Interrelation Between Molecular Motions and Structure in Solid Trimethylamine-boron-trichloride as Studied by NMR

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The temperature dependences of proton second-moment and spin-lattice relaxation times (T_1 and $T_{1\varrho}$) have been measured in solid $(CH_3)_3NBCl_3$. The nature of reorientation processes occurring in the complex has been established and the activation parameters determined. The motions are discussed in relation to the molecular structure of the complex.

Key words: NMR, Molecular motions.

Introduction

The charge transfer complex trimethylamine-boron-trichloride (TMABTCl), consisting of the electron donor trimethylamine and boron-trichloride, is a stable crystalline solid. Its molecular and crystal structure has been determined by Hess [1]. The crystals are monoclinic, space group $P2_1/m$, with $a = 6.492$, $b = 10.216$, $c = 6.649$ Å, $\beta = 116.0°$ and two molecules per unit cell. The bond lengths and the angle found indicate that the complex may not have the ideal C_{3v} symmetry. Since there is a close relation between the spatial arrangement of bounded atoms and the hindrance potential of motion of molecular subunits, these crystallographic differences should influence the motions in this complex; namely the rotation of the methyl groups about their three-fold symmetry axes (C_3 motion) and the axial rotation of the trimethylamine moiety about the N–B axis (C_3^- motion). To elucidate the relation between the structure and dynamic behaviour of the complex we have used NMR [2, 3].

Experimental

A pure sample of $(CH_3)_3NBCl_3$ was powdered and after degassing sealed under vacuum in a glass ampoule. The derivatives of the absorption curves were registered using an oscillator spectrometer operating at 28 MHz. The second moments found by numerical integration of the spectra were corrected for the finite modulated field [4]. T_1 and $T_{1\varrho}$ were measured at 25 MHz using a pulse spectrometer [5]. T_1 was determined by the saturation recovery method and $T_{1\varrho}$ by spin locking the magnetization in the rotating field [6]. The temperature of the sample was controlled by means of a gas-flow cryostat and monitored with a platinum resistor to an accuracy of about 1 K.

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Results

Figure 1, depicting the temperature dependence of the second moment (M_2), shows two plateau values of 0.074 and 0.016 mT^2. Figure 2 shows that T_1 displays a single, broad, and asymmetric minimum of 20.5 ms at 172.5 K, and that $T_{1\varrho}$ displays two minima of 0.33 and 0.82 ms at 111 and 266.5 K, respectively, for a spin-locking field of 2.2 mT, and of 0.09 and 0.31 ms at temperatures 105 and 256.5 K, respectively, for a spin-locking field of 0.7 mT.

Discussion

a) Second Moment

We have compared the measured values of M_2 with theoretical ones corresponding to possible motional states of the complex. The latter values are easy to calculate using Van Vleck's formula [7] because the crystal and the molecular structure of the complex are known [1] and allow for only certain well-defined motions. In the calculation all structural parameters

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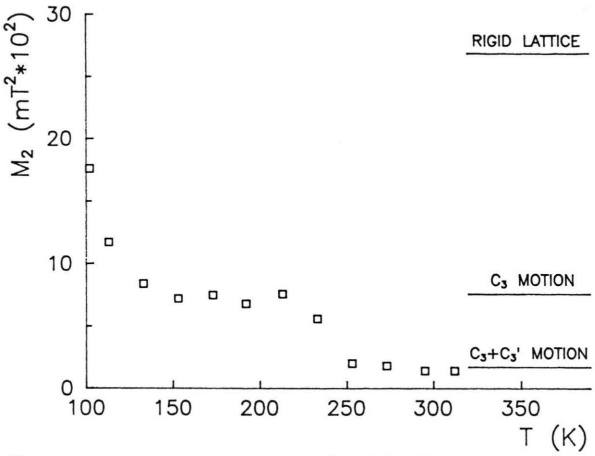

Fig. 1. Proton second moment in TMABTCl versus temperature. The values expected for rigid lattice, C_3 and $C_3+C_3^-$ motions are also shown.

