OURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 113–120 (1991)

INTERNAL ROTATION OF CH_3 GROUPS AND ENTROPY DIFFERENCE BETWEEN DIASTEREOISOMERS: A ^{13}C NMR STUDY VIA RELAXATION TIME MEASUREMENTS

Y. BRUNEL, C. COULOMBEAU AND S. LAVAITTE
Université Joseph Fourier, LEDSS, Bât. 52 – Chimie Recherche, BP 53X, 38401 Grenoble Cédex, France
AND
J. REISSE*
Laboratoire de Chimie Organique (CP 165), Université Libre de Bruxelles, 50 avenue F.D. Roosevelt, 1050 Brussels, Belgium

Overall and internal rotation can be studied by means of relaxation time measurements on carbon-13. Diffusion constants associated with overall rotation and internal rotation can be used to quantify the intermolecular and intramolecular motional constraints. During the course of the study, a very careful examination of monomethyl and dimethylnorbornanes was performed and the results were compared with data obtained by neutron inelastic scattering. This study led to a clear conclusion concerning the real usefulness of relaxation time measurements as a very good alternative method for the determination of entropy contributions, which are usually calculated on the basis of vibrational studies.

INTRODUCTION

Internal rotation and its influence on the entropy difference between isomers

For a set of molecules in a singlet fundamental electronic state, the entropy difference between isomers A and B in the perfect gas phase is the sum of different contributions[1] [equation (1)]:

$$\Delta S^\circ = \Delta S^\circ_{\text{rot.}} + \Delta S^\circ_{\text{int.rot.}} + \Delta S^\circ_{\text{vib.}} \qquad (1)$$

where rot. = overall rotation, int.rot. = internal rotation and vib. = vibration.

We shall not consider the trivial contributions to ΔS° associated with the symmetry number differences between A and B ($\sigma_A \neq \sigma_B$) on the one hand, and with the mixing entropy terms which may be different for A and B (when A and B are mixtures of sub-species) on the other.

Even in the gas phase, the different terms in equation (1) are not strictly independent. Moreover, the translational motion and the internal degrees of freedom (rotation, internal rotation and vibration) are coupled in the liquid phase. Strictly, this means that the translational degrees of freedom contribute to ΔS° in the liquid state. Nevertheless, as has been proved in the case of *cis*- and trans-1,2-dichloroethylene, the translational diffusion properties of diastereoisomers are probably very similar[2] and the coupling between translation and rotation is negligible for the kind of stereoisomers studied in this work.[3]

In the gas phase, $\Delta S^\circ_{\text{rot.}}$ between cyclohexane stereoisomers is generally less than 2 J mol^{-1} K^{-1} (see Table 1), a conclusion which can be generalized to the kind of stereoisomers examined in this work.

Table 1. $\Delta S^\circ_{\text{rot.}}$ (J mol^{-1} K^{-1}) between diastereoisomers in the gas phase at 300 K[4] [$\Delta S^\circ_{\text{rot.}} = (S^\circ_{\text{rot.}}) - (S^\circ_{\text{rot.}})_a$]

System[a]	X = Cl	X = Br	X = I
A	1·17	1·34	1·34
B	1·08	1·46	1·63
C	1·00	1·33	1·37

[a] System A: equatorial and axial halogenocyclohexanes. System B: *trans*- and *cis*-1-halogeno-4-*tert*-butylcyclohexanes (with an equatorial *tert*-butyl group). System C: equatorial and axial 2-halogeno-*trans*-decalins.

---

* Author for correspondence.

0894–3230/91/020113–08$05.00

Received 9 April 1990
Revised 4 September 1990

The net effect of the constraints acting on the solute molecules in solution can be described as a lowering of $S^{\circ}_{\mathrm{rot.}}$ for A and B, with $\Delta S^{\circ}_{\mathrm{rot.}}$ remaining small as soon as the diffusion tensor of the two isomers is approximately isotropic. Such a condition is certainly fulfilled for the isomers examined here.

