

Crystal Structure and Cationic Motion of *o*-Toluidinium Chloranilate and *m*-Toluidinium Chloranilate Studied by X-ray Diffraction and ^1H NMR

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The crystal structure of *o*-toluidinium chloranilate and *m*-toluidinium chloranilate, $2\text{CH}_3\text{C}_6\text{H}_4\text{-NH}_3^+ \cdot \text{C}_6\text{O}_4\text{Cl}_2^{2-}$, was determined by single crystal X-ray diffraction at room temperature. It was found that *o*-toluidinium chloranilate (I) is monoclinic, $\text{P}2_1/\text{n}$ (#14), $Z = 2$, $a = 5.2184(14)$, $b = 7.825(2)$, $c = 22.840(5)$ Å, and $\beta = 92.015(19)^\circ$, and *m*-toluidinium chloranilate (II) is monoclinic, $\text{P}2_1/\text{c}$ (#14), $Z = 2$, $a = 11.214(2)$, $b = 5.4844(10)$, $c = 16.379(6)$ Å, and $\beta = 105.21(2)^\circ$. In these salts, the cations are connected with the anions by N-H...O hydrogen bonds to form 2:1 units of $2\text{CH}_3\text{C}_6\text{H}_4\text{NH}_3^+ \cdot \text{C}_6\text{O}_4\text{Cl}_2^{2-}$ that are located on inversion centers. The $2\text{CH}_3\text{C}_6\text{H}_4\text{NH}_3^+ \cdot \text{C}_6\text{O}_4\text{Cl}_2^{2-}$ units in both salts are connected by other N-H...O hydrogen bonds to build a three-dimensional hydrogen-bond network. Motions of the toluidinium ions in solid (I) and (II) were studied by ^1H NMR spin-lattice relaxation time measurements. Reorientations of the NH_3^+ group about the C-N bond axis and the CH_3 group about the C-C bond axis were observed, and their motional parameters were evaluated. The internal rotational barriers of the NH_3^+ and CH_3 groups of an isolated *o*-toluidinium ion were estimated from *ab initio* molecular orbital calculations at HF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) levels of theory.

Key words: Crystal Structure; X-ray Diffraction; Hydrogen Bond; Cationic Motion; MO Calculation.

1. Introduction

Chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone), a strong dibasic acid endowed with hydrogen-bond donor as well as acceptor groups, appears particularly attractive as a template for generating tightly bound self-assemblies with polarizable bases [1–7]. Recently we have analyzed the crystal structures of the chloranilic acid-amine (1:1) system and found that these were classified into three types according to the hydrogen bonding patterns in the crystals [8]. Molecular motions in solid ethylammonium chloranilate, $\text{C}_2\text{H}_5\text{NH}_3^+ \cdot \text{C}_6\text{HO}_4\text{Cl}_2^-$, which is classified into Type 3c of the (1:1) system, were studied by ^1H NMR to investigate the role of the hydrogen bonds in stabilizing the orientations of the NH_3^+ and CH_3 groups in the crystal [9]. In the present study we have prepared the (1:2) salts of chloranilic acid with *o*-toluidine (2-aminotoluene) and *m*-toluidine (3-aminotoluene) to extend our work on the hydrogen-bonding in chloranilic acid-amine crystals to the (1:2) system. We have determined their crystal structure by single crystal X-ray diffraction and measured the ^1H

NMR spin-lattice relaxation time (T_1). We also estimated the internal rotational barriers for the NH_3^+ and CH_3 groups of an isolated *o*-toluidinium ion from *ab initio* molecular orbital (MO) calculations.

2. Experimental

o-Toluidinium chloranilate (I) and *m*-toluidinium chloranilate (II) were prepared by mixing chloranilic acid with the corresponding toluidine (molar ratio 1:2) in acetonitrile, respectively. Single crystals were grown by slow evaporation of the solutions at room temperature. Dark-brown prismatic crystals of *o*-toluidinium and *m*-toluidinium chloranilates were sealed in glass capillaries for the X-ray measurements. The diffraction data were collected using the ω - 2θ scan technique on a Rigaku AFC-5R diffractometer [10] with MoK_α radiation ($\lambda = 0.71073$ Å) at the X-ray Laboratory of Okayama University. The crystal lattice parameters were determined from 25 reflections in the 2θ range of 20 – 25° . The structures were solved by SIR92 [11], and the structure refinement was carried out by SHELXL97 [12]. All H atoms in (I)

Table 1. Crystal data and details of the structure determination for *o*-toluidinium chloranilate (I) and *m*-toluidinium chloranilate (II).

