October, 1990] © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* *63,* *2877—2880 (1990)*

^{1}H NMR Studies of Motions in Solid $(CH_3)_3CBr$, $(CH_3)_3CCl$, and $(CH_3)_3CNO_2$: Methyl Group and *t*-Butyl Group Uniaxial Reorientations

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(Received April 20, 1990)

^{1}H NMR line shapes and their second moments for *t*-butyl compounds {$(CH_3)_3CX$ where X=Br, Cl, and NO_2} have been studied as a function of temperature. It is shown that the methyl group and the *t*-butyl group uniaxial reorientations are distinguished by ^{1}H NMR technique. The dipolar interactions modulated by these motions are reported in three cases: the first where methyl reorientation is fast while *t*-butyl reorientation is slow, the second where *t*-butyl reorientation is faster than methyl reorientation, and the third where both reorientations are in almost the same rate. The results obtained here are consistent with the results of ^{1}H NMR relaxation studies reported previously.

Nuclear magnetic resonance can give valuable information on molecular dynamics in crystals. Recently many detailed studies of molecular motions in solid *t*-butyl compounds, $(CH_3)_3CX$, (particularly X=Cl, Br, I, NO_2, or CN) have been reported by various techniques.[1–11] On cooling these solids, overall molecular reorientation is usually the first motion to be restricted. This is followed by the internal motions of the *t*-butyl group (the uniaxial molecular reorientation about the C–X axis) and the methyl group (methyl group reorientation about the C–CH_3 axis). The relative rates of the latter two motions have been the subject of much recent debate.[1,8] An early study[12] of ^{1}H NMR line shapes for the *t*-butyl compounds did not discuss about the subject in detail. Ripmeester and Ratcliffe[9,13] have recently shown that it is possible to use ^{2}H NMR line shapes to determine which of these motions is faster in the vicinity of motional narrowing. On the other hand recent ^{1}H NMR relaxation studies[10,14,15] have settled this debate with the characterisation of molecular motions in the various phases of the *t*-butyl compounds. The ^{1}H NMR relaxation studies[14–16] characterized molecular motions as follows; in case $(CH_3)_3CBr$ the methyl motion is fast whereas the *t*-butyl motion is slow, in case $(CH_3)_3CCl$ the *t*-butyl motion is faster than the methyl motion, and in case $(CH_3)_3CNO_2$ both motions have similar rates of the reorientations. However measurements of proton resonance lines so far reported have been unable to make any distinctions of these motions. In order to confirm the conclusion of previous ^{1}H NMR relaxation studies, the auther challenged to measure ^{1}H NMR line shapes of three compounds (X=Br, Cl, and NO_2) more carefully above about 54 K using a magic-T type spectrometer. In this paper the temperature dependence of the proton line shapes and a comparison of these line shapes are shown. Second moments determined from the absorption line widths are also discussed.

Experimental

2-Bromo-2-methylpropane, $(CH_3)_3CBr$, obtained from Aldrich Chemical Company was purified by normal distillation after being neutralized by K_2CO_3, followed by dehydration using molecular sieve 4A. 2-Chloro-2-methylpropane, $(CH_3)_3CCl$, was obtained from Wako Pure Chemical Industries Ltd. It was purified by normal distillation. 2-Methyl-2-nitropropane, $(CH_3)_3CNO_2$, obtained from Aldrich Chemical Company was purified by a preparative gas chromatograph, followed by dehydration using molecular sieve 4A. They were further purified by two stage vacuum distillation and degassed by the usual freeze-pump-thaw technique. Specimens were sealed under vacuum in glass ampoules with an external diameter of 10 mm for NMR measurements and also in glass cells specially designed[17] for differential thermal analysis (DTA). The melting points of these specimens determined by the DTA were 256.8±0.3 K for $(CH_3)_3CBr$, 248.2±0.3 K for $(CH_3)_3CCl$, and 298.7±0.3 K for $(CH_3)_3CNO_2$, respectively.

Proton NMR line shapes were measured on a bench made magic-T type spectrometer[18,19] operating at 13.0 MHz. The Bruker B-E33Nf electromagnet and B-H11D field controller were used. The main magnet field was modulated by a coil carrying 38 Hz current and the modulation width was about 20% of a resonance line width. Measurements were carried out between ca. 54 K and the melting point of the samples. Experimental second moments were determined from the derivative line tracings using the NEC PC-9801 VX personal computer, and were corrected for modulation effects.[20]

The temperature was measured with a chromel-P/constantan thermocouple to an accuracy of ±0.3 K and was controlled to within 0.2 K.