In this study we shall be concerned essentially with $\Delta S^{\circ}_{\mathrm{int.rot.}}$ The distinction between $\Delta S^{\circ}_{\mathrm{int.rot.}}$ and $\Delta S^{\circ}_{\mathrm{vib.}}$ in equation (1) is usual in statistical thermodynamics,[6] even if the internal rotation degrees of freedom are no more than low-frequency vibrational modes. This means that the calculation of $S^{\circ}_{\mathrm{vib.}}$ for A and B is the sum of $3N-6-m$ terms, where N is the number of atoms in A (and B) and m is the number of internal rotation degrees of freedom described as localized group vibrations. In our examples, m will be 1 or 2, depending on the number of internal CH_3 rotors present in the molecule. As has been shown previously[6] with particular reference to the bicyclic molecules studied in this work (Figure 1), empirical force fields are able to provide a good estimation of $\Delta S^{\circ}_{\mathrm{vib.}}$, but give poor results at the level of $\Delta S^{\circ}_{\mathrm{int.rot.}}$ $\Delta S^{\circ}_{\mathrm{vib.}}$ can also be estimated provided that the low-frequency vibrational modes of A and B are known. Neutron inelastic scattering is a good experimental method for exploring the low-frequency region of a vibrational spectrum, but this method remains difficult to handle.[7,8] This is one of the main reasons why we decided to use T_1 measurements in NMR to measure the barriers hindering the rotation of CH_3 rotors.

It is generally accepted that the internal rotation of CH_3 group is only slightly perturbed by the solvent. The $S^{\circ}_{\mathrm{rot.int.}}$ values will therefore be estimated using the general expressions that are strictly valid for gas-phase molecules (one-dimensional rotation hindered by a threefold potential barrier). The estimation of $S^{\circ}_{\mathrm{rot.int.}}$ requires a knowledge of the symmetry number of the rotor (σ'), its reduced moment of inertia I_r with respect to its rotational axis and V_3, the barrier hindering the internal rotation of the CH_3 group.[5] Equation (2) gives the relationship between E (internal energy), V_3 and θ (dihedral angle) as soon as the series $E = f(\theta)$ is truncated to its first non-constant term:

$$E = V_3(1+\cos 3\theta)/2 \qquad (2)$$

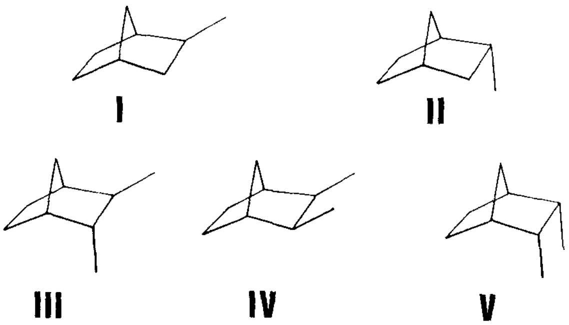

Figure 1. Derivatives studied.

Determination of rotational barriers by relaxation time measurements in ^{13}C NMR

Over the last 20 years many papers have been devoted to the determination of rate constants for internal rotation via the measurement of the dipole–dipole contribution to the T_1 values in ^{13}C NMR. All these publications have been based on the seminal papers by Woessner,[9] Woessner *et al.*[10] and Kuhlmann and Grant.[11]

The Woessner model rests on various assumptions:

1. The overall motion of the molecule is given as a diffusion motion.
2. The overall diffusion tensor is characterized by one diffusion constant D (spherical top), two diffusion constants $D_{\parallel}$ and $D_{\perp}$ (symmetrical top) and three diffusion constants D_{xx}, D_{yy}, D_{zz} (asymmetric top). This last case was only recently dealt with by Craik *et al.*[12] and Bastard *et al.*[13]
3. The internal rotation of the CH_3 group is described either as a diffusion motion characterized by an internal diffusion constant, R_D, or as a jump motion characterized by an internal rate constant, R_I.
4. The internal rotational axis makes an angle α (which can be 0°) with the principal axis of the diffusion tensor in the case of the symmetrical top, or any angle involving the three principal axes of the diffusion tensor in the case of the asymmetrical top.

The dipole–dipole contribution to the longitudinal relaxation time of one particular carbon nucleus can be determined by means of the equation

$$(T_1^{\mathrm{DD}})^{-1} = \sum_i [\gamma_H^2\gamma_C^2\hbar^2/r_{\mathrm{CH}_i}{}^6]\,T_c^{\mathrm{eff}} \qquad (3)$$

where the sum is taken over all H_i atoms of the molecule. r_{CH_i} corresponds to the distance between the carbon atom and H_i. T_c^{eff} is the effective correlation time and the other symbols have their usual meanings. In the absence of cross-relaxation and cross-correlation terms, equation (3) is valid under extreme narrowing conditions. Cross-relaxation is suppressed by the broadband decoupling of the H nuclei, and the cross-correlation effects seem to be negligible in the cases under study.[14]