	(I)	(II)
<i>Crystal Data</i>		
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
$a / \text{\AA}$	5.2184(14)	11.214(2)
$b / \text{\AA}$	7.825(2)	5.4844(10)
$c / \text{\AA}$	22.840(5)	16.379(6)
$\beta / ^\circ$	92.015(19)	105.21(2)
$V / \text{\AA}^3$	932.1(4)	972.1(4)
Z	2	2
$D_x / \text{Mg m}^{-3}$	1.508	1.446
$\mu (\text{Mo K}\alpha) / \text{mm}^{-1}$	0.379	0.363
$F(000)$	440	440
Crystal Size / mm	$0.40 \times 0.40 \times 0.50$	$0.20 \times 0.30 \times 0.40$
<i>Data Collection</i>		
T / K	299	299
$\theta_{\min}, \theta_{\max} / ^\circ$	1.8, 29.0	1.9, 29.0
h	$-1 \rightarrow 7$	$-1 \rightarrow 15$
k	$0 \rightarrow 10$	$0 \rightarrow 7$
l	$-31 \rightarrow 31$	$-22 \rightarrow 21$
No. of measured reflections	3226	3263
No. of independent reflections	2463	2590
Reflections with $I > 2\sigma(I)$	1914	1590
R_{int}	0.049	0.045
<i>Refinement</i>		
Refinement on	F^2	F^2
No. of reflections and parameters used in refinement	2463	2590
Absorption correction	ψ scans [13]	ψ scans [13]
T_{\min}, T_{\max}	0.808, 0.863	0.873, 0.930
$R[F^2 > 2\sigma(F^2)]$	0.038	0.049
$wR[F^2]$	0.102	0.130
S	1.07	1.01
Weighting scheme	(a)	(b)
$(\Delta/\rho)_{\max}$	0.01	0.01
$\Delta/\rho_{\min} / \text{e \AA}^{-3}$	-0.25	-0.25
$\Delta/\rho_{\max} / \text{e \AA}^{-3}$	0.26	0.28

(a) $w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.2389P]$, $P = (F_o^2 + 2F_c^2)/3$;
 (b) $w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 0.2339P]$, $P = (F_o^2 + 2F_c^2)/3$.

were refined isotropically. Refined distances are C-H = 0.93(2)–1.00(2) and N-H = 0.90(3)–0.97(2) Å. For (II), the H atoms in methyl groups were treated as riding atoms with C-H = 0.96 Å and $U_{\text{iso}}(\text{methyl H}) = 1.5 U_{\text{eq}}(\text{methyl C})$, while other H atoms were refined isotropically. The refined distances are C-H = 0.88(4)–1.01(3) and N-H = 0.87(4)–0.93(3) Å. Crystal data and experimental details are given in Table 1¹.

¹Crystal data of (I) and (II) have been deposited at the Cambridge

Table 2. Selected bond lengths (Å) determined for *o*-toluidinium chloranilate (I) and *m*-toluidinium chloranilate (II).

	(I)	(II)		(I)	(II)
Cl-C2	1.7386(17)	1.735(3)	O1-C1	1.2454(19)	1.262(3)
O2-C3	1.257(2)	1.233(3)	C1-C2	1.401(2)	1.380(3)
C1-C3 ⁱ	1.546(2)	1.540(4)	C2-C3	1.396(2)	1.416(3)
N-C4	1.473(2)	1.468(3)	C4-C5	1.386(2)	1.376(4)
C5-C6	1.395(3)	1.385(4)	C6-C7	1.386(3)	1.380(4)
C7-C8	1.380(3)	1.386(5)	C8-C9	1.384(3)	1.384(5)
C4-C9	1.381(2)	1.372(4)	C5-C10	1.498(3)	
C6-C10		1.504(5)			

Symmetry code: ⁱ $1 - x, 2 - y, -z$.

Table 3. Hydrogen-bonding geometry for *o*-toluidinium chloranilate (I) and *m*-toluidinium chloranilate (II).

