_{m}(i) 1/2 \left\{ \left[ \frac{1}{2\omega_{i}} + \frac{1}{\omega_{i} + \frac{2}{t_{e}}} \right] D_{m,n}^{(2)}(\alpha_{i}, \beta_{i}, 0) D_{m,n}^{(2)}(\alpha_{i}, \beta_{i}, 0) + \right. \]

\[ + D_{m,n}^{(2)}(\alpha_{i}, \beta_{j}, 0) D_{m,n}^{(2)}(\alpha_{i}, \beta_{j}, 0) \left[ \left[ \frac{1}{2\omega_{i}} - \frac{1}{\omega_{i} + \frac{2}{t_{e}}} \right] D_{m,n}^{(2)}(\alpha_{i}, \beta_{i}, 0) D_{m,n}^{(2)}(\alpha_{i}, \beta_{j}, 0) \right. \]

\[ + D_{m,n}^{(2)}(\alpha_{i}, \beta_{j}, 0) D_{m,n}^{(2)}(\alpha_{i}, \beta_{j}, 0) \} \]  

(15)

Instead of trying to reduce this expression to a simpler analytical form, we have chosen to write it in a computer program and to calculate \(\tau_{c}\) numerically.

Finally, for a given temperature we have, three experimental correlation times given by equation (3), that we can fit to equation (15) by adjusting the dynamical parameters \(D_{xx}, D_{yy}, D_{zz}\) and \(\tau_{e}^{-1}\) and the geometrical ones corresponding to the polar angles of the CH vector before and after the jump. We have checked that equation (15) gives the same result as Huntress's formula (Eq. 3-B.6 of reference [24]) in the limit of the rigid asymmetric top obtained when \(\tau_{e}^{-1} = 0, \alpha_{1} = \alpha_{2} \) and \(\beta_{1} = \beta_{2}\). Results in agreement with those given by Baldo et al. (Eq. (23) of reference [14]) are also obtained in the limit where the CH vector lies in the librating plane.
3. Experimental conditions.

Commercial cyclopentene (FLUKA 99.9 %) was carefully distilled under partial vacuum and then degassed and sealed in a 5 mm diameter glass tube. Indeed, atmospheric oxygen seems to initiate some polymerization [22a].

This tube is placed in a larger one of 10 mm diameter containing a few drops of hexadeutero-benzene dissolved in carbon disulfide in order to provide a 2H signal for the field frequency stabilization.

As already pointed out, from the 13C NMR point of view, the cyclopentene molecule has three distinct sites which can be classified in A { X } (ethylenic carbon) and A { X2 } systems.

The relaxation of an A { X } spin system under decoupling conditions can be obviously described by a single exponential; on the other hand, for an A { X2 } system, even when it is decoupled the neglect of cross-correlation spectral densities could in some instances lead to serious misinterpretation [9a, 9b]. In fact, an exponential recovery (as shown in Fig. 2) does not necessarily mean that cross-correlation can be neglected; this pure exponential character, which may be anyway difficult to detect experimentally, could be accidental due to a particular type of cross-correlation. Furthermore, these quantities are involved in the NOE factor. However a previous study involving the 13C[(IH)2J spin system of cyclopropane [9c] has shown that the influence of the JHCH dipolar cross-correlation spectral density was negligible because of its small value as compared with the autocorrelation spectral density; this is essentially due to geometrical reasons.

Therefore, we have studied the three 13C sites of cyclopentene in natural abundance under proton decoupling conditions. The T1 measurements have been performed at 22.628 MHz with a Bruker HX 90 spectrometer connected to a NICOLET 1080 computer. The inversion-recovery pulse sequence \( \{ 180^\circ - r - 90^\circ \} n \) has been used with waiting times \( T \) of the order of 5 \( T_1 \). In order to improve the signal-to-noise ratio, four free induction decays (FID) have been accumulated. The NMR spectrum has then been calculated by Fourier transform of the resulting FID in a spectral range of 600 Hz. During the measurement the saturation of the proton transitions at 90 MHz has been achieved with a broad-band decoupler BRUKER BSV 3P.

Finally to correct the data for any temporal drift of the spectrometer, the 13C longitudinal magnetization at thermal equilibrium and under proton irradiation has been performed at the beginning and after five measurements of the magnetization. The values at time \( \tau \) are then deduced by linear interpolation [17].

