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tert-Butylammonium Chloride at 115 K

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Abstract. $C_4H_{12}N^+Cl^-$, $M_r = 109.6$, orthorhombic, *Pbca*, $a = 17.770$ (8), $b = 8.877$ (4), $c = 8.647$ (3) Å, $V = 1364.0$ Å³, $Z = 8$, $D_x = 1.067$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 1.98$ cm⁻¹, $F(000) = 480$, $T = 115$ K, $R = 0.043$ for 1073 unique reflections with $I > 2\sigma(I)$. The *tert*-butylammonium ion in this ionic crystal is in its fully staggered conformation (all H atoms were found and their positions refined), and is hydrogen bonded to three neighboring Cl⁻ ions. The analysis was performed at 298 K as well as 115 K; the structure does not change, but the torsional motion of the *tert*-butyl group about the C–NH₃⁺ axis increases appreciably, as observed in other structures, from an r.m.s. amplitude of about 5° to nearly 12°.

Introduction. The *tert*-butylammonium ion is frequently used as a perching guest in host–guest chemistry (Cram

& Trueblood, 1981). The present analysis was carried out to provide information on the conformation of this simple ion and on its internal torsional motion (Trueblood & Dunitz, 1983). The current Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) reports only ten structures that contain this ion; the only ones that give H-atom parameters are from this laboratory.

Experimental. Crystals were obtained unexpectedly from chloroform–benzene during an attempt at preparation of a *tert*-butylammonium salt of a *para*-cyclophane crown (Helgeson, 1978) and were initially believed to be such a salt. Colorless single crystal, 0.23 × 0.22 × 0.44 mm; Syntex PI diffractometer

equipped with a variable temperature device (Strouse, 1976), graphite monochromator; unit-cell parameters* at 115 K by least-squares refinement of 15 reflections ($8 \leq 2\theta \leq 17^\circ$), θ - 2θ scan, $2.0^\circ \text{ min}^{-1}$ from 1.2° below $K\alpha_1$ to 1.2° above $K\alpha_2$, $2\theta_{\text{max}} = 55^\circ$ for the range $0 \leq h \leq 22$, $0 \leq k \leq 11$, $0 \leq l \leq 11$, three reflections monitored every 97 reflections with maximum 5% intensity variation from average, 1562 unique data, 1386 with $I > 0$, 1073 with $I > 2\sigma(I)$ used in refinement, Lorentz and polarization but no absorption correction ($\mu = 1.98 \text{ cm}^{-1}$); structure solved by phasing with Cl^- found in a Patterson map; all atoms located on Fourier and difference Fourier maps, anisotropic displacement parameters for all non-H atoms; all atoms refined by full-matrix least-squares procedure based on $|F|$ with a maximum $\sin\theta/\lambda = 0.65 \text{ \AA}^{-1}$; refinement of 103 parameters converged to $R = 0.043$, $wR = 0.051$ ($wR = 0.055$ for all 1562 reflections), $w = 1/\sigma^2(F_o)$, goodness of fit = 1.40, ratio of maximum least-squares shift to e.s.d. in a position parameter in the final cycle of 0.07 for a non-H atom and 0.36 for H, average ratios 0.02 and 0.1 respectively; maximum and minimum heights in final difference map 0.14 and -0.08 e \AA^{-3} ; atomic factors from *International Tables for X-ray Crystallography* (1974); all calculations on a DEC VAX 11/780 and VAX 11/750, using *SHELX76* (Sheldrick, 1976) and local programs for least squares (*FMLS*), molecular geometry (*MG84*) and molecular motion (*THMA11*: Trueblood, 1978; Schomaker & Trueblood, 1984).

Discussion. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 1† and selected bond lengths and bond angles are given in Table 2.