D-H...A	D-H / Å	H...A / Å	D...A / Å	D-H...A / °
(I)				
N-H5...O1	0.97(2)	1.88(2)	2.842(2)	173.4(19)
N-H6...O2 ⁱ	0.89(2)	2.26(3)	3.104(2)	157(2)
N-H6...O1 ⁱⁱ	0.89(2)	2.26(2)	2.913(2)	130(2)
N-H7...O2 ⁱⁱⁱ	0.95(3)	1.90(3)	2.842(2)	173(2)
C10-H10...O2 ⁱ	0.98(2)	2.58(2)	3.420(3)	143.8(18)
(II)				
N-H5...O1	0.94(3)	1.87(3)	2.784(4)	165(3)
N-H6...O1 ^{iv}	0.87(3)	2.11(3)	2.902(3)	152(3)
N-H6...O2 ^v	0.87(3)	2.29(3)	2.969(3)	135(3)
N-H7...O1 ^{vi}	0.91(3)	2.49(3)	3.295(4)	148(3)
N-H7...O2 ^{vii}	0.91(3)	2.13(3)	2.894(3)	140(3)
C9-H4...O2 ^{viii}	0.89(4)	2.43(4)	3.286(4)	163(3)

Symmetry codes: ⁱ $-1 + x, -1 + y, z$; ⁱⁱ $-x, 1 - y, -z$;

ⁱⁱⁱ $x, -1 + y, z$; ^{iv} $-x, -1/2 + y, 1/2 - z$; ^v $x, 1/2 - y, 1/2 + z$;

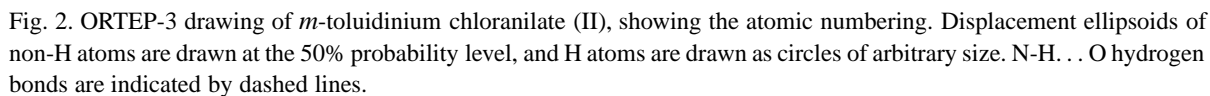
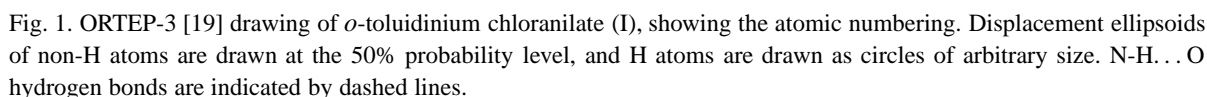
^{vi} $x, -1 + y, z$; ^{vii} $-x, -y, -z$; ^{viii} $x, -1/2 - y, 1/2 + z$.

The ¹H NMR spin-lattice relaxation time (T_1) was measured at 32 MHz by the $180^\circ - \tau - 90^\circ$ method, using the pulse spectrometer reported in [14]. The experimental uncertainty was estimated to be within 10% for T_1 . MO calculations were performed using the Gaussian 98 package [15]. Hartree-Fock (HF) with the 6-31G(d,p) basis set was used for constrained geometry optimizations. The second-order Möller-Plesset (MP2) [16] and Beck's three parameter hybrid DFT-HF [17] with the Lee-Yang-Parr correlation functional (B3LYP) [18] with the 6-31G(d,p) basis set were used for full geometry optimizations and vibrational frequency calculations.

3. Results and Discussion

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively. Selected bond lengths

Crystallographic Data Centre (CCDC) as supplementator publication No. CCDC 220653 and CCDC 220654. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html.



other, and one bifurcated hydrogen bond (N-H6...O2ⁱ and N-H6...O1ⁱⁱ). In (II), one N-H...O hydrogen bond (N-H5...O1) forms the 2:1 unit and two bifurcated hydrogen bonds (N-H6...O1^{iv}, N-H6...O2^v, N-H7...O1^{vi}, and N-H7...O2^{vii}) connect the 2:1 units. A C-H...O hydrogen bond connecting the 2:1 units is observed in (I) between the methyl group and the anion, and in (II) between the benzene ring and the anion.