The measurement of the NOE factor is performed in two steps. The area \( S_0 \) of the 13C resonance signal at thermal equilibrium is first evaluated under proton decoupling conditions and after the sequence \( 90^\circ - \text{acquisition} - T \) \( n \) where \( T = 10 T_1 \).

The area \( S_\infty \) in the absence of proton decoupling is measured with a gated decoupling sequence [9d] in which the irradiation frequency is shifted by 100 KHz and the decoupler simultaneously switched from the modulation to the C.W. mode during the acquisition of the first induction decay. In addition,
the first induction decays corresponding to continuous proton irradiation \((S_{0})\) and to gated proton irradiation \((S_{0})\) were alternatively acquired and stored in separate memory blocks in order to avoid eventual instrumental drifts having a different effect on the spectra obtained with and without NOE. The factor \(\eta\) characterizing the Nuclear Overhauser Effect is then defined as 
\[ \eta = \frac{(S_{0} - S_{0})}{S_{0}}. \]

4. Results.

The evolution of the logarithm of the magnetization for the three different \(^{13}\)C nuclei of cyclopentene is linear at all temperatures (Fig. 2) and the spin-lattice relaxation time \(T_{1}\) can easily be deduced (Table III).

In particular, it can be pointed out that this linearity persists for carbons 1 and 2 over times longer than \(T_{1}\) confirming the negligible rôle of the cross-correlation terms. The values of \(\eta\) are also reported in table III and allow the dipolar relaxation time \(T_{1}\) and the experimental correlation time \(\tau_{c}\) to be deduced with help of equations (1) and (3) and of the measured \(T_{1}\) values.

One can remark that the precise measurement of the NOE effect is of crucial importance for cyclopentene since \(\eta\) is found to be smaller than 2 at all temperatures.

5. Discussion.

For each temperature we have three experimental correlation times which can be fitted by a system of three equations of the type

\[ \tau_{c}^{\text{calc.}} = \tau_{c}(D_{xx}, D_{yy}, D_{zz}, \tau_{c}^{-1}, \alpha_{1}, \beta_{1}, \alpha_{2}, \beta_{2}). \]  

For carbons 1 and 2 which have \(n = 2\) equivalent protons, \(\tau_{c}^{\text{calc.}}\) is obtained from the average of the two contributions.

The question now is to know whether both internal and external motions or only the latter are responsible for the \(^{13}\)C relaxation. This makes a great difference since, for three equations, there are at least 10 important parameters in the first case, whereas there are only 3 for the reorientational motion of the rigid molecule of known geometry, making possible the determination of the three diffusion coefficients \(D_{xx}, D_{yy}, D_{zz}\).

So we have first supposed as a working hypothesis that the molecule is rigid \((\tau_{c}^{-1} = 0)\) and the geometry is varied inside limits which go from the planar configuration to the bent one with a maximum puckering angle \(\alpha_{0} = 30^{\circ}\). The information on the equilibrium geometry mainly comes from NMR H-H dipolar couplings analysis. Lemarié et al. [19] found \(\alpha_{0} = 23^{\circ}\) for liquid cyclopentene at room temperature and Stephenson et al. [20] \(30.8^{\circ}\) in a nematic solvent. Although this latter value could be slightly modified by following a different method of analysis of the data [21], it is probable that the \(\alpha_{0}\) value lies in the range 20-30\(^{\circ}\). For a given \(\alpha_{0}\) value, there is in principle no problem to deduce \(D_{xx}, D_{yy}\) and \(D_{zz}\) values by a least-square fitting procedure applied to the three equations similar to (15). The results thus obtained are reported in table IV for the room temperature experiment and for various \(\alpha_{0}\) values.

Table III. — Experimental parameters \(T_{1}\) and \(\eta\) for liquid cyclopentene and corresponding \(T_{1}^{D}\) and \(\tau_{c}\) values.

