Structural Parameters and Internal Rotational Barriers of tert-Butylammonium Ion: AM1 and ab initio Calculations

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Semiempirical and ab initio MO calculations were performed to estimate the structural parameters of tert-butylammonium ion and its potential energies for the internal rotation of the CH_3 and NH_3^+ groups. The barrier height for the rotation of NH_3^+ was found to be lower than for that of CH_3, corresponding to the C–N bond being longer than the C–C bond.

Recently we have studied the ^1H NMR spin-lattice relaxation time (T_1) and second moment (M_2) of ^1H NMR absorption in crystals of $[(CH_3)_3CNH_3]_2TeX_6$ (X = Cl, Br), $[(CH_3)_3CNH_3]_2SnCl_6$, and their partially deuterated analogs in the temperature range 77–405 K [1, 2]. We found three reorientational modes of the cations, namely C_3 reorientation of CH_3 and NH_3^+ about the respective C–C and C–N bonds and C_3' reorientation of the tert-butyl group about the C–N bond. The activation energies of these motions are quite small compared to those in halides [3–5]. This implies that the cations are loosely bound in the crystals and hence the values for the CH_3 and NH_3^+ groups are mostly due to the respective internal barrier to rotation about the C–C and C–N bonds, respectively. Among the three motions, the NH_3^+ motion did occur at the lowest temperature with activation energies (7.9–10.1 kJ mol^{-1}), which are smaller than those for the CH_3 groups (7.9–19.7 kJ mol^{-1}). This was surprising because a higher activation energy for NH_3^+ than for CH_3 results even for the isolated cation if the C–N bond (1.47 Å) is taken to be shorter than the C–C bond (1.54 Å), as is normally done in calculations of T_1 and M_2 of the tert-butylammonium ion [1–6]. These bond lengths were, however, not based on experimental data of this cation but on the molecular parameters of other alkylamines or alkylammonium ions [7–9]. This suggests that these values are not adequate for the present cation. In fact, recent crystal structure studies on tert-butylammonium salts gave comparable C–N and C–C bond lengths, as shown in Table 1 [10–12].

In the present investigation we have made semiempirical and ab initio MO calculations for the tert-butylammonium cation. We have calculated the geometrical parameters of the cation and elucidated the internal rotational barriers for the CH_3 and NH_3^+ groups.

Semiempirical MO calculations using the AM1 method were carried out with the MOPAC Ver. 5.0 from JCPE [13–16]. Ab initio calculations were performed with the Gaussian 88 program [17] using STO-3G, 4-31G, and 6-31G basis sets. The all-staggered conformation of the cation was found to be the most stable from AM1 calculation, as expected from nonbonded repulsions between the hydrogen orbitals.

The structural parameters of the cation calculated by AM1 and ab initio MO with the restriction to the all-staggered conformation are listed in Table 1. These values compare quite well with the parameters derived from X-ray studies. The AM1 calculations showed almost the same C–C and C–N bond lengths of 1.529 and 1.528 Å, respectively, while the ab initio calculations gave somewhat longer C–N bonds of 1.565–1.569 Å. These values are ca. 0.1 Å longer than the length adopted so far for the C–N bond.

The potential height for the internal rotation of the CH_3 group was evaluated from the difference between the total energies for the all-staggered conformation and the conformation where only one CH_3 group is rotated by 60° about the C–C bond axis from the all-staggered form, i.e. if one CH_3 group is eclipsed with respect to the C–C and C–N bonds. The potential barrier for the NH_3^+ rotation was obtained in a similar manner. All calculations gave the barrier for NH_3^+ smaller than for CH_3, as shown in Table 1. These results strongly support our conclusion reached on the basis of the previous NMR studies on $[(CH_3)_3CNH_3]_2MX_6$ (M = Sn, Te; X = Cl, Br) [1, 2]. The calculated barriers of the NH_3^+ group, except one

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Table 1. Computed and experimental structural parameters of the $(CH_3)_3CNH_3^+$ ion and its potential energies (V) for the CH_3 and NH_3^+ group rotations.

	AM1	STO-3G	4-31G	6-31G	$(CH_3)_3CNH_3Cl$	$(CH_3)_3CNH_3Br$	$[(CH_3)_3CNH_3]_2TeCl_6$
r(C–C)	1.529	1.547	1.525	1.528	1.521–1.528 [a]	1.499–1.517 [d]	1.51–1.57 [f]
r(C–N)	1.528	1.565	1.569	1.566	1.517	1.501	1.542–1.548
r(C–H)	1.118	1.086	1.082	1.083	0.90–1.03	1.08	
r(N–H)	1.023	1.041	1.009	1.009	0.88–0.99	1.08	
∢ CCC	109.9	112.6	112.7	112.7	111.7–112.1	111.9–112.2	110.2–114.0
∢ CCN	109.1	106.1	106.0	106.0	106.7–107.2	104.8–107.8	106.0–108.4
∢ CCH	110.5	110.2	110.9	110.9			
∢ CNH	109.5	111.4	110.6	110.7			
V (CH_3)/kJ mol^{-1}	8.09	14.85	17.56	17.21	9.8–22.7 [b,*]	10.6–21.0 [b,c,*]	10.9–16.7 [g,*]
V (NH_3^+)/kJ mol^{-1}	4.19	11.27	12.38	12.41	44.2 [c,*]	38.5 [c,*]	10.1 *

[a] Ref. [10], [b] Ref. [3], [c] Ref. [5], [d] Ref. [11], [e] Ref. [4], [f] Ref. [12], [g] Ref. [1].
* Activation energies derived from temperature dependences of ^{1}H NMR T_1. One should take into account the zero-point energy for comparison with the calculated potential energies.

from AM1 which is less reliable, are comparable to the experimental activation energies of the NH_3^+ reorientation in these complexes, when one takes into account the zero-point energy (ca. 1.4 kJ mol^{-1} roughly estimated for the potential barrier of 12.4 kJ mol^{-1} [18]). The barriers for the CH_3 rotation obtained from the ab initio MO are close to the 17–20 kJ mol^{-1} reported for the barrier of the CH_3 rotation as obtained by measuring IR and Raman spectra on $[(CH_3)_4N]_2MX_6$ (M = Te, Pt; X = Cl, Br) [19], which cations, isoelectronic with $(CH_3)_3CNH_3^+$, are also known to be loosely packed in crystals owing to the bulky complex anions [20]. On the other hand, the activation energies experimentally derived for the CH_3 reorientation in $[(CH_3)_3CNH_3]_2MX_6$ (M = Sn, Te; X = Cl, Br) range from 7.9 to 19.7 kJ mol^{-1} [1, 2], some of which are considerably small as compared with the calculated barriers, even if one subtracts the zero-point energy from the barrier height. This may be explained in terms of the distortion of the cation due to the crystal field.

The AM1 and ab initio calculations were performed at the Okayama University Computer Center and the Computer Center of Kyushu University, respectively.

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