MO calculations using the HF/6-31G(d,p) level of theory were performed on an isolated *o*-toluidinium cation in order to elucidate the stable conformation and the internal rotational barriers for the NH_3^+ and CH_3 groups around the C-N and C-C bonds, respectively. For the rotation of the NH_3^+ group one of the C-C-N-H torsion angles is defined by ϕ , and for the CH_3 rotation a C-C-C-H torsion angle is φ :

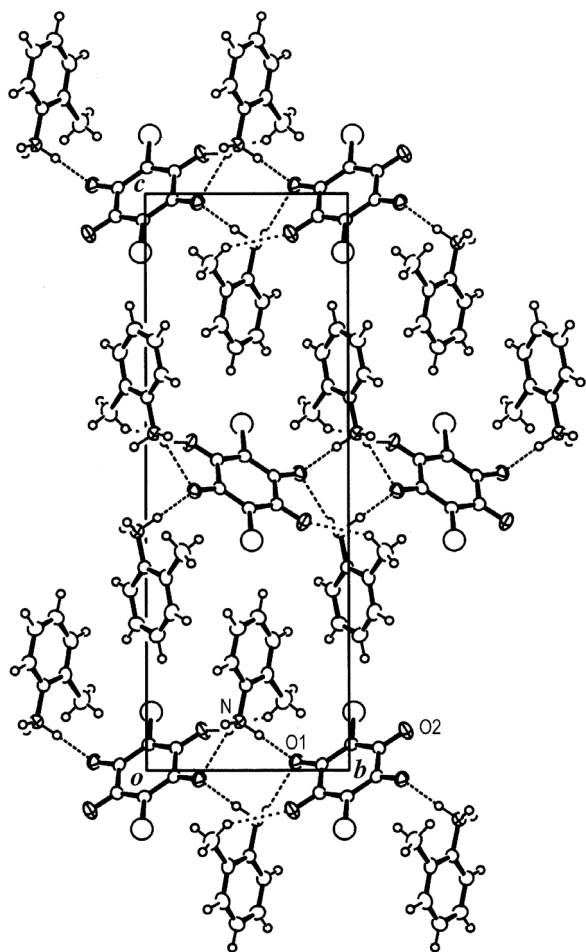
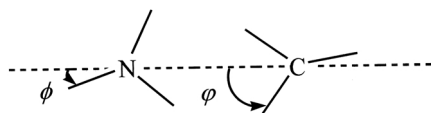


Fig. 3. Packing diagram of (I) viewed down the *a* axis. N-H...O and C-H...O hydrogen bonds are shown by dashed lines.



The dashed line indicates the plane of the benzene ring. The geometrical optimization of all parameters, except the two torsion angles (ϕ and φ), was carried out every 10° , from ϕ being -60° to 60° and from φ being 0° to 120° . Figure 5 shows the relative energies of *o*-toluidinium ions as a function of ϕ and φ . The energy minimum was found around $\phi = 0^\circ$, $\varphi = 60^\circ$. The minimum energy path of NH_3^+ rotation between two such stable conformers passes $\phi = 60^\circ$, $\varphi = 60^\circ$, and that of CH_3 passes $\phi = 0^\circ$, $\varphi = 0^\circ$. No implication of a coupling rotation or a geared rotation of

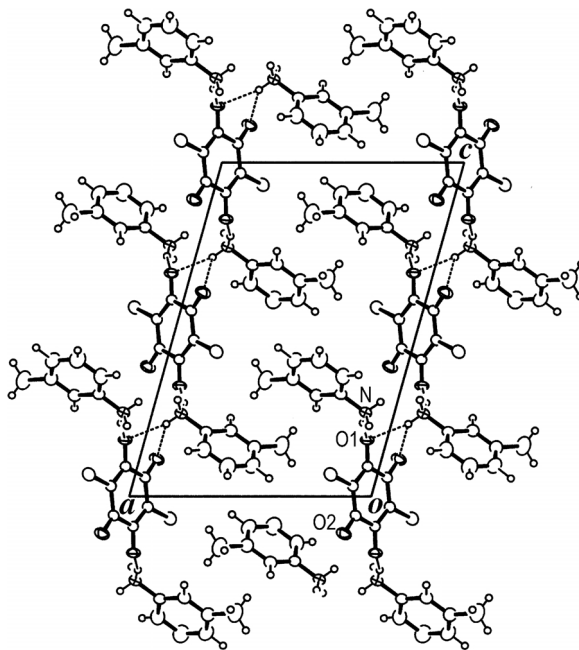


Fig. 4. Packing diagram of (II) viewed down the *b* axis. N-H...O hydrogen bonds are shown by dashed lines.