<table>
<thead>
<tr>
<th>(T_{1}) (s) (*)</th>
<th>(\eta) (*)</th>
<th>(T_{1}^{P}) (s) (*)</th>
<th>(\tau_{c}) (ps) (*)</th>
<th>(T_{1}) (s)</th>
<th>(\eta)</th>
<th>(T_{1}^{P}) (s)</th>
<th>(\tau_{c}) (ps)</th>
<th>(T) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{1})</td>
<td>33.8</td>
<td>32.5</td>
<td>29.7</td>
<td>300</td>
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<td></td>
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<tr>
<td></td>
<td>(2.0)</td>
<td>(2.0)</td>
<td>(1.0)</td>
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<tr>
<td></td>
<td>(0.68)</td>
<td>(0.72)</td>
<td>(0.73)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(T_{1}) (s) (*)</td>
<td>32.5 ± 1.6</td>
<td>29.5 ± 1.6</td>
<td>25.4 ± 1.1</td>
<td>300</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(\eta) (*)</td>
<td>1.41 ± 0.14</td>
<td>1.43 ± 0.15</td>
<td>0.79 ± 0.06</td>
<td>63.94</td>
<td></td>
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<tr>
<td>(T_{1}^{P}) (s) (*)</td>
<td>45.84</td>
<td>41.03</td>
<td>63.94</td>
<td>300</td>
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<tr>
<td>(\tau_{c}) (ps) (*)</td>
<td>0.504</td>
<td>0.56</td>
<td>0.67</td>
<td>63.94</td>
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<tr>
<td>(T_{1}) (s)</td>
<td>24.6 ± 1.0</td>
<td>23.0 ± 0.7</td>
<td>26.2 ± 0.8</td>
<td>260</td>
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<tr>
<td>(\eta)</td>
<td>1.65 ± 0.11</td>
<td>1.75 ± 0.12</td>
<td>1.16 ± 0.10</td>
<td>44.92</td>
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<tr>
<td>(T_{1}^{P}) (s)</td>
<td>29.65</td>
<td>26.14</td>
<td>44.92</td>
<td>260</td>
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<tr>
<td>(\tau_{c}) (ps)</td>
<td>0.78</td>
<td>0.886</td>
<td>0.96</td>
<td>44.92</td>
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<tr>
<td>(T_{1}) (s)</td>
<td>16.1 ± 1.0</td>
<td>14.6 ± 0.8</td>
<td>19.6 ± 1.5</td>
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<tr>
<td>(\eta)</td>
<td>1.66 ± 0.15</td>
<td>1.70 ± 0.16</td>
<td>1.51 ± 0.08</td>
<td>220</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_{1}^{P}) (s)</td>
<td>19.29</td>
<td>17.08</td>
<td>25.81</td>
<td>220</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tau_{c}) (ps)</td>
<td>1.2</td>
<td>1.36</td>
<td>1.66</td>
<td>220</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) Experimental values of Grant et al. [25]. The values in parentheses have been recalculated to unify the presentation.
Table IV. — Rotational diffusion constants calculated with equation (15) from the experimental $^{13}$C NMR correlation times in the hypothesis of the rigid molecule for various conformations of liquid cyclopentene at 300 K.

<table>
<thead>
<tr>
<th>$\phi_0$ (degrees)</th>
<th>$D_{xx}$ (ps$^{-1}$)</th>
<th>$D_{yy}$ (ps$^{-1}$)</th>
<th>$D_{zz}$ (ps$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (*)</td>
<td>0.29</td>
<td>0.21</td>
<td>0.17</td>
</tr>
<tr>
<td>0</td>
<td>0.446</td>
<td>0.269</td>
<td>0.137</td>
</tr>
<tr>
<td>22.2$^\circ$ (**)</td>
<td>0.450</td>
<td>0.276</td>
<td>0.133</td>
</tr>
<tr>
<td>25$^\circ$</td>
<td>0.452</td>
<td>0.279</td>
<td>0.131</td>
</tr>
<tr>
<td>30$^\circ$</td>
<td>0.456</td>
<td>0.283</td>
<td>0.127</td>
</tr>
</tbody>
</table>

(*) Values determined by Grant et al. [25].
(**) Puckering angle of the gas phase equilibrium geometry [18].

The most important conclusion to be drawn from these results is the important anisotropy of rotation. Moreover, the orders of magnitude of each diffusion constant in the sequence $D_{xx} > D_{yy} > D_{zz}$ are very little dependent on the puckering angle $\phi_0$ and the same tendencies are observed at lower temperature. Grant et al. [25], in a short study of near ellipsoidal molecules, report $T_1$ and NOE results (Table III) for liquid cyclopentene at room temperature which differ noticeably from ours. Their calculated diffusion coefficients are of course also different (Table IV). Nevertheless, the general trends persist and these authors already remark on the surprising sequence of $D$ values in particular the smallness of $D_{zz}$ which is associated with the pseudo-$C_5$ axis of the molecule, i.e. with the greatest cylindrical symmetry.