As far as the carbon atoms of the molecular skeleton are concerned, T_c^{eff} is related to the overall diffusion constant D by equation (4) if the diffusion is considered as isotropic:

$$T_c^{\mathrm{eff}} = 1/6D \qquad (4)$$

For the CH_3 group, T_c^{eff} is given by

$$T_c^{\mathrm{eff}} = A/6D + B/(6D + D_i') + C/(6D + D_i'') \quad (5)$$

where A, B and C are geometrical factors.[10] As was clearly shown by Blunt and Stothers,[15] the C—C—H bond angles of the CCH_3 group directly affect the value of the geometrical parameters A, B and C. D_{i-} and D_i'' are characteristics of the internal rotational motion. D_i' and D_i'' are simply related to R_{D} or R_{I} depending on the model used to describe the internal rotation.[14] If the internal rotation can be described as a series of random jumps between three equivalent positions (jump motion model),

$$D_i' = D_i'' = 3/2R_{\mathrm{I}} \quad (6)$$

where R_{I} is the number of jumps per second. If the rotation is described as a stochastic diffusion motion,

$$D_i' = 1/4D_i'' = R_{\mathrm{D}} \quad (7)$$

where R_{D} is the internal rotation diffusion constant.

Following Kuhlmann and Grant R_{I} is related to the barrier hindering internal rotation, V_{I} by the equation

$$R_{\mathrm{I}} = 3/2(kT/I_{\mathrm{r}})^{1/2}\exp(-V_{\mathrm{I}}/RT) \quad (8)$$

while the relationship between R_{D} and V_{D} is given by

$$R_{\mathrm{D}} = (kT/I_{\mathrm{r}})^{1/2}\exp(-V_{\mathrm{D}}/RT) \quad (9)$$

Equations similar to equations (8) and (9) are available and describe other and more complex situations including the fully anisotropic diffusion motion.[12,13,16]

A problem which is important in the context of this study is the effect of r_{CH} values on T_c^{eff} and the extent of the influence of the H atoms not directly connected to the carbon atom observed.

Is it justifiable to take only H atoms into account which are directly bonded to the ^{13}C atom observed? In the case of 2-methyladamantane (solvent $CDCl_3$, $T = 280$ K), we compared the T_c^{eff} values calculated via equation (3) on the one hand with values calculated by taking into account only the directly bonded hydrogen atoms on the other.[17] A systematic difference of *ca* 1% was observed for CH_3, whereas this difference was *ca* 3% for CH_2 and less than 10% for CH. Considering the experimental error on T_c^{eff} it seems acceptable, but certainly not wholly correct, to limit the summation to the directly bonded H atoms (this procedure, which is generally used, will be discussed later).

Another question concerns the exact value of r_{CH} to be incorporated into equation (3). This question is a difficult one because C—H bond lengths are generally not known with any degree of accuracy. Moreover, as has been demonstrated by Harris and Newman,[18] the relevant distance in NMR is $r_{\mathrm{CH}} \equiv \langle r^{-3} \rangle^{1/3}$ if the analytical form of the correlation function is taken into account. This average distance is different from the average distances obtained via diffraction experiments or rotational spectroscopy.[18] It nevertheless seems very difficult to calculate $\langle r^{-3} \rangle^{1/3}$ properly and the common practice of introducing into the calculation the r_{CH} distance obtained via other techniques is the only possible procedure even if it is not strictly correct.

If the overall motion was isotropic, if all the r_{CH} values were identical, if the directly bonded hydrogen acted alone as a relaxing species and if cross-correlation was negligible, all the T_c^{eff} would be identical for the carbon nuclei of the rigid skeleton. Nevertheless, different T_c^{eff} values for the carbon atoms of a same molecule are not definite evidence *per se* for an anisotropic overall motion,[3] but are an indication which must be taken into account.

Molecules very similar to those studied in this work have been examined previously by other workers.[19-22] It appears clear that, in all cases, the diffusion tensor is anisotropic. However, at the same time, it is also clear that anisotropy is much less important for hydrocarbons such as bicyclooctane of norbornane[19] than for the corresponding substituted systems, the substituents being voluminous atoms such as halogens or a hydrogen-bonding group such as OH, NH_2 or COOH.[19,20] In the case of norbornane itself, the ratio between the values of the principal components of the diffusion tensor is of the order of 2 whereas for α-androstane, for example, this ratio is higher than 7.[16]

