# Redetermination of triethylammonium chloride in the space group $P31c$

**Andrei V. Churakov$^{a}$\* and Judith A. K. Howard$^{b}$**

$^{a}$N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Science, 31 Leninskii Prospect, Moscow 119991, Russia, and $^{b}$Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England

Correspondence e-mail: churakov@igic.ras.ru

The structure of triethylammonium chloride, $C_6H_{16}N^+ \cdot Cl^-$, has been redetermined in the space group $P31c$. In contrast with previous refinements in the space group $P6_3mc$, no disorder of the triethylammonium cation was observed.

## Comment

The structure of triethylammonium chloride has been reported four times to date (Hendricks, 1928; Genet, 1965; James *et al.*, 1985; Ilyukhin, 2000). All four structure determinations were made in the space group $P6_3mc$ (No. 186) and showed 'propeller'-like disorder of the cation (Fig. 1) caused by a crystallographic mirror plane. Two closely related models were used in the later refinements. In the first, both independent C atoms occupy general positions [12 (*d*): *x, y, z*; Genet, 1965; James *et al.*, 1985; Fig. 1(*a*)]. In the second, the methylene C atom lies on a general position, while the methyl C atom lies on the mirror plane [6 (*c*): *x, x̄, z*; Ilyukhin, 2000; Fig. 1(*b*)].

Such disorder is a common feature of the $Et_3NH^+$ cation. A total of 379 structures containing the triethylammonium cation are reported in the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002). Of these, 126 structures are disordered (33.2%) and 76 structures (20.1%) possess the disordered cation. These figures are noticeably higher than the statistical appearance of disorder in the CSD (18.2%; Allen, 2002). The same type of disorder was observed previously for some other trialkylammonium derivatives with approximate $C_{3v}$ symmetry, namely silatranes (Zaitseva *et al.*, 1996) and germatranes (Karlov *et al.*, 2001). These two structures were refined in the space group *Pnma*. However, refinements in the lower-symmetry space group $Pna2_1$ retain the 'propeller'-like disorder, with occupancy ratios $\simeq$ 0.5:0.5. On the contrary, the refinement of [NHEt$_3$][Sn(acac)Cl$_4$] in the lower-symmetry group led to an ordered cation, but was not found to be convincing (Korte *et al.*, 1988). Against this background, we present here a further redetermination of the structure of triethylammonium chloride, (I) (Fig. 2).

A new data set for (I) was collected on a Bruker SMART CCD diffractometer at 120 K. The systematic absences were consistent with the space groups $P31c$ (No. 159) and $P6_3mc$. Comparison of the $|F_o(hkl)|$ and $|F_o(hk\bar{l})|$ values points to $P6_3mc$, since their equality holds in $P6_3mc$ but not in $P31c$. However, the mean value of $|E^2 - 1|$ (0.678) was lower than expected for non-centrosymmetric crystals (Herbst-Irmer & Sheldrick, 1998).

$$\left[ H-N \right]^+ \cdot Cl^-$$

(I)
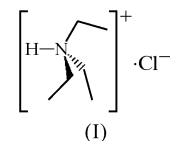
At first, the structure was refined in the higher symmetry group $P6_3mc$. The model of Ilyukhin (2000) was found more appropriate and the final refinement converged to $R_1 = 0.054$ for 395 independent reflections with $I > 2\sigma(I)$ and 29 parameters. The highest difference peak was 0.55 e Å$^{-3}$. However, the Flack (1983) parameter was found to be poorly determined [0.00 (39)], and the use of the racemic TWIN instruction did not led to any improvement of results. Subsequently, the structure was solved and refined in the space group $P31c$. The disorder of the cation disappeared and the refinement led to a residual $R_1 = 0.072$ for 661 reflections with $I > 2\sigma(I)$ and 47 parameters. The highest difference peak was 0.82 e Å$^{-3}$.

The factor $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$ for low-intensity reflections was slightly greater than 1 and did not directly indicate the presence of twinning (Herbst-Irmer & Sheldrick,
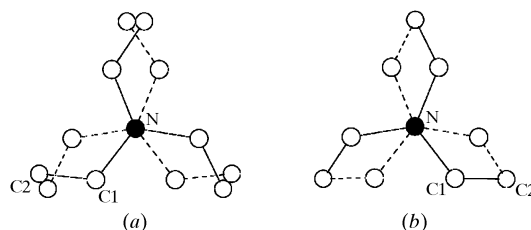


**Figure 1**
The 'propeller'-like disorder of the $Et_3NH^+$ cation, viewed along the *c* axis, showing (*a*) the model of Genet (1965) and (*b*) the model of Ilyukhin (2000).

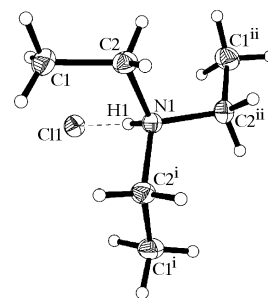

**Figure 2**
The ordered structure of the $Et_3NH^+$ cation of (I), showing 50% probability displacement ellipsoids. The N—H$\cdots$Cl hydrogen bond is denoted by a dashed line [symmetry codes: (i) $1 - y, 1 + x - y, z$; (ii) $y - x, 1 - x, z$].