The interatomic distances are quite normal (Table 2); the N—H and C—H distances, not shown, averaged 0.92 (5) and 0.97 (4) Å, ranging a little more than one e.s.d. above and below the average. These distances are about 0.1 Å shorter, as is usual, than those that would be found by neutron diffraction, but the *angular positions* of the twelve H atoms are probably much more reliable. All of the H—X—X—H torsion angles fall into two groups, two thirds being very nearly *gauche* [average of $24 = 60$ (5)°, range 52 – 72°] and the others very nearly antiperiplanar. The *tert*-butylammonium ion is thus in the fully staggered conformation, as

* The structure analysis was also performed at 298 K. Space group and structure were the same; $a = 18.007$ (8), $b = 8.962$ (4), $c = 8.677$ (4) Å, $V = 1400 \text{ \AA}^3$, $D_x = 1.040 \text{ g cm}^{-3}$; 1241 unique reflections, 778 with $|F| > 3\sigma(F)$ used in refinement, converged to $R = 0.050$, $wR = 0.050$, $S = 1.31$.

† Lists of anisotropic displacement parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43576 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

expected for the isoelectronic neopentane. We have observed this conformation in every structure containing this ion that we have examined, more than ten in all.

Because there is significant motion of the ion even at 115 K, corrections to the bond distances for rigid-body motion (Schomaker & Trueblood, 1968) average nearly 0.006 Å; these corrections have been noted in Table 2. Corrections for thermal motion are more than three times larger at room temperature, averaging about 0.019 Å, but the corrected distances are nearly identical, because the *apparent* distances are foreshortened appreciably. The motion of the ion in the crystal

Table 1. *Positional and displacement parameters for tert-butylammonium chloride at 115 K*

Displacement parameters are commonly called vibrational parameters. Units of $\langle u^2 \rangle$ are \AA^2 . Units of each e.s.d., in parentheses, are those of the least significant digit of the corresponding parameter.

	x	y	z	$\langle u^2 \rangle$
Cl	0.32633 (4)	0.41843 (7)	0.31331 (8)	0.024
N(1)	0.3170 (1)	0.0871 (3)	0.1803 (3)	0.021
C(1)	0.3872 (2)	0.0044 (3)	0.2307 (3)	0.023
C(2)	0.3836 (2)	-0.1522 (4)	0.1597 (4)	0.032
C(3)	0.3863 (2)	-0.0013 (5)	0.4059 (4)	0.038
C(4)	0.4539 (2)	0.0948 (4)	0.1703 (4)	0.031
H(1N)	0.320 (2)	0.187 (4)	0.230 (4)	0.04 (1)*
H(2N)	0.279 (2)	0.041 (4)	0.224 (4)	0.04 (1)*
H(3N)	0.317 (2)	0.090 (4)	0.076 (5)	0.05 (1)*
H(21)	0.434 (2)	-0.198 (3)	0.179 (4)	0.03 (1)*
H(22)	0.380 (2)	-0.141 (4)	0.051 (4)	0.03 (1)*
H(23)	0.337 (2)	-0.205 (4)	0.204 (4)	0.05 (1)*
H(31)	0.344 (2)	-0.052 (4)	0.436 (4)	0.03 (1)*
H(32)	0.431 (2)	-0.049 (4)	0.441 (4)	0.04 (1)*
H(33)	0.390 (2)	0.094 (4)	0.441 (4)	0.05 (1)*
H(41)	0.500 (2)	0.044 (4)	0.197 (4)	0.05 (1)*
H(42)	0.457 (2)	0.196 (4)	0.219 (4)	0.04 (1)*
H(43)	0.454 (2)	0.109 (4)	0.057 (5)	0.05 (1)*

* Denotes an atom refined isotropically. Other isotropic values are $1/8\pi^2$ times the 'equivalent B value' for an anisotropic atom, as defined by Hamilton (1959).

Table 2. *Bond distances (Å) and angles (°) for tert-butylammonium chloride at 115 K*

E.s.d.'s are in parentheses, in units of the least significant digit of the corresponding value.

	Uncorrected	Corrected*	
N—C(1)	1.513 (4)	1.517 (5)	
C(1)—C(2)	1.520 (5)	1.527 (6)	
C(1)—C(3)	1.515 (4)	1.521 (5)	
C(1)—C(4)	1.523 (4)	1.528 (5)	
N—C(1)—C(2)	107.0 (2)	C(2)—C(1)—C(3)	111.9 (3)
N—C(1)—C(3)	107.2 (3)	C(2)—C(1)—C(4)	112.1 (3)
N—C(1)—C(4)	106.7 (2)	C(3)—C(1)—C(4)	111.7 (3)
Hydrogen-bonding geometry†			
	Angle N—H...Cl	N...Cl	H...Cl
N—H(1N)...	173 (3)	3.162 (3)	2.18 (4)
N—H(2N)...	174 (3)	3.170 (3)	2.30 (3)
N—H(3N)...	175 (3)	3.178 (3)	2.28 (4)

* Corrections for rigid-body motion (see text).