Experimental Results

Figure 1 shows temperature dependence of the line width on the lowest temperature solid phase. Here the line width is defined as the separation between the pairs of peeks in the observed derivative of the absorption line. In these compounds the line shapes are complex at the lowest temperature studied (below ca. 100 K) and have the structure of the outer and inner pairs of peaks of the derivative line shape. The line has begun to narrow at the temperature between 80 and 90 K for all samples.

Second moment, M_2, as a function of temperature for these samples is plotted in Fig. 2. This figure is the behavior of the second moment on the lowest temperature phase of each sample. The second moment of the samples except $(CH_3)_3CNO_2$ shows a two-step decrease with increasing temperature. The lower-temperature decreasing of M_2 for $(CH_3)_3CBr$ occurs at ca. 80 K from 0.269±0.017 mT^2 to 0.110 ±0.020 mT^2 and the second decrease at ca. 115 K causes M_2 to be 0.019±0.002 mT^2. A rigid lattice value of 0.274±0.026 mT^2 for $(CH_3)_3CCl$ drops at 85 K to 0.075±0.014 mT^2, and next dropping to 0.021±0.003 mT^2 occurs at 112 K. In case $(CH_3)_3CNO_2$ a motional narrowing around 90 K is accompanied by a change in M_2 from 0.259±0.018 mT^2 to 0.020±0.003 mT^2.

Figure 3 reproduces the smoothed line shapes observed for $(CH_3)_3CBr$, $(CH_3)_3CCl$, and $(CH_3)_3CNO_2$; only halves of the derivative curves are shown. The ordinate is proportional to an intensity of derivative curves and its scale is normalized. Abscissas are in mT unit. These data are roughly consistent with the previously reported results[12,16] measured above 77 K.

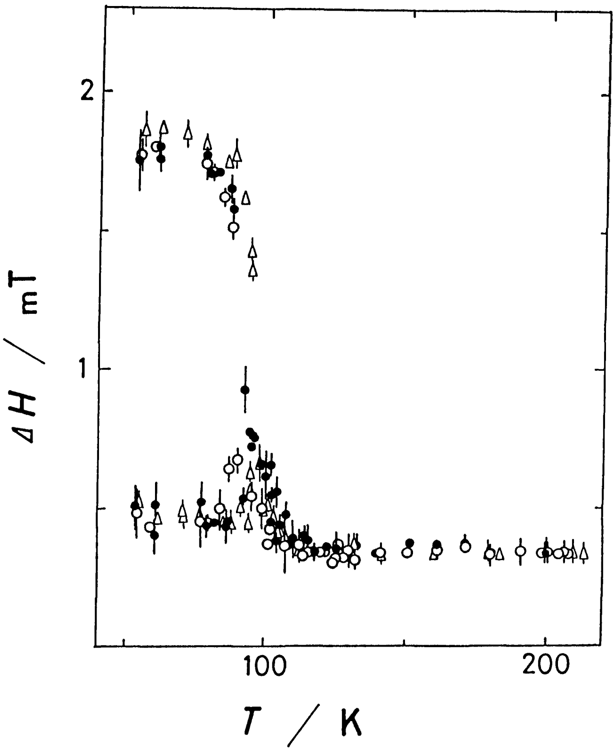

Fig. 1. Experimental line width for $(CH_3)_3CBr$ (○), $(CH_3)_3CCl$ (●), and $(CH_3)CNO_2$ (△) versus temperature.

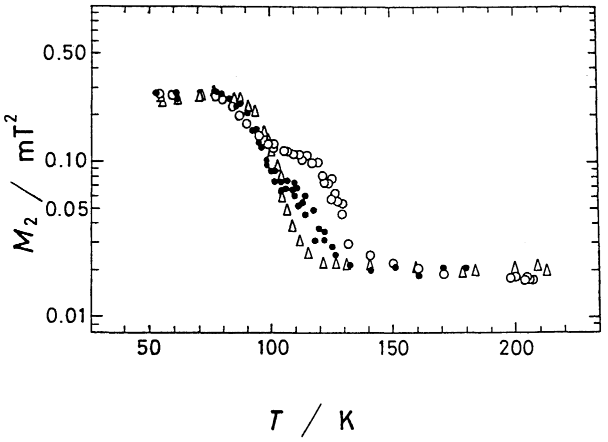

Fig. 2. Second moments for $(CH_3)_3CBr$ (○), $(CH_3)_3CCl$ (●), and $(CH_3)_3CNO_2$ (△) versus temperature.