# organic compounds

1998). Later, the TWIN operator relative to the mirror plane ($\bar{1}00$, 110, 001) was included. This immediately resulted in the significant decrease of $R_1$ to 0.019 [48 parameters, Flack parameter 0.06 (6), highest difference peak 0.18 e $\text{Å}^{-3}$]. The volume fraction of twin components converged to 0.5. Kahlenberg (1999) noted that, in such cases, standard Yeates and Britton statistical tests for merohedral twinning fail. Thus, the choice of the space group may be made on the basis of the final residual parameters only.

## Experimental

Crystals of (I) were grown from a solution in ethanol–water (1:1). Long needles (15 mm) were cut into small pieces of suitable size.

*Crystal data*

| | |
|---|---|
| $C_6H_{16}N^+\cdot Cl^-$ | Mo $K\alpha$ radiation |
| $M_r = 137.65$ | Cell parameters from 3089 |
| Trigonal, $P31c$ | reflections |
| $a = 8.2542\ (2)$ Å | $\theta = 2.8–30.0°$ |
| $c = 6.9963\ (2)$ Å | $\mu = 0.38\ \text{mm}^{-1}$ |
| $V = 412.81\ (2)\ \text{Å}^3$ | $T = 120\ (2)$ K |
| $Z = 2$ | Block, colourless |
| $D_x = 1.107\ \text{Mg m}^{-3}$ | $0.40 \times 0.10 \times 0.10$ mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | $R_{int} = 0.014$ |
| | $\theta_{max} = 28.0°$ |
| $\omega$ scans | $h = -5 \rightarrow 10$ |
| 3185 measured reflections | $k = -10 \rightarrow 9$ |
| 665 independent reflections | $l = -9 \rightarrow 9$ |
| 661 reflections with $I > 2\sigma(I)$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.019$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.047$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.04$ | $\Delta\rho_{max} = 0.18$ e $\text{Å}^{-3}$ |
| 665 reflections | $\Delta\rho_{min} = -0.09$ e $\text{Å}^{-3}$ |
| 48 parameters | Absolute structure: Flack (1983), |
| All H-atom parameters refined | with 297 Friedel pairs |
| | Flack parameter = 0.06 (6) |

The ammonium H atom was found from a difference Fourier synthesis. Other H atoms were placed in calculated positions. Both positional and displacement parameters for all H atoms were refined.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C2 | 1.5053 (13) | C1—C2 | 1.5160 (18) |
| C2—N1—C2$^i$ | 111.18 (11) | N1—C2—C1 | 112.23 (13) |

Symmetry code: (i) $1 - y, 1 + x - y, z$.

structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-Plus*.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (1998). *SMART.* Version 5.049. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SHELXTL-Plus.* Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT.* Version 6.04. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Genet, F. (1965). *Bull. Soc. Fr. Mineral. Cristallogr.* **88**, 463–482.
Hendricks, S. B. (1928). *Z. Kristallogr.* **67**, 472–481.
Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* B**54**, 443–449.
Ilyukhin, A. B. (2000). Private communication to the Cambridge Structural Database, refcode ETAMCL02. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
James, M. A., Cameron, T. S., Knop, O., Neuman, M. & Falk, M. (1985). *Can. J. Chem.* **63**, 1750–1758.
Kahlenberg, V. (1999). *Acta Cryst.* B**55**, 745–751.
Karlov, S. S., Shutov, P. L., Churakov, A. V., Lorberth, J. & Zaitseva, G. S. (2001). *J. Organomet. Chem.* **627**, 1–5.
Korte, L., Mootz, D., Scherf, M. & Wiebcke, M. (1988). *Acta Cryst.* C**44**, 1128–1130.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Zaitseva, G. S., Karlov, S. S., Churakov, A. V., Avtonomov, E. V., Lorberth, J. & Hertel, D. (1996). *J. Organomet. Chem.* **523**, 221–225.

# supporting information

# Redetermination of triethylammonium chloride in the space group *P*31*c*

## Andrei V. Churakov and Judith A. K. Howard

## Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-Plus*.