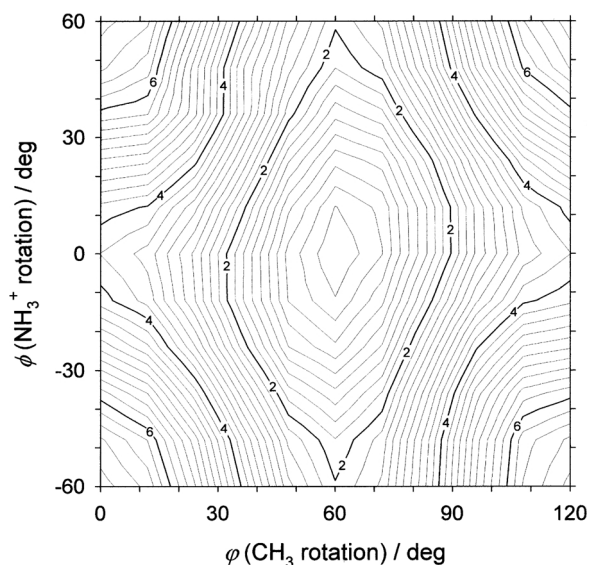


Fig. 5. Relative energies (kJ mol^{-1}) of the *o*-toluidinium cation, evaluated by HF/6-31G(d,p) as a function of the torsion angles of NH_3^+ and CH_3 groups. Contour lines indicate conformations with the same relative energy.

NH_3^+ and CH_3 groups was observed at this level of theory. At the minimum point ($\phi = 0^\circ$, $\varphi = 60^\circ$) and the transition states [TS1 ($\phi = 60^\circ$, $\varphi = 60^\circ$) and TS2

	Stable	TS1	TS2	cryst.
N - C4	1.4876 (1.4976)	1.4902 (1.5002)	1.4895 (1.4998)	1.473(2)
C4 - C5	1.3971 (1.3986)	1.3966 (1.3979)	1.3961 (1.3968)	1.386(2)
C5 - C6	1.3998 (1.4005)	1.4015 (1.4021)	1.4018 (1.4035)	1.395(3)
C6 - C7	1.3962 (1.3955)	1.3950 (1.3939)	1.3942 (1.3929)	1.386(3)
C7 - C8	1.3955 (1.3951)	1.3963 (1.3963)	1.3962 (1.3967)	1.380(3)
C8 - C9	1.3952 (1.3941)	1.3940 (1.3931)	1.3933 (1.3916)	1.384(3)
C4 - C9	1.3893 (1.3895)	1.3904 (1.3907)	1.3919 (1.3925)	1.381(2)
C5 - C10	1.5058 (1.5099)	1.5077 (1.5121)	1.5079 (1.5117)	1.498(3)
C9 - C4 - N - H5	-120.86 (-120.59)	-60.19 (-60.29)	-119.52 (-119.54)	-116.1(14)
C9 - C4 - N - H6	118.99 (119.24)	180.00 (180.00)	119.53 (119.50)	121.6(17)
C9 - C4 - N - H7	-0.95 (-0.68)	60.19 (60.29)	0.00 (-0.03)	-2.8(16)
C4 - C5 - C10 - H8	-61.37 (-61.14)	-61.49 (-61.53)	-120.49 (-120.65)	-66.7(19)
C4 - C5 - C10 - H9	179.70 (179.83)	180.00 (180.00)	120.54 (120.80)	165.0(16)
C4 - C5 - C10 - H10	60.75 (60.77)	61.49 (61.53)	0.03 (0.08)	47.9(16)

Table 4. Selected bond lengths (Å) and torsion angles (°) of *o*-toluidinium ion in stable and transition states optimized by MP2/6-31G(d,p) and B3LYP/6-31G(d,p) (in parentheses).

The atomic numbering is the same as that used in Fig. 1. ϕ and ϕ in the text correspond to the torsion angles of C9-C4-N-H7 and C4-C5-C10-H10, respectively.