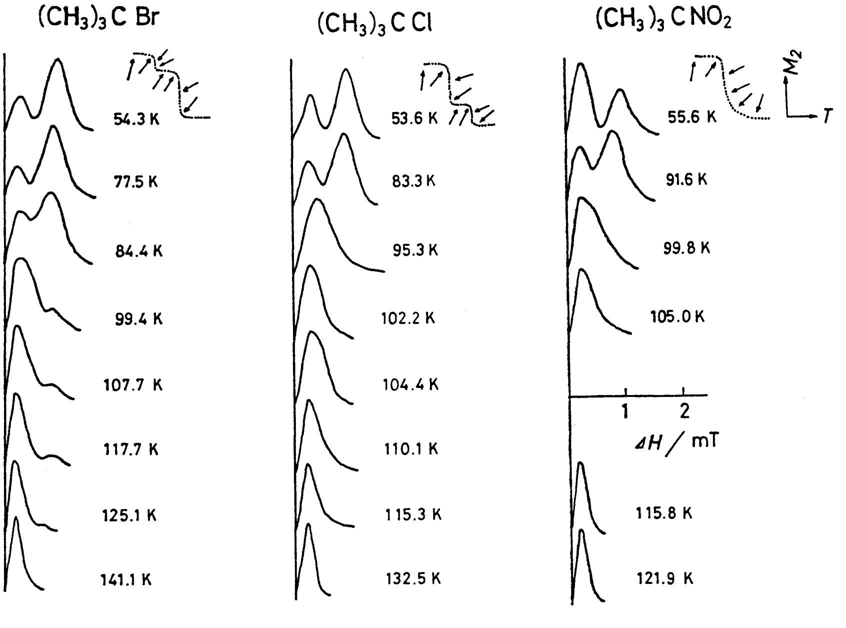

Fig. 3. Temperature dependence of ^1H NMR absorption line derivatives for $(CH_3)_3CBr$, $(CH_3)_3CCl$, and $(CH_3)_3CNO_2$. These are right side portions of the derivative line shapes.

Discussion

The derivative line shapes shown in Fig. 3 have two peaks at the lowest temperature studied; the inner peak is mainly affected by the intramethyl group dipolar interaction and the outer peak is hardly affected by others which are intermethyl, intermolecular, etc. So it is reasonable to hold that the outer peak of the derivative line shape is more affected by the *t*-butyl reorientation rather than the methyl reorientation. The outer peaks of $(CH_3)_3CCl$ and $(CH_3)_3CNO_2$ disappeared at the first motional narrowing. On the other hand the outer peak of $(CH_3)_3CBr$ did not disappear at the first motional narrowing but disappeared at the second narrowing with increasing temperature as shown in Figs. 1, 2, and 3. The rates of molecular motions excited are distinctly reflected on the difference among these line shapes. In order to explain these differences quantitatively, turn to the discussion of M_2 of ^{1}H NMR absorption line. At this stage it is necessary to review the expression of ^{1}H NMR relaxation on $(CH_3)_3CX$ type molecules. The relaxation rate produced by modulation of the dipolar interaction within the molecule undergoing methyl and *t*-butyl reorientations is given as follows:

$$T_1^{-1}=\sum_{i=2}^{3}\frac{\gamma^4\hbar^2}{120r_{1i}^6}\{8B(\tau_m)+8B(\tau_M)+19B(\tau_c)\}+\frac{9}{40}\sum_{j=4}^{9}\frac{\gamma^4\hbar^2}{l_{1j}^6}B(\tau_M) \tag{1}$$

where r_{1i} is the interproton distance in a methyl group, l_{1j} is the distance between the proton 1 and the proton j of other methyl groups in the same molecule, γ is the proton gyromagnetic ratio, τ_m and τ_M are the correlation times for the methyl and the *t*-butyl reorientations, respectively, and τ_c is defined by

$$1/\tau_c=1/\tau_m+1/\tau_M. \tag{2}$$

The spectral density function $B(\tau)$ is assumed to have the form

$$B(\tau)=\tau/(1+\omega^2\tau^2)+4\tau/(1+4\omega^2\tau^2) \tag{3}$$

where ω is the resonant angular frequency. Here it is assumed that methyl and *t*-butyl motions are mutually independent and all correlations between these motions are ignored.

Consider M_2 of the proton absorption line reduced by these motions in three cases: the first where the methyl reorientation is fast while the *t*-butyl reorientation is slow {i.e. $\tau_m<\tau_M$ in Eq. 1 found in $(CH_3)_3CBr$}; the second where the *t*-butyl reorientation is faster than the methyl reorientation {i.e. $\tau_m>\tau_M$ in Eq. 1 detected in $(CH_3)_3CCl$}; the third where these two motions are in almost same time scale {i.e. $\tau_m\approx\tau_M$ in Eq. 1 observed in $(CH_3)_3CNO_2$}.