What is the influence of the assumption of isotropic motion on the value of a barrier hindering the internal rotation of a CH_3 group? The answer depends on the degree of anisotropy. In the case of α-androstane, Levy *et al.*[16] have compared the values of internal rotation rate constants obtained by treating the overall diffusion motion as anisotropic or isotropic. From their results compared with other results previously published in the literature, these authors were able to show that the methyl rotation rates of $(CH_3)_{18}$ and $(CH_3)_{19}$ in androstane derivatives are 2–3 times smaller when calculated using isotropic overall motion. Nevertheless, the case of α-androstane is particular because this molecule is highly anisotropic. The anisotropy is much less in the case of the methyl derivatives of norbornane and the assumption of isotropicity seems acceptable – a point that has already been proved for 1-methyladamantane.[17] Moreover, the adjustment of the six parameters (three diffusion constants and three angles) necessary to describe an overall anisotropic rotation is a difficult task. Even in the case of 5α-androstane, where 17 relaxation times were measured, the authors were obliged to assume that the inertia and diffusion tensors were simultaneously diagonal. It appears clear that a gap exists between the theoretical treatment and its application to real systems. We therefore consider that our approach of carefully selecting the molecules in order to perform measurements on 'approximately spherical objects' is satisfactory and makes it possible to refrain from adjusting too many parameters with respect to the number of data.

Physical meaning of rotational barriers determined via relaxation time measurements

It seems interesting to make some comments on the different problems related to the V_I or V_D determinations via equations (8) and (9). What is the physical sense of V_I and V_D? Taking into account the fact that, depending on the model used, V_I or V_D values can be obtained starting from the same series of T_1 values, neither V_I nor V_D can be strictly equal to V_3 [equation (2)]. If V_I (or V_D) were physically identical with V_3, it is obvious that the choice between the two models describing the internal motion would be easy. Kowalewski and co-workers,[25] have examined this problem in great detail. They also discussed a different approach which leads to the determination of an activation energy E_a from the study of the temperature effect on R_1. On the basis of simulation experiments they concluded that E_a values are similar to V_3 (only 2–4 per cent lower). The general conclusions which they arrived at are as follows: E_a gives a better estimate of V_3 than V_I; and the physical meaning of V_I is not perfectly clear.

This problem is of real interest firstly if the fact is taken into account that our final goal is the estimation of $\Delta S^{\circ}_{\text{int.rot.}}$ between isomers and secondly if it is considered that the use of Pitzer's theory implies a knowledge of V_3. The arguments put forward by Kowalewski and co-workers[14,25] are not totally convincing given that their own experimental results[14] do not confirm the conclusions based on simulation experiments. Indeed, their V_0 values (equivalent to V_X in our work) are closer to V_3 values than E_a values.

The correlation between $\Delta S^{\neq}$ and $\Delta H^{\neq}$ obtained by them is reasonably good, but this observation does not necessarily reflect a true physical phenomenon. Indeed, it is surprising to see some $\Delta S^{\neq}$ values in the range -12 to $-19\ \text{J mol}^{-1}\text{K}^{-1}$. $\Delta S^{\neq}$ could be predicted as being near zero for a process such as a 120° jump by a CH_3 group. Moreover, these very negative $\Delta S^{\neq}$ values are associated with surprisingly low $\Delta H^{\neq}$ values. Finally, other workers have observed that when a comparison is possible, V_I values are similar to V_3 values obtained by other methods.[23,24]

Under these conditions, we consider that the comparison between V_3, V_I (or V_D) and E_a remains a useful approach in order to determine which of the parameters V_I, V_D or E_a is the best approximation of V_3.

We decided to investigate the norbornane derivatives essentially because the same molecules had been studied previously by inelastic neutron scattering (INS).[7,8] In this way, a direct comparison between V_3 and the barriers obtained by NMR would be possible for a set of similar molecules.

DISCUSSION OF RESULTS

Table 2 gives a complete series of parameters describing the overall and internal dynamics of some norbornane derivatives.

The D^{BH} values given in the first row of Table 2 correspond to the isotropic diffusion constant associated with the overall motion. These values were calculated by considering that the directly bonded H atoms (BH) only contribute to the dipole–dipole relaxation of the various carbon nuclei. These values themselves are averages calculated over the seven carbon atoms of the rigid skeleton of the norbornane derivatives.