($\phi = 0^\circ$, $\phi = 0^\circ$) of NH_3^+ and CH_3 rotations full optimizations and frequency calculations were performed at MP2/6-31G(d,p) and B3LYP/6-31G(d,p) levels. The stable state was confirmed to correspond to a potential energy minimum from the vibrational analysis, which shows only real frequencies for the optimized conformer. TS1 and TS2 were found to be a saddle point of first order from the presence of one imaginary frequency. Optimized C-N and C-C bond lengths and torsion angles of the NH_3^+ and CH_3 groups are shown in Table 4 together with the present crystal data. In the transition states, the N-C4, C5-C6, C7-C8, C4-C9, and C5-C10 bonds become longer than in the stable state, while the other C-C bonds become shorter. Short bond lengths of C-C and C-N in the crystal compared with the calculated bond lengths are explainable by thermal vibration or libration of the cation in the crystal. The CH_3 group in the crystal rotates by *ca.* 10° from the stable conformation, probably due to the C-H...O hydrogen bond. Rotation barriers of the NH_3^+ group, evaluated by MP2 and B3LYP as a difference in total energy between the stable state and the transition state, are 1.48 and 1.09 kJ mol^{-1} , respectively, while those of the CH_3 group are 3.90 and 3.32 kJ mol^{-1} , in the same order.

The temperature dependence of T_1 in *o*-toluidinium chloranilate observed at 32 MHz is shown in Figure 6. A T_1 minimum and a T_1 maximum appear around 385 and 230 K, respectively. Referring to the crystal data that show no disorder in atomic positions, the conceivable reorientational motions of the ions responsible for T_1 are the reorientation of NH_3^+ and CH_3 groups in the cation. Since the NH_3^+ groups were linked with the anion through strong hydrogen bonds, we can assign the T_1 minimum to the NH_3^+ group motion, and the T_1 decrease with decreasing temperature below 230 K

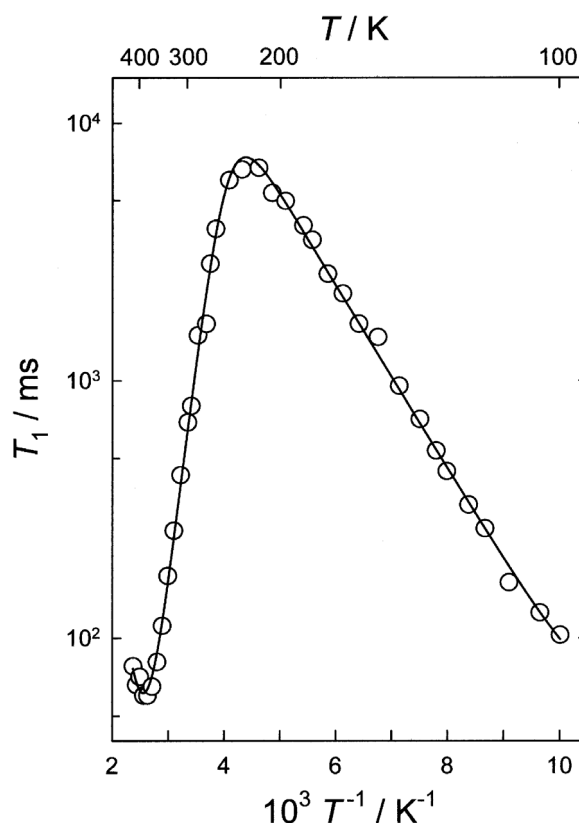


Fig. 6. Temperature dependence of ^1H T_1 observed at 32 MHz in (I). The solid line indicates the best fit theoretical values.

to the CH_3 group motion. For these motions, T_1 can be expressed by the sum of the two BPP equations associated with the NH_3^+ and CH_3 group motions [20]:

$$T_1^{-1} = C_1 f(\tau_1) + C_2 f(\tau_2), \quad (1)$$

$$f(\tau_i) = \tau_i / (1 + \omega^2 \tau_i^2) + 4\tau_i / (1 + 4\omega^2 \tau_i^2), (i = 1, 2), \quad (2)$$

where τ_1 and τ_2 are correlation times for the NH_3^+ and CH_3 group motions, respectively, and ω is the Larmor frequency. C_1 and C_2 are the motional constants for the NH_3^+ and CH_3 groups, respectively. Since τ_2 is considered to be short enough to satisfy the relation $\omega\tau_2 \ll 1$ in the temperature range studied, $f(\tau_2)$ can be rewritten as