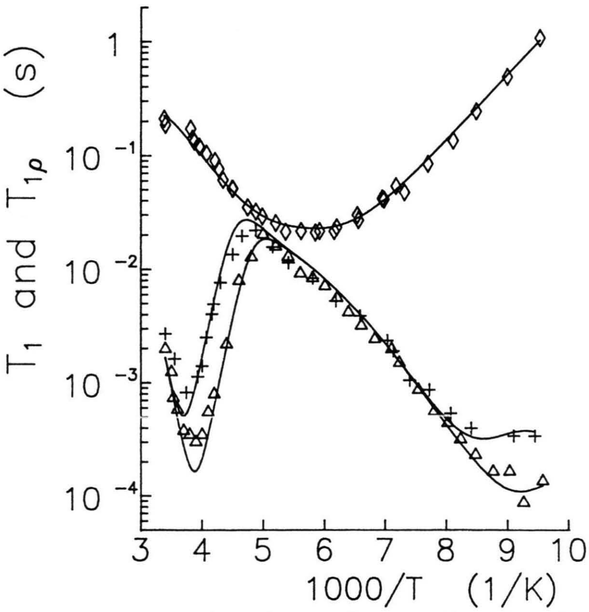

Fig. 2. Temperature dependences of proton T_1 and $T_{1\varrho}$ in TMABTCl. ◇: T_1 (25 MHz), +: $T_{1\varrho}$ (2.2 mT), △: $T_{1\varrho}$ (0.7 mT).

except for the CH bond distance are taken from the X-ray study [1]. Since the CH bond length in the X-ray data is shorter than usual, following previous papers [8] we assumed this distance to be about 1.1 Å. The results of the calculation are summarized in Table 1. In view of the number of studies that have been made on compounds having similar symmetry, we considered it unnecessary to give all details of the calculation. The interested reader is referred to [9–11].

The theoretical value of the second moment for a rigid lattice is 0.269 mT^2. We did not reach a temperature low enough to measure this value in the present experiment. However, by comparing the observed and calculated values of the second moment it can be concluded that the low temperature variation of M_2 reflects the onset of hindered rotation of the methyl groups (C_3 motion). The calculation indicates that for methyl reorientation M_2 should be of 0.076 mT^2. The fact that the experimental value of M_2 between 140–220 K is 0.074 mT^2 shows that in this temperature interval only CH_3 reorientation is fast enough to reduce the proton dipolar interactions. With increasing temperature above 220 K M_2 decreases again, approaching the high temperature plateau value of 0.016 mT^2, which is consistent with the rotation of the trimethylamine moiety about the N–B axis (C_3^- motion) in addition to the methyl reorientation.

b) Relaxation Time

Taking into account the discussion of the second moment given above, the T_1 minimum observed at about 173 K and the low temperature minima of $T_{1\varrho}$ should be attributed to the reorientation of the CH_3 groups. On the other hand, the high temperature minima of $T_{1\varrho}$ are due to axial rotation of the trimethylamine moiety.

The relaxation rates in species like TMABTCl can be expressed by the empirical formula

$$1/T_1 = (1/T_1)^{\mathrm{ME}} + (1/T_1)^{\mathrm{ME\text{-}ME}}, \quad (1)$$

describing contributions due to interaction between protons in the same methyl group (the dominant relaxation contribution) and between protons in different groups.

The dipolar interactions of protons within the methyl group are modulated by the complex motion that this group undergoes too, i.e. by the methyl rotation about its symmetry axis in addition to the anisotropic reorientation of the $[N(CH_3)_3]$ unit about the NB axis. Assuming that these motions are thermally activated and independent of each other it was shown that [12, 13] (2)

$$(1/T_1)^{\mathrm{ME}} = 9/80\, \gamma^4 \hbar^2 r^{-6} [A\, g(\tau_1) + B\, g(\tau_2) + C\, g(\tau_3)],$$

where r is the distance between protons in the methyl group,

$$g(\tau_i) = \tau_i/(1 + \omega^2 \tau_i^2) + 4\,\tau_i/(1 + 4\omega^2 \tau_i^2), \quad (2\mathrm{a})$$

Table 1. Observed and calculated second moments ($mT^2 \cdot 10^2$) for trimethylamine-boron-trichloride complex.

Motion	M_2 calculated	M_2 observed	Temperature range
Rigid structure	26.9		
C_3	7.6	7.4	140–220 K
$C_3 + C_3^-$	1.7	1.6	>250 K

Table 2. Activation energies and pre-exponential factors yielding best agreement between calculated [a] and observed T_1 and $T_{1\varrho}$ values.

Molecular group	Motion	E_a (kJ/mol)	τ_0 (s)
$(2 \cdot CH_3)_A$	C_3	11.0	$1.2 \cdot 10^{-12}$
$(1 \cdot CH_3)_B$	C_3	14.8	$4.4 \cdot 10^{-13}$
$N(CH_3)$	C_3^-	51.1	$4.6 \cdot 10^{-16}$

[a] Temperature-dependent T_1 and $T_{1\varrho}$ were fit simultaneously. An iterative reconvolution routione utilized a non-linear least-squares algorithm based on the Marquardt technique [24]. Although six adjustable parameters were involved in the fitting procedure, not more than four of them were introduced into the fitting routine at the some time. The best fit was judged to be that with the lowest χ^2.

