Motions of Ethylammonium Ions in Solid Ethylammonium Chloranilate Studied by ^{1}H Nuclear Magnetic Resonance

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The motions of the ethylammonium ion in solid ethylammonium chloranilate, $C_2H_5NH_3^+ \cdot C_6HO_4Cl_2^-$, are studied by ^{1}H NMR second moment (M_2) and spin-lattice relaxation time (T_1) measurements. Reorientations of the CH_3 group about the C–C bond axis and the NH_3^+ group about C–N bond axis were observed and their motional parameters were evaluated. The internal rotational barriers of the CH_3 and NH_3^+ groups of an isolated $C_2H_5NH_3^+$ ion were estimated from *ab initio* molecular orbital calculations.

Key words: Nuclear Magnetic Resonance; Molecular Motion; Ethylammonium Ion; HF.

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 cations [1–6].

The title compound, $C_2H_5NH_3^+ \cdot C_6HO_4Cl_2^-$, crystallizes in the triclinic system (space group $P\bar{1}$) with a = 7.201(2), b = 10.348(2), c = 7.190 (2) Å, α = 95.59(2)°, β = 92.95(2)°, γ = 98.47(2)°, V = 526.3(2) Å^3, and Z = 2 at room temperature [7]. A packing view of the crystal is shown in Figure 1. The molecules of the chloranilate ion form an O–H…O hydrogen-bonded dimer,

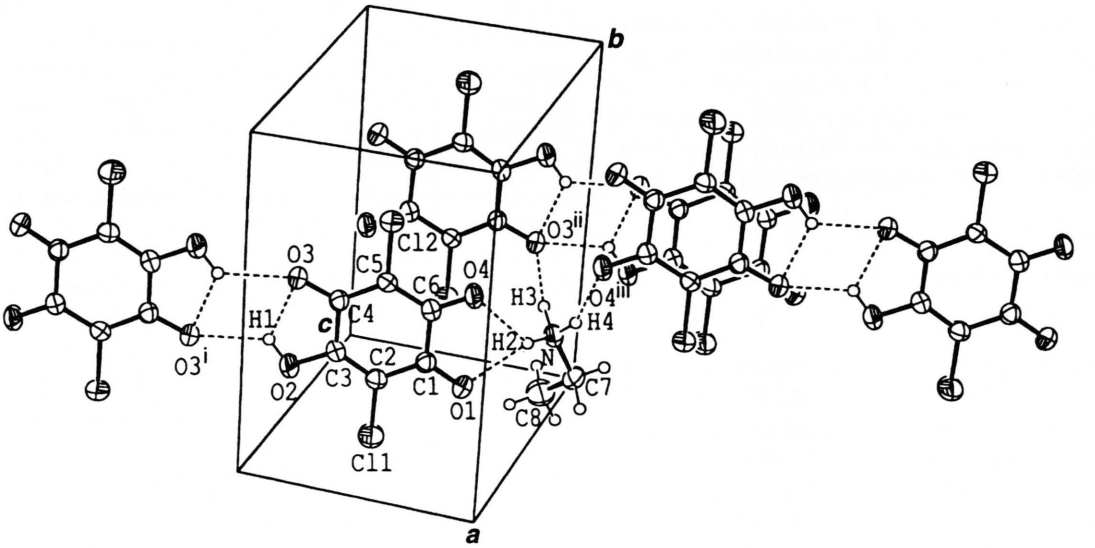

Fig. 1. ORTEP-3 [8] drawing of ethylammonium chloranilate. Thermal ellipsoids of non-H atoms are drawn at the 50% probability level, and H atoms are drawn as circles of arbitrary size. O–H…O and N–H…O hydrogen bonds are indicated by dashed lines [symmetry codes: (i) 2–x, 1–y, 2–z; (ii) 1–x, 1–y, 1–z; (iii) 1–x, 1–y, –z].

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in which the molecules are related to each other by an inversion center. The ethylammonium ion links the three dimers of the chloranilate ion through N-H...O hydrogen bonds [N–H2...O1, N–H2...O4, N–H3 ...O3^{ii}, and N–H4...O4^{iii}], forming a three-dimensional hydrogen-bond network. A weak C–H...O interaction between the methyl group of the cation and the anion is also observed [C8–H7...O1]. In the present study, we have measured the ^{1}H NMR spin-lattice relaxation time (T_1) and second moment (M_2) of the ^{1}H MNR linewidth in order to investigate the role of the hydrogen bonds in stabilizing the orientations of the NH_3 and CH_3 groups in the crystal. We also estimated the internal rotational barriers for the CH_3 and NH_3^+ groups of an isolated $C_2H_5NH_3^+$ ion from *ab initio* molecular orbital (MO) calculations.