In the first case {in case $(CH_3)_3CBr$}, M_2 reduction by the methyl motion, ΔM_2, would produce T_1 {with $\tau_M\rightarrow\infty$ in Eq. 1} given by

$$T_1^{-1}=\sum_{i=2}^{3}\frac{9\gamma^4\hbar^2}{40r_{1i}^6}B(\tau_m)=\frac{2}{3}\Delta M_2\,B(\tau_m). \tag{4}$$

Using r_{1i}=0.180 nm, ΔM_2 is calculated to be 0.158 mT^2. The other M_2 reduction by the *t*-butyl motion, $\Delta M_2'$, would produce the relaxation rate given by

$$\begin{aligned}T_1^{-1}&\approx\left\{\sum_{i=2}^{3}\frac{\gamma^4\hbar^2}{15r_{1i}^6}+\sum_{j=4}^{9}\frac{9\gamma^4\hbar^2}{40l_{1j}^6}\right\}B(\tau_M)\\&=\frac{2}{3}\Delta M_2'\,B(\tau_M).\end{aligned} \tag{5}$$

Also using l_{1j}=0.310 nm in Eq. 5 the value of $\Delta M_2'$ is calculated to be 0.065 mT^2. The experimental M_2 value for the rigid lattice is 0.269 mT^2 and the apparent M_2 reduced by methyl motion is 0.110 mT^2. The reduced second moment by the first motion is 0.159 mT^2. This agrees with the calculated value (0.158 mT^2). The experimental M_2 for the *t*-butyl motion is 0.019 mT^2. So the dipolar interaction modulated by the *t*-butyl motion is 0.091 (0.110—0.019) mT^2. The value of 0.091 mT^2 is larger than the calculated value of 0.065 mT^2. The calculated value contains only intramolecular contribution. The difference of 0.026 mT^2 would be assigned to the intermolecular contribution and experimental errors. The result of calculation is in reasonable agreement with the experimental result.

In the second case {in case $(CH_3)_3CCl$} ΔM_2 by the *t*-butyl motion is evaluated from Eq. 1 (with $\tau_m\rightarrow\infty$) to be 0.176 mT^2. The following motion (methyl motion) reduces M_2 to 0.047 mT^2. The experimental M_2 for the rigid lattice of $(CH_3)_3CCl$ is 0.274 mT^2 and M_2 is reduced by *t*-butyl motion and becomes 0.075 mT^2. M_2 after the second motion (methyl motion) is 0.021 mT^2. So the first motion modulates the dipolar interaction giving ΔM_2=0.199 (0.274—0.075) mT^2 and the second motion reduces M_2 by 0.054 (0.075—0.021) mT^2. Comparing with the result of $(CH_3)_3CBr$, the experimental value of 0.199 mT^2 is somewhat larger than the calculated value of 0.176 mT^2 containing only intramolecular interaction. However these results support the expectation that the first motion excited with increasing temperature is the *t*-butyl group reorientation.

In the third case {in case $(CH_3)_3CNO_2$} the experimental second moment value for the rigid lattice is 0.259 mT^2 and the apparent second moment after exciting of both of these motions is 0.020 mT^2. So the experimental M_2 reduced by these motions is 0.239 mT^2. The calculated M_2 due to both of these motions is expected from Eq. 1 (with $\tau_m=\tau_M$) to be 0.223 mT^2. These are in better agreement than those of the two cases mentioned above.

It is interesting to know the consistency between the second moment data and the previous ^{1}H NMR relaxation data,[14-16] i.e. it is to estimate the temperatures of

Table 1. Estimated Temperatures from T_1 Data and Experimental Temperatures Derived from M_2 for the Onset of Motional Narrowing for Methyl and *t*-Butyl Reorientations

		$(CH_3)_3CBr$	$(CH_3)_3CCl$	$(CH_3)_3CNO_2$
Methyl reorientation	Estimated temperature /K from T_1	85	121	94—102 (Estimated) 88—92 (Experimental)
	Experimental temperature /K from M_2	78—85	112—118	
t-Butyl reorientation	Estimated temperature /K from T_1	126	91	
	Experimental temperature /K from M_2	114—120	85—90	

the motional narrowing using the ^{1}H NMR relaxation data. The estimated temperatures are listed in Table 1 together with the present experimental results. They are in good agreement. This agreement supports that the results of ^{1}H NMR second moment study are consistent with the results of previous ^{1}H NMR relaxation studies.[14–16] The conclusion of previous studies of the author and coworkers is confirmed as mentioned above.

The author is grateful to Miss Rie Sato and Mr. Kazuaki Kazama for their assistance.

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