## Triethylammonium chloride

*Crystal data*

| | |
|---|---|
| $C_6H_{16}N^+ \cdot Cl^-$ | $D_x = 1.107$ Mg m$^{-3}$ |
| $M_r = 137.65$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Trigonal, $P31c$ | Cell parameters from 3089 reflections |
| Hall symbol: P 3 -2c | $\theta = 2.9$–$30.0°$ |
| $a = 8.2542$ (2) Å | $\mu = 0.38$ mm$^{-1}$ |
| $c = 6.9963$ (2) Å | $T = 120$ K |
| $V = 412.81$ (2) Å$^3$ | Block, colourless |
| $Z = 2$ | $0.40 \times 0.10 \times 0.10$ mm |
| $F(000) = 152$ | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 661 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.014$ |
| Graphite monochromator | $\theta_{max} = 28.0°$, $\theta_{min} = 2.9°$ |
| $\omega$ scans | $h = -5 \rightarrow 10$ |
| 3185 measured reflections | $k = -10 \rightarrow 9$ |
| 665 independent reflections | $l = -9 \rightarrow 9$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | All H-atom parameters refined |
| $R[F^2 > 2\sigma(F^2)] = 0.019$ | $w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$ |
| $wR(F^2) = 0.047$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.04$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 665 reflections | $\Delta\rho_{max} = 0.18$ e Å$^{-3}$ |
| 48 parameters | $\Delta\rho_{min} = -0.09$ e Å$^{-3}$ |
| 1 restraint | Absolute structure: Flack (1983), with xx Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Absolute structure parameter: 0.06 (6) |
| Secondary atom site location: difference Fourier map | |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger. The structure was solved by direct methods (Sheldrick, 1990) and refined by full-matrix least-squares on $F^2$(Sheldrick, 1997), with anisotropic thermal parameters for all non-H atoms.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)*

|      | *x*          | *y*           | *z*        | $U_{iso}$*/$U_{eq}$ |
| ---- | ------------ | ------------- | ---------- | ------------------- |
| Cl1  | 0.3333       | 0.6667        | 0.1486     | 0.02172 (12)        |
| N1   | 0.3333       | 0.6667        | 0.5913 (2) | 0.0165 (3)          |
| C1   | 0.1785 (2)   | 0.31876 (16)  | 0.5507 (2) | 0.0263 (3)          |
| C2   | 0.17835 (16) | 0.47886 (15)  | 0.6567 (3) | 0.0213 (2)          |
| H1   | 0.3333       | 0.6667        | 0.466 (6)  | 0.032 (8)*          |
| H1A  | 0.074 (3)    | 0.204 (3)     | 0.592 (3)  | 0.045 (6)*          |
| H1B  | 0.284 (3)    | 0.306 (3)     | 0.572 (3)  | 0.030 (4)*          |
| H1C  | 0.154 (6)    | 0.333 (2)     | 0.412 (3)  | 0.042 (7)*          |
| H2A  | 0.067 (2)    | 0.4754 (19)   | 0.644 (4)  | 0.026 (4)*          |
| H2B  | 0.197 (2)    | 0.467 (3)     | 0.793 (2)  | 0.028 (4)*          |

*Atomic displacement parameters ($Å^2$)*

|      | $U^{11}$     | $U^{22}$     | $U^{33}$     | $U^{12}$     | $U^{13}$     | $U^{23}$     |
| ---- | ------------ | ------------ | ------------ | ------------ | ------------ | ------------ |
| Cl1  | 0.02437 (15) | 0.02437 (15) | 0.01642 (17) | 0.01218 (7)  | 0.000        | 0.000        |
| N1   | 0.0163 (4)   | 0.0163 (4)   | 0.0167 (7)   | 0.0082 (2)   | 0.000        | 0.000        |
| C1   | 0.0262 (6)   | 0.0180 (5)   | 0.0338 (7)   | 0.0102 (4)   | −0.0013 (7)  | −0.0018 (4)  |
| C2   | 0.0186 (4)   | 0.0182 (5)   | 0.0241 (5)   | 0.0070 (4)   | 0.0022 (6)   | 0.0026 (7)   |

*Geometric parameters ($Å$, º)*

| | | | |
| --- | --- | --- | --- |
| N1—C2[i]     | 1.5053 (13) | C1—H1B     | 0.94 (3)     |
| N1—C2        | 1.5053 (13) | C1—H1C     | 1.01 (2)     |
| N1—C2[ii]    | 1.5053 (13) | C2—H2A     | 0.914 (18)   |
| N1—H1        | 0.87 (4)    | C2—H2B     | 0.976 (15)   |
| C1—C2        | 1.5160 (18) | Cl1—H1     | 2.22 (4)     |
| C1—H1A       | 0.95 (2)    |            |              |
|              |             |            |              |
| C2[i]—N1—C2  | 111.18 (11) | C2—C1—H1C   | 106.6 (15)  |
| C2[i]—N1—C2[ii] | 111.18 (11) | H1A—C1—H1C | 106 (2)     |
| C2—N1—C2[ii] | 111.18 (11) | H1B—C1—H1C  | 114 (3)     |
| C2[i]—N1—H1  | 107.70 (12) | N1—C2—C1    | 112.23 (13) |
| C2—N1—H1     | 107.70 (12) | N1—C2—H2A   | 109.1 (11)  |
| C2[ii]—N1—H1 | 107.70 (12) | C1—C2—H2A   | 111.4 (12)  |

| C2—C1—H1A | 108.8 (14) | N1—C2—H2B | 107.7 (12) |
| C2—C1—H1B | 115.2 (14) | C1—C2—H2B | 108.9 (10) |
| H1A—C1—H1B | 106 (2) | H2A—C2—H2B | 107.3 (19) |

Symmetry codes: (i) −*x*+*y*, −*x*+1, *z*; (ii) −*y*+1, *x*−*y*+1, *z*.