Table 1. Optimized geometry (Å, °) for the all-staggered, the CH_3-eclipsed, and the NH_3^+-eclipsed conformations of the ethylammonium ion.

	Staggered	CH_3-eclipsed	NH_3^+-eclipsed
C–C	1.517	1.533	1.517
C–N	1.518	1.517	1.534
C–H (CH_3)	1.093 (× 2)	1.090 (× 2)	1.093 (× 2)
	1.092 (× 1)	1.095 (× 1)	1.092 (× 1)
C–H (CH_2)	1.091	1.090	1.090
N–H	1.025	1.024 (× 2)	1.024 (× 2)
		1.025 (×1)	1.025 (× 1)
C–C–N	110.2	110.4	110.3
C–C–H (CH_3)	111.5 (× 2)	110.8 (× 2)	111.4 (× 2)
	108.6 (× 1)	111.8 (× 1)	108.7 (× 1)
C–C–H (CH_2)	112.5	113.0	112.3
C–N–H	110.9 (× 2)	111.0 (× 2)	112.0 (× 2)
	112.2 (× 1)	112.0 (× 1)	111.1 (× 1)

Experimental

$C_2H_5NH_3^+ \cdot C_6HO_4Cl_2^-$ was prepared by mixing an acetonitrile solution of chloranilic acid with an aqueous solution of ethylamine. The obtained crystal was recrystallized twice from methanol. The ^{1}H NMR spin-lattice relaxation time (T_1) was measured at 32 MHz by the $180° - \tau - 90°$ method using the pulse spectrometer described in [9]. The experimental uncertainty was estimated to be within 10% for T_1. The ^{1}H NMR spectra were recorded on a JEOL JNM-MW-40S spectrometer operated at 40 MHz. MO calculations were performed using the Gaussian 98 package [10]. The second-order Møller-Plesset (MP2) method [11] with the 6-311G(d, p) basis set was used for geometry optimization and vibrational frequency calculations.

Results and Discussion

A. Molecular Orbital Calculation

In order to elucidate the internal rotational barriers for the CH_3 and NH_3^+ groups around the C–C and C–N bond axes, respectively, in an isolated ethylammonium ion, we have made *ab initio* MO calculations with MP2/6-311G(d,p) level. The full optimizations without symmetry restrictions were carried out for three kinds of conformations of the cation: (i) the all-staggered conformation, (ii) the CH_3-eclipsed conformation, i.e. the conformation where only the CH_3 group is rotated by 60° about the C–C bond axis from the all-staggered form, (iii) the NH_3^+-eclipsed conformation, i.e., the conformation where only the NH_3^+ group is rotated by 60° about the C–N bond axis from the all-staggered form. For the optimized geometry of the three conformers see Table 1. The geometry of the all-staggered form is the same as that reported by Zeroka et al. [12]. The all-staggered conformation was confirmed to correspond to a potential energy minimum from the vibrational analysis, which shows only real frequencies for the optimized conformer. On the other hand, the CH_3- and NH_3^+-eclipsed conformations were found to correspond to a saddle point of first order from the presence of one imaginary frequency. The potential height for the internal rotation of the CH_3 group was evaluated from the difference in the electronic energy between the all-staggered conformation and the CH_3-eclipsed conformation. The potential height for the NH_3^+ rotation was obtained in a similar manner. The potential heights obtained are 14.1 and 11.9 kJ mol^{-1} for the CH_3 and NH_3^+ rotations, respectively. Thus, the internal rotational barriers were estimated to be 12.5 and 9.1 kJ mol^{-1} for the CH_3 and NH_3^+ groups, respectively, taking account of zero-point vibrational energies. The zero-point energies were approximated by one-half of the CH_3 and NH_3^+ torsional frequencies, which were calculated to be 270 and 461 cm^{-1}, respectively, by Zeroka et al. [12].