τ_1 and τ_2 are correlation times for C_3 and C_3^- motions, respectively,

$$\tau_3^{-1} = \tau_1^{-1} + \tau_2^{-1}, \tag{2b}$$

$$A = 3/2 \sin^4 \delta, \quad B = \sin^2 2\delta + \sin^4 \delta,$$

$$C = 1/2\,(8 - 3 \sin^4 \delta), \tag{2c}$$

δ is the angle between two internal rotation axes, i.e. between C–N and N–B bonds. All other symbols have their usual meaning.

The relaxation contributions due to the interaction between protons placed in different methyl groups can be approximated as [14]

$$(1/T_1)^{\text{ME-ME}} = 27/20\, \gamma^4 \hbar^2 R^{-6} g(\tau_2), \tag{3}$$

where R is the distance between the triangles formed by the protons of each methyl group.

Equations (1)–(3) can be easily applied to the descriptions of $T_{1\varrho}$ for spin-locking fields greater than local dipolar fields, and the result only differs in the function $g(\tau_i)$ being replaced by [14]

$$g_\varrho(\tau_i) = 3/2\, \tau_i/(1 + 4\omega_1^2 \tau_i^2) + 5/2\, \tau_i/(1 + \omega^2 \tau_i^2) + \tau_i/(1 + 4\omega^2 \tau_i^2). \tag{4}$$

It is seen from the M_2 study that at low temperatures the axial motion of the $[NCCH_3)_3]$ unit is very sluggish ($\omega \tau_2 \gg 1$). Hence $(T_1^{-1})^{\text{ME-ME}} \cong 0$ and (T_1^{-1}) reduces to the well known formula for rotation of the methyl group about it three-fold axis [15]

$$(1/T_1) = 9/20\, \gamma^4 \hbar^2 r^{-6} g(\tau_1). \tag{5}$$

The observed relaxation minimum, which is asymmetric and broad, can not be fitted to this theoretical equation for a motion of all methyl groups with a unique correlation time τ_1. Also, the experimental value of the T_1 minimum is higher than that calculated for a single motion.

The data can be successfully explained if one assumes that two of the methyl groups responsible for relaxation differ in their motional freedom from the third group. Such a dynamic inequivalency may be expected on the basis of the X-ray study [1], which shows that the methyl groups in trimethylamine-boron trichloride complex are structurally different.

Hence the relaxation rates in this compound should be described by two superimposed relaxation curves weighted by coefficients 2/3 and 1/3, respectively:

$$(1/T_1) = [2/3(1/T_1)_A^{\text{ME}} + 1/3(1/T_1)_B^{\text{ME}}] + (1/T_1)^{\text{ME-ME}}, \tag{6}$$

since there are three methyl groups in the trimethylamine moiety and two of them (denoted as A) are dynamically different from the third one (denoted as B).

The activation parameters for the motions revealed by M_2, obtained by fitting (6) and (2)–(4) to the experimental data, are summarized in Table 2. The fitted curves are shown by the solid lines in Figure 2. The agreement between the measured T_1 and $T_{1\varrho}$ values and the calculated ones is satisfactory, especially if one considers that the data measured at very different field strengths are fitted simultaneously with the same parameters. The obtained results compare well with the values of activation energies reported for C_3 motion in trimethylamine complexes [9, 10, 16]. The activation energy for the C_3^- motion falls into the ranges of the highest values (43–73 kJ) for this motion reported in [16–19]. Albert and Ripmeester [20] suggest that a high barrier for this motion may occur if C_3^- is not a symmetry axis. Observations of this work corraborate this statement.

The distortion of symmetry in boron trihalide-trimethylamine complexes manifests itself in the NQR spectra of the halogen atom linked to boron, where it gives rise to two resonance lines with an intensity ratio of 2:1 [21, 22]. The fact that these lines fade out far below the melting point has been attributed to the hindered rotation of the boron trihalide. It has been suggested that in BCl_3- and BBr_3-trimethylamine this motion consists in rotation of the whole complex about the N–B bond rather than uncorrelated motion of the two moieties. Lucken-Ardjomande and Lucken [23] have studied the dynamics of the BCl_3-chloropyridine complexes and discussed the possibility of a quantitative analysis of the NQR data. They found that, although internal rotation shows up clearly in the temperature dependences of the quadrupole resonance frequencies, deriving the barrier to this rotation is a difficult problem.

Summary

In solid $C(CH_3)_3NBCl_3$ methyl group rotation and axial reorientation of the trimethylamine moiety occur. The anomalous low temperature relaxation minima of $T_{1\varrho}$ and minimum of T_1, explained in terms of dynamic inequivalency of the methyl groups, prove the differences in bond lengths and angles found in this complex by X-ray diffraction.

Acknowledgements

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