As is shown in Table 3, the individual D^{BH} values are

Table 2. Dynamic properties of norbornane methyl derivatives at 273 K (1 mol dm^{-3} in $CDCl_3$)[a]

Compounds		I	II	III methyl exo	III methyl endo	IV	V
D^{BH}	1	5·92	6·22	4·43	4·43	4·11	4·70
D^{T}	2	6·18	6·90	4·74	4·74	4·37	5·01
R_D^{BH}	3	3·91	5·81	3·46	2·20	2·33	2·97
R_D^{T}	4	3·42	5·38	2·82	1·63	1·82	2·44
R_D^{BH}	5	7·35	10·74	6·45	4·20	4·41	5·59
R_I^{T}	6	6·48	10·03	5·28	3·15	3·50	4·65
V_D^{BH}	7	12	11	12	14	13	13
V_D^{T}	8	13	11	13	14	14	13
V_I^{BH}	9	12	11	12	13	13	12
V_I^{T}	10	12	11	12	14	13	13
V_3 neutrons	11	15	14	14	13	14	15
E_a	12	8·5 ± 2·4	8·7 ± 2·9	8·8 ± 3·6	14·4 ± 2·7	13·6 ± 3·1	10·7 ± 1·3

[a] *Units*: lines 1 and 2 in 10^{10} rad^2.sec^{-1}; lines 3–6 in 10^{10} s^{-1}; lines 7–12 in kJ.mole^{-1}; line 12: the error indicated corresponds to one standard deviation.

Table 3. D^{BH} and D^{T} for **I** at 273 K (1 mol dm^{-3} in CDCl$_3$)[a]

Atom[b]	δ(ppm)	D^{BH}	D^{T}
C-1	43·04	5·78	6·33
C-2	36·38	5·62	6·27
C-3	39·86	6·37	6·34
C-4	36·94	5·53	6·11
C-5	30·02	6·31	6·51
C-6	28·75	5·93	5·45
C-7	34·77	5·87	6·04

[a] For the definition of the symbols, see text (D values in 10^{10} rad^2 s^{-1}).
[b] The numbering of the carbon atoms of the norbornane skeleton is classical (C-1 corresponds to the bridgehead in this 2-methylnorbonornane).

not identical for each carbon of compound **I** (the same conclusion can be reached from the study of the other molecules), but the differences are so small that the assumption of overall isotropic rotation discussed in the Introduction seems acceptable.

The D^{T} values given in the second row of Table 2 were obtained firstly by considering that all the H atoms play a role in the relaxation of each carbon nucleus and then by taking the same average over the various carbon atoms of the skeleton in the case of D^{BH}.

Structural parameters are not available for all the componds under study. We have kept the geometry of the norbornane[26] for their skeletal framework, but have added the methyl groups in a staggered conformation with standard geometrical parameters: $r_{CH} = 1{\cdot}115$ Å and CCH = 109·5°. The D^{T} values are systematically slightly higher than D^{BH}, but we consider this difference to be negligible (see below). Considering the values of D^{T} (or D^{BH}), it becomes clear that the shape of the molecule has an observable (but small) effect on the overall rotation of the molecules under study. Compound **II** (or **V**) diffuses more rapidly than **I** (or **IV**) on a systematic basis. This is probably related to the more globular shape of the *endo* (or di-*endo*) species. We can conclude that the entropy of rigid rotation in solutions is not identical for each diastereiosomer in the monomethyl or dimethyl series. It is even slightly different in the gas phase,[6] and the loss of entropy on passing from gas to solution is thus slightly higher for the *exo* than for the *endo* isomer and for the di-*exo* than for the di-*endo* isomer, with the *endo–exo* isomers being characterized by a behaviour pattern intermediate between those of the di-*exo* and the di-*endo* isomers. It is impossible to calculate this decrease in entropy but, considering the great similarity between the D^{T} values for the isomers of methylnorbornane or dimethylnorbornane, the overall rotation entropy must remain very similar in solutions (as in the gas phase).

In the third and fourth rows of Table 2, the internal rate constants for methyl rotation were calculated by considering internal rotation as a diffusion process [equation (7)]. The values in the third row were calculated by taking into account only the directly bonded H atoms as relaxing partners, whereas the values in the fourth row were established by taking all the H atoms of the molecule into account. The same difference exists between the calculation procedures used to estimate the values given in the fifth and sixth rows. Nevertheless, in this ease, the internal rate constants were estimated by considering internal rotation as a jump motion [equation (6)]. The rate constants (third and fourth rows) are related to the barriers given in the seventh and eighth rows via equation (9), while the rate constants given in the fifth and sixth rows are related to the barriers given in the ninth and tenth rows via equation (8).

Comparing the barriers obtained by using different data treatment (diffusional-BH or diffusional-T, inertial-BH or inertial-T), it appears that the various kinds of treatment give slightly different values, which is normal. Moreover, and very important, the kind of data treatment does not lead to any inversion of sequence when one derivative is compared with another.