B. ^{1}H NMR

The temperature dependence of the second moment (M_2) obtained from the resonance spectra is shown in Figure 2. The M_2 value at 117 K is (31.7 ± 2.0) G^2 (1 G = 1 × 10^{-4} T). With increasing temperature, M_2 de-

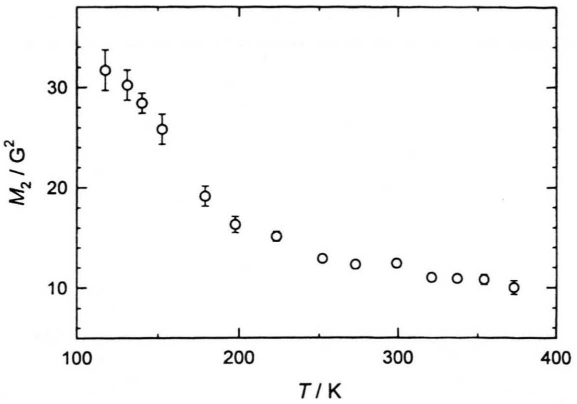

Fig. 2. Temperature dependence of the second moment (M_2) of ^{1}H NMR linewidth observed for ethylammonium chloranilate at a Larmor frequency of 40 MHz (1 G = 10^{-4} T).

Table 2. Calculated second moment (M_2) of ^{1}H NMR linewidth in ethylammonium chloranilate

	M_2/G^2 (1 G = 10^{-4} T)		
	Rigid	CH_3 reorient.	$CH_3 + NH_3^+$ reorient.
Intra-cation	25.7	19.0	9.8
Inter-ion	3.5	2.4	1.8
Total	29.2	21.4	11.6

creases and a constant value of (11 ± 1) G^2 is obtained above 320 K. To interpret the M_2 values, we calculated the values for each of the following motional states of the cation: (i) the rigid lattice, (ii) the C_3 reorientation of the CH_3 group about the C–C bond axis, (iii) the C_3 reorientation of the NH_3^+ group about the C–N bond axis in addition to the CH_3 reorientation. In the calculation, all the bond angles except the C–C–N angle were assumed to be tetrahedral. The C–C–N angle and the bond lengths of C–C and C–N and were taken to be 111.0°, 1.497, and 1.490 Å, respectively, from the crystal data of the salt [7]. The C–H and N–H lengths were taken to be 1.092 and 1.025 Å from the result of the MO calculation as described above. Inter molecular magnetic dipole-dipole interactions were calculated from the crystal data. The calculated values for the motional modes are given in Table 2. By comparing the observed M_2 values with the calculated ones, the cations are expected to be rigid below 117 K. The M_2 values above 320 K can be explained by a model of the C_3 reorientations of the CH_3 and NH_3^+ groups.

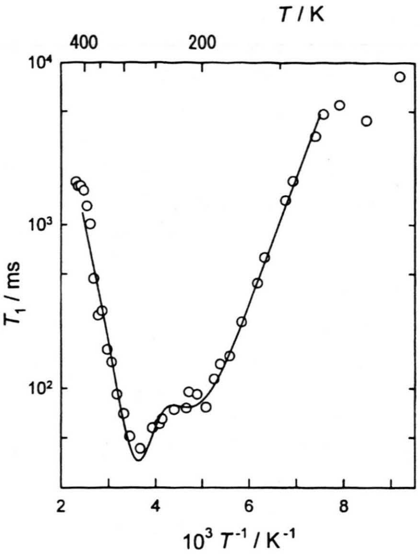

Fig. 3. Temperature dependence of the spin-lattice relaxation time (T_1) of ^{1}H NMR observed for ethylammonium chloranilate at a Larmor frequency of 32 MHz. The solid line shows the best-fitted values.

The temperature dependence of T_1 observed at 32 MHz is shown in Figure 3. A T_1 shoulder and a T_1 minimum appear around 200 and 270 K, respectively. Referring to the above discussion on M_2, we can assign the T_1 shoulder to the reorientation of the CH_3 group motion and the T_1 minimum to the NH_3^+ group motion. For these motions, T_1 can be expressed by the sum of the two BPP equations associated with the CH_3 and NH_3^+ group motions [13]:

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

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

where τ_1 and τ_2 are correlation times for the CH_3 and NH_3^+ group motions, respectively, and ω is the Larmor frequency. C_1 and C_2 are the motional constants for the CH_3 and NH_3^+ groups, respectively. An Arrhenius-type relationship between τ and the activation energy (E_a) for the reorientation process was assumed:

$$\tau = \tau_0 \exp(E_a/RT)\,, \tag{3}$$

where τ_0 is the correlation time at infinite temperature. Equations (1)–(3) were fitted to the T_1 data using a least-squares method. The E_a values of (15.1 ± 0.6) and (34 ± 3) kJ mol^{-1} were obtained for the CH_3 and NH_3^+ group reorientations, respectively. 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. On the other hand, the E_a value for the CH_3 group being slightly larger than the corresponding rotational barrier indicates the reorientation of the CH_3 group to be under a low interionic potential, probably originating from the C–H...O interaction.

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