We have now obtained further evidence which makes us think that these results, obtained in the rigid molecule approximation, have little physical meaning. Firstly, as already pointed out, it would be very unusual for a molecule which is nearly a symmetric top to have its rotation inertially controlled. In general, the faster rotation occurs about the axis of higher symmetry [1-3] which corresponds here to the higher moment of inertia. Actually, for molecules, which are not strictly symmetric tops such as furan or thiophen, the rotation has been found to be nearly isotropic inside the error limits [26, 27].

Secondly, we have performed quasielastic neutron scattering experiments on liquid cyclopentene at 300 K, 182 and 179 K [22]. After a separate determination of the self diffusion coefficient at these temperatures, we have deconvoluted the whole quasielastic profile from the resolution function and the translational Lorentzian component by using Sears’s spherical rotation model [28]. Indeed, it would be illusory to fit more parameters, as required by a model with a symmetric top or a fortiori asymmetric top molecule. If the rotational and ring-puckering motions are not coupled it is easy to show that the latter does not affect the profile at low values of momentum transfer because its incoherent structure factor is close to 1. With the above assumptions, the profiles have been very satisfactorily reproduced at all temperatures and the $D$ values given for comparison in figure 3 have been obtained.

Thirdly, we have performed IR and Raman bandshape analysis on liquid cyclopentene between 150 and 300 K [23]. Rather few bands are well isolated and free from combinations or hot-bands involving the ring-puckering; however it has been possible to select two bands in IR and two in Raman which seem to be only affected by vibrational and rotational relaxation.

The results indicate that $D_{xx}, D_{yy}, D_{zz}$ are of the same order of magnitude in the liquid phase (Fig. 3).

As soon as the jump rate becomes faster than $10^{10}$ s$^{-1}$ there is an important modification of the $D_{xx}$ and $D_{zz}$ values which converge towards the rather constant $D_{yy}$ one to give the situation of a nearly isotropic rotor with $D_{xx} \approx D_{yy} \approx D_{zz}$ values close to $1/6 \tau_c$.
Fig. 4. — Calculated values of the $D_{xx}$, $D_{yy}$ and $D_{zz}$ constants for various temperatures, puckering angles and jump rates. The horizontal dotted lines give the average $D_0$ value obtained by other techniques. The vertical line indicates the values of $t_e^{-1} = 5 \times 10^{12}$ s$^{-1}$ at 300 K and $10^{12}$ s$^{-1}$ at 220 K.

The $D_0$ value previously deduced from the IR, Raman and quasielastic neutron scattering results.

The crossing is now strongly dependent on $\alpha_0$. It occurs in a reasonable range of $t_e^{-1}$ values for $\alpha_0 = 25^\circ$ or $30^\circ$ but not for smaller angles. On the other hand, it seems difficult to envisage higher $\alpha_0$ values [19-21]. The crossing also depends slightly on the temperature. As indicated in figure 4 a $t_e^{-1}$ value of $5 \times 10^{12}$ s$^{-1}$ for $\alpha_0 = 30^\circ$ seems to be reasonable at 300 K whereas at 220 K a better situation seems to be $t_e^{-1} = 10^{12}$ s$^{-1}$ and $\alpha_0 = 30^\circ$.

One can remark that the "reasonable» $t_e^{-1}$ values are limited to a maximum value of $10^{14}$ s$^{-1}$. Indeed we know from inelastic neutron scattering or IR and Raman spectroscopies that the frequency distribution corresponding to the transitions in the ring-puckering potential has its maximum at about 170 cm$^{-1}$ [22]. This corresponds to a mean frequency of $3.2 \times 10^{13}$ s$^{-1}$ for the oscillations of the molecule in one of its two equivalent bent conformations. The jump rate cannot be faster than these oscillations. Actually the values of $10^{12}$ s$^{-1}$ and $5 \times 10^{12}$ s$^{-1}$ found at 220 and 300 K indicate that the molecule executes some ten oscillations during the residence time $t_e$.

Two kinds of experimental limitations prevent the extraction of more precise information. First of all, the rotational constants $D_{xx}$, $D_{yy}$ and $D_{zz}$ cannot be found from optical and neutron spectroscopies with a precision better than $10\%$. It is obvious from figure 4 that in the crossing region, a precise knowledge of these three constants would allow a precise determination of both $\alpha_0$ and $t_e^{-1}$.