† Cl' is at $(\frac{1}{2}-x, y-\frac{1}{2}, z)$; Cl'' at $(x, \frac{1}{2}-y, z-\frac{1}{2})$.

probably has an appreciable contribution from internal torsional motion about the C(1)–NH₃⁺ bond (Trueblood & Dunitz, 1983); it is noteworthy that the principle eigenvector of **L**, when rigid-body motion is assumed, is only 12° from the direction of the C(1)–N bond. In attempting to assess this contribution, it is necessary to add additional atoms to avoid singularities, and for this purpose the three hydrogen-bonded Cl⁻ ions were included. The analysis was done using both the direct Dunitz–White approach, ignoring any correlation of internal and overall motion, and the approach of Schomaker & Trueblood (1984), including such correlations. In each case, the r.m.s. amplitude about the C–N bond was 5 (1)°; however, the analyses were flawed by the fact that one eigenvalue of **L** became slightly negative [mean square amplitude less than 1 (°)², smaller than its e.s.d.], presumably a consequence of the inclusion of the Cl⁻ ions in the analysis – they hardly can be expected to move in concert with the cation. Furthermore, the data are only of mediocre quality by the Hirshfeld (1976) test. Nonetheless, we believe this result is meaningful; it parallels the findings in many other structures containing this ion (Maverick, Grossenbacher & Trueblood, 1979; Trueblood & Maverick, 1979). At room temperature, the r.m.s. torsional amplitude about the C–N bond is about 12 (2)°.

The *tert*-butylammonium ion is hydrogen bonded to three neighboring Cl⁻ ions (Table 2), which are in nearly ideal positions for accepting these bonds, the N–H...Cl angles being nearly 180° and the C(1)–N...Cl angles about tetrahedral (104–109°). It is

characteristic of this ion in host–guest structures that it forms three hydrogen bonds in much this fashion, although often the receptor atoms in the guest structures are less ideally positioned (Cram & Trueblood, 1981; Maverick, Grossenbacher & Trueblood, 1979). There are no other short intermolecular (interionic) interactions.

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Dimethyl *exo*-5-(Dibromomethyl)-*endo*-5-methyl-6-oxobicyclo[2.2.2]octa-2,7-diene-2,3-dicarboxylate*

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Abstract. C₁₄H₁₄Br₂O₅, *M_r* = 422.1, monoclinic, *P*2₁, *a* = 7.859 (1), *b* = 10.406 (2), *c* = 9.888 (2) Å, β = 103.98 (1)°, *U* = 784.7 Å³, *D_x* = 1.79 Mg m⁻³, *Z* = 2, *Mo Kα*, λ = 0.71069 Å, μ = 5.13 mm⁻¹, *T* = 295 K, *F*(000) = 416, *R* = 0.032 for 1349 observed [*I* > 3σ(*I*)]

* Although the *endo* and *exo* designations are not strictly applicable to the bicyclo[2.2.2]octadiene system, we use them for the sake of simplicity with the following convention: substituents are designated as being *endo* or *exo* with respect to the unsaturated bridge of lower priority (Yates & Auksi, 1979).

reflections. Dimethyl acetylenedicarboxylate reacts preferentially on the methyl face of 6-(dibromomethyl)-6-methyl-2,4-cyclohexadien-1-one to give the title compound. In the bicyclo[2.2.2]octadiene system torsion angles (τ) about the double bonds are 0.4 (6) and 2.7 (7)°, while the C(5)–C(6) bond is slightly twisted [τ = 7.1 (5)°] due to contacts involving the CHBr₂ substituent. The two methoxycarbonyl groups are canted by 5.5 (8) and 78.1 (8)° with respect to the plane of the C(2)=C(3) double bond.