It appears clear than when the barriers are translated into internal rotation entropy values, the kind of data treatment has no significant effect on the entropy of the various derivatives. This last statement is easy to prove.

The tables of Pitzer and Gwinn[5] give the entropy of internal rotation as a function of V/RT for different values of $1/Q_F$, i.e. the inverse of the partition function of a free CH$_3$ rotor. If we consider the two barrier values obtained by means of the two different data treatments ($V_D^{BH} = 12$ kJ mol^{-1}, $V_D^{T} = 13$ kJ mol^{-1}) for **I**, it is easy to calculate that the internal rotation entropy calculated using one value or the other will differ by less than 0·7 J mol^{-1} K^{-1}. Such a difference is of no significance. Even if we calculate the entropy contribution for **I** on the basis of V_I^{T} on the other hand, and of V_3 (INS) on the other, the two entropy values will differ by less than 1·5 J mol^{-1}K^{-1}. Again, this difference can be neglected for all practical purposes.

Table 4 gives the contributions to the entropy due to the hindered internal rotation of the CH$_3$ rotor(s) for the various derivatives studied.

Table 4. Entropy contribution at 273 K associated with internal rotation (compounds **I**–**V**)

Compound	$S^{\circ}_{\text{int.rot.}}$ (J mol^{-1} K^{-1})[a]
I	8·9
II	9·2
III	16·8
IV	16·6
V	15·9

Table 5. Temperature effect on the entropy of internal rotation (for compound **I**)

Temperature (K)	$S_{\text{int.rot.}}$ (J mol^{-1} K^{-1})[a]
273	8·9
303	9·2
313	9·1
323	9·5
330	9·3

[a]Values are based on V_I^T (Table 2).

Table 5 gives for **I** the contribution to the entropy for the hindered internal rotation of the CH_3 rotor at various temperatures. This contribution seems to increase slightly with increasing temperature, but the variation is less than the experimental error (see experimental).

In the case of dimethyl derivatives, entropy was estimated by applying an additivity rule on the premise that the two internal rotors were independent and that the truncated Fourier series [equation (2)] remained valid in the dimethyl series. The theoretical model used in this study does not allow a demonstration of the existence (or the non-existence) of any sort of coupling between the two methyl rotors in the dimethyl derivatives. The existence of such a coupling has been clearly demonstrated by means of INS in the case of di-*endo*- and di-*exo*-dimethyl derivatives,[7] but this coupling is small (*ca* 25 cm^{-1}) in relation to the height of the barrier ($V_3 \approx 1200$ cm^{-1}). Its neglect has no significant influence on the entropy difference between isomers associated with the internal rotation[27] of the methyl group. A comparison between the internal rotation entropy in the various norbornane derivatives shows clearly how similar these contributions are when isomers are compared. This conclusion had already been reached on the basis of a vibrational study in the low-frequency range.[7,8] Nevertheless, if we take into account the difficulty of INS studies or at least their time-consuming aspect, and if we also take into account that INS studies are performed at 10 K on a solid-state sample, it becomes possible to put forward T_1 measurement as a convenient alternative method.

At the end of their paper, Ericsson *et al.*[14] stated, 'the results presented here do not provide definitive evidence supporting (or contradicting) our previous suggestion that the Arrhenius activation energy, obtained by NMR relaxation studies, should not be a good approximation to the potential barrier.' We think that the results of this study will clarify this problem because it now becomes possible to compare V_X (or V_D) barriers [obtained via equations (7) and (8)] with V_3 values determined by INS;[7,8] cf. Table 2, eleventh row). In the twelfth row of Table 2, E_a values are also given that were calculated according to the example of Kowalewski and Liljefors[25] by plotting R_I^T determined at five temperatures as a function of $1/T$, and by searching for the best exponential curve through the five points (Arrhenius law). It appears clearly (Table 2) that the E_a values differ systematically from V_3 determined by INS.

As we pointed out previously, a similar observation was made by Ericsson *et al.*[14] themselves. It therefore seems that V_I (or V_D) values determined by NMR are better estimates of the true V_3 values. Moreover, the error in E_a is probably due to the fact that the number of points is too small to arrive at an accurate determination not only of the E_a value, but also of the pre-exponential term. This being the case, it would be absurd to try to determine E_a via a linear semilogarithmic plot of R_I versus $1/T$: such a method would obviously be more inaccurate than the unsatisfactory exponential plot.