The second kind of limitation comes from the imprecision of the NMR correlation times $\tau_c$. Its consequences are illustrated in figure 5 for $\alpha_0 = 30^\circ$ and $T = 300$ K. Three distinct series of $\tau_c$ values are chosen : the normal ones 0.5, 0.56 and $0.67 \times 10^{12}$ s (Table III) and two others which differ by $\pm 10\%$. The determination of the best $D$ values has been performed for these three series of $\tau_c$. In this way, one can visualize the consequences of the imprecision on $\tau_c$. Although large areas are now associated to each diffusion constant, the general trend persists and one can define a crossing area which does not fundamentally modify the previous conclusions. It simply shows the kind of precision to be expected in the present state of the experimental data. The quality of the fits can be appreciated in figure 6 where for each $t_e^{-1}$ value, the experimental and calculated $\tau_c$ are compared. It is interesting to see that the best fits are obtained for a $t_e^{-1}$ value of about $10^{13}$ s$^{-1}$ and the normal series of experimental correlation times.

Finally, it must be concluded that a rather large uncertainty is attached to the $t_e^{-1}$ values thus determined : at 300 K, $t_e^{-1} = (5 \pm 4).10^{12}$ s$^{-1}$, at 220 K $t_e^{-1} = (1 \pm 0.5).10^{12}$ s$^{-1}$. In particular, it would be illusory to deduce an order of magnitude for the activation energy.

Fig. 5. — Rotational diffusion constants calculated as a function of $t_e^{-1}$ for $T = 300$ K and $\alpha_0 = 25^\circ$. Curves «a» correspond to the normal series of $\tau_e^{\text{np}}$ (see Table III); curves «b» and «c» correspond respectively to $(\tau_e^{\text{np}} + 10\%)$ and $(\tau_e^{\text{np}} - 10\%)$.  

Fig. 6. — Comparison of the calculated $\tau_0$ values (solid line) with the experimental ones. The three series of $\tau_0$ defined in figure 4 are marked by horizontal lines. The vertical line corresponds to $\tau_0 = 10^{13}$ s$^{-1}$.

After discussing the experimental limitations it is necessary to recall that the simple models used in the treatment of the data also bring their own limitations. It is not guaranteed that the whole molecule rotation and the ring-puckering are uncoupled. Nor is it evident that the jump model between two sites is a good representation of the internal motion. However more sophisticated theories would bring further parameters that could not be evaluated with the present data. A more efficient way to complete and improve the analysis could rather be to search for independent evidence of the internal motion by other techniques.

This seems to be possible by studying the infrared and Raman spectra of specifically deuterated molecules [29]. We have monodeuterated the cyclopentene molecule on carbons 1 or 2 and instead of observing one single $\nu_{CD\text{D}}$ stretching vibration, we obtain a complex spectral density at low temperature two intense bands distant by a few tens of cm$^{-1}$ reflect the presence of CD bonds in the axial or equatorial positions. When the temperature increases they merge into a continuous and broad-band. This coalescence is very similar to that observed currently in NMR but on a different time scale. A conformational exchange occurring with a rate of $5 \times 10^{12}$ s$^{-1}$ is quite likely to produce the observed phenomena.

6. Conclusion.

The aim of the present work was to apply the $^{13}$C NMR relaxation technique to a flexible molecule in the liquid state and to compare the results with those obtained by infrared, Raman and quasielastic neutron scattering.

The cyclopentene molecule executes a well defined ring-puckering motion and presents, for the $^{13}$C NMR three distinct sources of information. Rather simple hypotheses have been made in the analysis of the three series of $T_1$ and NOE data obtained between 220 and 300 K. The dipolar energy relaxation between the carbons and the directly bonded protons has been interpreted as resulting from quasi isotropic rotational diffusion and from internal jumps between two bent conformations. Orders of magnitude for the relevant parameters have been obtained. The puckering angle $\alpha_0$ seems to be in the range 25-30$^\circ$ the jump rate $\tau_0^{-1}$ of about $5 \times 10^{12}$ s$^{-1}$ at 300 K with a small activation energy and the mean rotational constant $D_0$ of about $0.22 \times 10^{12}$ s$^{-1}$ at the same temperature with an activation energy of 5.1 kJ.mole$^{-1}$.

Although the model is rather crude, there is good evidence at a qualitative level for the influence of the internal motion on the $^{13}$C relaxation time.

However the necessity to use complementary techniques to improve the analysis is evident. Selectively deuterated molecules could well open a new interesting field of investigation for these non-rigid molecules in the condensed state.

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References

[22b] Lassegues, J. C., Fouassier, M., Besnard, M., Jobic, H. and Dianoux, A. J. (Part II, following paper).