$$f(\tau_2) = 5\tau_2. \quad (3)$$

Assuming an Arrhenius-type relationship between τ_i and the activation energy E_{ai} for the reorientation process:

$$\tau_i = \tau_{0i} \exp(E_{ai}/RT). \quad (4)$$

Equations (1–4) were fitted to the T_1 data using a least-squares method. The motional parameters $E_{a1} = 33.5(7) \text{ kJ mol}^{-1}$, $\tau_{01} = 1.0(2) \times 10^{-13} \text{ s}$, and $C_1 = 23.0(8) \times 10^8 \text{ s}^{-2}$ were obtained for the NH_3^+ group reorientation, while $E_{a2} = 6.82(14) \text{ kJ mol}^{-1}$ and $\tau_{02}C_2 = 6.2(10) \times 10^{-4} \text{ s}^{-1}$ were obtained for the CH_3 group. The much larger E_a value for the NH_3^+ group than the calculated internal rotational barrier of the NH_3^+ group is interpreted in terms of the presence of strong N-H...O hydrogen bonds formed between the cation and the anion. The E_a value for the CH_3 group, which is also larger than the corresponding rotational barrier, indicates that the reorientation of the CH_3 group is under an intermolecular potential, probably originating from the C-H...O interaction.

The temperature dependence of T_1 at 32 MHz in *m*-toluidinium chloranilate is shown in Figure 7. A T_1 minimum appears around 310 K, which is attributed to the NH_3^+ motion. T_1 below 200 K is too long to determine it precisely. The long T_1 can be explained by the CH_3 group of (II) reorienting much faster than that of (I) in the temperature range studied. In other words, the hindering barrier to the CH_3 group reorientation in (II) is much lower than that in (I). The low barrier is expected from the crystal structure, where no effective C-H...O interaction is found between the CH_3 group

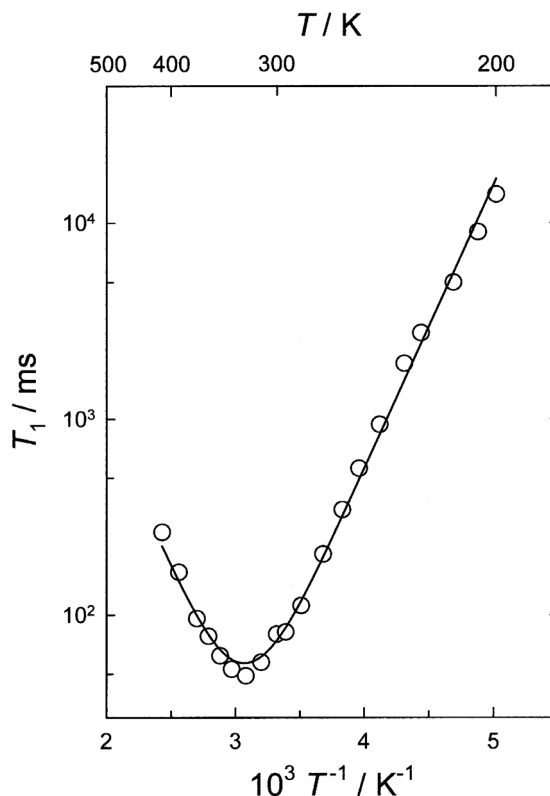


Fig. 7. Temperature dependence of ^1H T_1 observed at 32 MHz in (II). The solid line indicates the best fit theoretical values.

and the anion in (II). For the NH_3^+ motion we have fitted the T_1 expression

$$T_1^{-1} = C_1 f(\tau_1) \quad (5)$$

to the T_1 data, using the Arrhenius-type relationship given by (4). $E_{a1} = 27.7(5) \text{ kJ mol}^{-1}$, $\tau_{01} = 1.1(2) \times 10^{-13} \text{ s}$, and $C_1 = 25(1) \times 10^8 \text{ s}^{-2}$ were obtained for the reorientation. Although these values are comparable to those of (I), a somewhat small E_a value was obtained for (II). Since the shortest hydrogen bonding distance (H5...O1) in (I) is comparable to that in (II), this difference can be attributed to the presence of two bifurcated N-H...O hydrogen bonds in (II), which causes the potential minimum of the NH_3^+ reorientation to be shallow and broad.

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