In Table 2, a systematic difference emerges between V_I or V_D and V_3 (INS), but, as discussed previously, this difference is negligible when translated into an entropy contribution.

The ease of determining the dynamic properties of molecules by NMR will certainly lead to important developments in the future. The consequences of the low-frequency, large-amplitude motions of molecules probably remain underestimated in many fields of chemistry.

EXPERIMENTAL

All the monomethyl and dimethyl derivatives of bicycloheptane were synthesized and purified according to published procedures.[8] The measurements were performed on solutions in $CDCl_3$ carefully degassed and sealed in 5- and 10-mm tubes. The concentrations of the solutions were always 1 mol dm^{-3}.

The NMR measurements were performed on Bruker AM300 spectrometers and AM400 by the progressive saturation (PS) method. The exponential curve was obtained using ten points. Each point corresponded to 32 scans performed by adding four independent series of eight successive scans. The FID curves were treated in the usual way before proceeding to the Fourier transformation.

The T_1 values (Table 6) of the fully decoupled ^{13}C signals were determined by means of a three-parameter exponential regression fitting of the experimental point distribution. Considering the range of T_1 values, the PS method was used instead of the well known IRFT method. The accuracy of the PS method, well documented in the literature,[29] was tested by comparing T_1 values obtained by this method with corresponding T_1 values obtained via the IRFT method applied to norbornane molecule.[19] Taking experimental errors (±5%) into account, the agreement between the two sets of values was excellent.

Table 6. T_1values in seconds at 273 K[a]

Atom[b]	I	II	III	IV	V
C-1	18·5 ± 0·3	20·0 ± 0·1	13·5 ± 1·1	13·2 ± 0·8	14·5 ± 0·2
C-2	18·0 ± 0·7	20·2 ± 0·2	13·5 ± 0·8	12·6 ± 0·7	14·3 ± 0·3
C-3	10·2 ± 0·3	11·3 ± 0·2	13·9 ± 0·4	12·6 ± 0·7	14·3 ± 0·3
C-4	17·7 ± 0·5	18·1 ± 0·3	13·8 ± 0·7	13·2 ± 0·8	14·5 ± 0·2
C-5	10·1 ± 0·2	11·0 ± 0·3	7·4 ± 0·1	7·0 ± 0·4	8·0 ± 0·1
C-6	9·5 ± 0·1	10·6 ± 1·1	7·7 ± 0·8	7·0 ± 0·4	8·0 ± 0·1
C-7	9·4 ± 0·1	12·1 ± 0·2	7·2 ± 0·3	6·4 ± 0·4	7·7 ± 0·2
C-Me (*exo*)	8·0 ± 0·2	—	6·2 ± 0·2	5·4 ± 0·3	—
C-Me (*endo*)	—	9·5 ± 0·8	5·7 ± 0·1	—	6·3 ± 0·1

[a] The statistical errors correspond to a 90% confidence limit.
[b] The numbering of the carbon atoms is the same as in Table 3.

Table 7. NOE values ($\eta + 1$) for compound **II** at different temperatures

Atom[a]	273 K	305 K	313 K	323 K	330 K
C-1	2·9	2·8	2·8	2·8	2·6
C-2	2·9	2·8	2·9	2·9	2·7
C-3	2·9	2·8	2·8	2·9	2·6
C-4	2·8	2·8	2·8	2·8	2·7
C-5	2·9	2·8	2·9	2·7	2·5
C-6	2·8	2·8	2·9	2·9	2·7
C-7	2·9	2·9	2·9	3·0	2·6
C-Me	3·0	2·9	2·9	2·8	2·6

[a] The numbering of the carbon atoms is the same as in Table 3.

The signal assignments of the various carbon nuclei of the molecules were performed according to Stothers *et al.*[30] Within the temperature range covered during our experiments, the Overhauser factor measured for **II** (Table 7) using a gated decoupling technique was equal to its maximum value for all the signals except at 330 K. Otherwise the study on NOE effect made by Vandenbosch[17] on methyladamantane derivatives shows clearly that the spin rotation contribution is negligible below 320 K. We therefore consider that the experimental T_1 values can be identified with the dipole–dipole components at 273 K.

Errors in the dynamic parameters determined by relaxation time measurements. It is extremely difficult to arrive at a proper estimate of the errors in the different values given in Table 2. Some of these errors are systematic, e.g. those associated either with a particular choice for the model describing the overall motion (isotropic motion) or with a particular choice for the r_{C-H} value . Other errors are statistical and primarily related to errors in T_1($\pm 5\%$).

Considering the relationship between T_c^{eff} and V_I (or V_D), it is normal that errors on T_c^{eff} should affect rotation barrier values in a complex fashion. On the basis of simulation experiments we were able to conclude that, with respect to the most probable value, the maximum error on the barrier values was *ca* 20 per cent and not necessarily symmetrical. Errors of this order do not significantly affect the calculations of entropy contributions.

REFERENCES

1. K. B. Wiberg, *Physical Organic Chemistry*. Wiley, New York (1963).
2. M. Claessens, P. Fiasse, O. Fabre, D. Zimmermann and J. Reisse, *Nouv. J. Chim.* **8**, 357–363 (1984).
3. J. Grandjean and P. Laszlo, *Mol. Phys.* **30**, 413–424 (1975).
4. M. Leit and J. Reisse, unpublished results.
5. K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **10**, 428–440 (1942); G. J. Janz, *Thermodynamic Properties of Organic Compounds*. Academic Press, New York (1967).
6. Y. Brunel, C. Coulombeau and A. Rassat, *Nouv. J. Chim.* **4**, 663–669 (1980).
7. Y. Brunel, C. Coulombeau, Ce. Coulombeau and H. Jobic, *J. Phys. Chem.* **90**, 2008–2015 (1986).
8. Y. Brunel, C. Coulombeau, Ce. Coulombeau and H. Jobic, *J. Phys. Chem.* **89**, 937–949 (1985).
9. D. E. Woessner, *J. Chem. Phys.* **36**, 1–4 (1962).
10. D. E. Woessner, B. S. Snowden, Jr, and G. H. Meyer, *J. Chem. Phys.* **50**, 719–721 (1969).
11. K. F. Kuhlmann and D. M. Grant, *J. Chem. Phys.* **55**, 2998–3007 (1971).
12. D. J. Craik, A. Kumar and G. C. Levy, *J. Chem. Inf. Comput. Sci.* **23**, 30–38 (1983).
13. J. Bastard, J. M. Bernassau, Do Khae Duc, M. Fetizon and E. Lesueur, *J. Phys. Chem.* **90**, 3936–3941 (1986).
14. A. Ericsson, J. Kowalewski, T. Liljefors and P. Stilbs, *J. Magn. Reson.* **38**, 9–22 (1980).
15. J. W. Blunt and J. B. Stothers, *J. Magn. Reson.* **27**, 515–519 (1977).
16. G. C. Levy, A. Kumar and D. Wang, *J. Am. Chem. Soc.* **105**, 7536–7540 (1983).
17. J. Vandenbosch, Thesis, Université Libre de Bruxelles (1978).
18. R. H. Harris and R. H. Newman, *Mol. Phys.* **38**, 1315–1327 (1979).

19. D. M. Grant, R. J. Pugmire, E. P. Black and K. A. Christensen, *J. Am. Chem. Soc.* **95**, 8465–8467 (1973).
20. H. Beierbeck, R. Martino and J. K. Saunders, *Can. J. Chem.* **58**, 102–109 (1980).
21. H. Beierbeck, R. Martino and J. K. Saunders, *Can. J. Chem.* **57**, 1224–1228 (1979).
22. S. Berger, F. R. Kreissl, D. M. Grant and D. Robert, *J. Am. Chem. Soc.* **97**, 1805–1808 (1975).
23. J. M. Bernassau, M. Fetizon, I. Hanna and J. A. Pinheiro, *Phys. Chem.* **90**, 3941–3943 (1986).
24. S. W. Collins, T. D. Alger, D. M. Grant, K. F. Kuhlmann and J. C. Smith, *J. Phys. Chem.* **79**, 2031–2037 (1975).
25. J. Kowalewski and T. Liljefors, *Chem. Phys. Lett.* **64**, 170–174 (1979).
26. A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.* **44**, 2356–2363 (1971); D. F. Chiang, C. F. Wilcox, Jr, and S. H. Bauer, *J. Am. Chem. Soc.* **90**, 3149–3157 (1968).
27. L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4786–4795 (1970).
28. R. J. P. Williams, *Angew. Chem., Int. Ed. Engl.* 766–777 (1977).
29. G. C. Levy and J. R. Peat, *J. Magn. Reson.* **18**, 500–521 (1975); J. L. Markley, W. J. Horsley and M. P. Klein, *J. Chem. Phys.* **55**, 3604–3605 (1971)
30. J. B. Stothers, C. T. Tan and K. C. Teo, *Can. J. Chem.* **51**, 2893–2901 (1973).