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The crystal structure of *N*-tertiary butyl propylamine.

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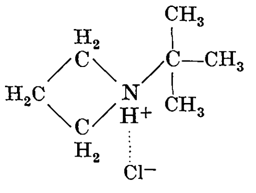
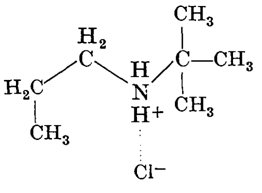
A compound previously assumed to be tertiary butyl azetidine hydrochloride (I) (Meyers, 1961) has been shown instead, by a three-dimensional X-ray diffraction study, to be the hydrochloride salt of *N*-tertiary butyl propylamine (II). The relation of its molecular parameters to those in other amines is of interest, particularly with respect to the N–C distance and to any indications of intermolecular hydrogen bonding.



(I)



(II)

Crystal data

Long needle-like crystals elongated along (001) were grown from a solution of ethyl alcohol–ethyl acetate. The space group ($Pna2_1$) and cell dimensions ($a=14{\cdot}15$, $b=8{\cdot}90$, $c=7{\cdot}73$ Å) were determined from precession photographs taken with Mo $K\alpha$ radiation. The observed density was 1·03 g.cm^{-3} as compared with the density calculated for $z=4$ which is 1·02.

Structure determination

Intensity data were collected of the zero and four upper levels about the [100] axis, and the zero and two upper levels about the [010] axis, all at a precession angle of 30°. Intensities were estimated visually, a scale of timed exposures of a selected 'typical' reflection being used. A total of 564 independent reflections were observed. Lorentz and polarization corrections were made in the usual manner (Waser, 1951).

Extinctions of all $0kl$ where $k+l$ was odd, $h0l$ where h was odd and $00l$ where l was odd conformed with space group $Pna2_1$ which was subsequently shown to be correct. The chlorine position was determined from the three Patterson syntheses. Structure factors using chlorine only and assuming an isotropic temperature factor, $B=3{\cdot}4$ Å^2, led to $r=0{\cdot}83$, $R=0{\cdot}40$ (Dickerson, Wheatley, Howell & Lipscomb, 1957). A three dimensional Fourier map was computed on the Remington–Rand 1103 computer, the phases calculated from the chlorine position being used, and four of the eight atoms were identified. Calculation of structure factors at this stage led to $r=0{\cdot}48$ and $R=0{\cdot}31$ and a new Fourier map was calculated using these phases. The remainder of the atoms (excluding hydrogen) were easily identifiable and it was then apparent that we were dealing with the propylamine salt rather than the azetidine salt. Peak heights combined with previous chemical knowledge made it possible to distinguish the nitrogen atom from the carbon atoms. Starting with $r=0{\cdot}18$ and $R=0{\cdot}19$ and using isotropic temperature factors equal to 3·4 Å^2 for all atoms, five cycles of least squares reduced these discrepancy factors to $r=0{\cdot}12$ and $R=0{\cdot}15$. Since the maximum shift in the coordinates was now less than 0·01 Å, a difference Fourier synthesis was calculated in the hope of finding the hydrogen atom positions. Although no peaks of height greater than 0·4 e^{2}Å^{-3} were observed, the background was so diffuse that no attempt was made to place the hydrogen atoms

Table 1. *Fractional coordinates and isotropic temperature factors*

Atom	x	y	z	B
Cl	0·406	0·117	0·255	4·08
N	0·100	0·537	0·160	2·44
C(1)	0·037	0·943	0·255	5·77
C(2)	0·022	0·780	0·202	2·84
C(3)	0·108	0·683	0·259	3·43
C(4)	0·185	0·436	0·176	2·70
C(5)	0·172	0·284	0·069	4·58
C(6)	0·279	0·506	0·139	3·97
C(7)	0·178	0·378	0·366	4·59

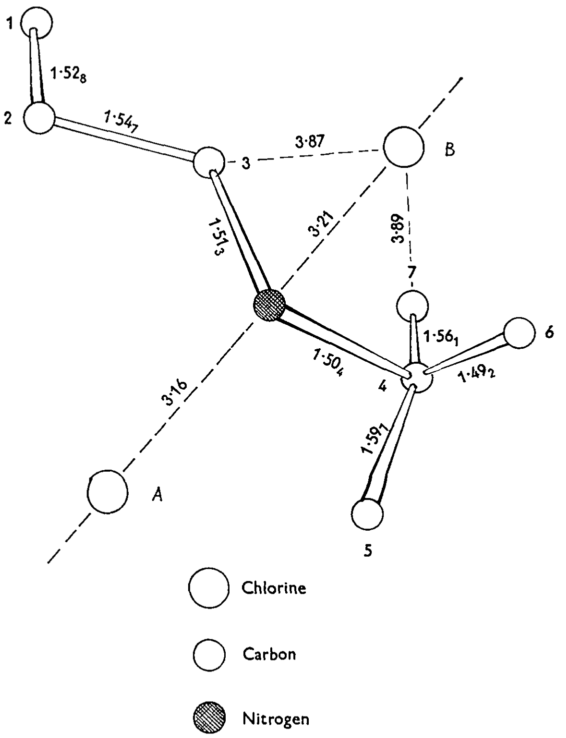


Fig. 1. Crystal structure of *N*-tertiary butyl propyl amine hydrochloride

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on the basis of this difference Fourier synthesis. Instead, the difference map indicated anisotropic vibrations in the light atom positions, particularly C_1. The fractional coordinates and isotropic temperature factors obtained are listed in Table 1 and bond distances are given in Fig. 1.

Discussion

With these parameters $C–C = 1{\cdot}55 \pm 0{\cdot}03$ Å and $C–N = 1{\cdot}51 \pm 0{\cdot}03$ Å, with the CNC bond angle equal to 114° and all other angles averaging to $109° \pm 3°$. The C–N distance appears to be somewhat long if it is compared with the 1·48 Å in studies on simpler amines by Atoji & Lipscomb (1951), Jellinek (1958) and Gabe (1961). However, it is comparable to the 1·51 Å which has been obtained in somewhat more complicated molecules for $C–N^+$ distances. To cite only a few examples one can look at the studies by Senko & Templeton (1960), Kartha, Ahmed & Barnes (1960), Rerat (1960) and Raman, Reddy & Lipscomb (1963). It seems likely that when one is considering all but the very simple molecules, a distinction should be made between $C–N^+$ distances and C–N distances. A survey of the literature indicates that a pattern of systematically longer distances (about 0·03 Å) is emerging when there is a positive charge in the vicinity of the nitrogen atom.

Hydrogen bonding through $Cl(A) \cdots N \cdots Cl(B)$ is indicated by the distances of 3·16 and 3·21 Å, which are significantly shorter than the corrected van der Waals distance of 3·30 Å given by Pimental & McClellan (1960). All other non-bonding distances are greater than 3·87 Å.

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References

ATOJI, M. & LIPSCOMB, W. N. (1957). *Acta Cryst.* **6**, 770.
DICKERSON, R. E., WHEATLEY, P. J., HOWELL, P. A. & LIPSCOMB, W. N. (1957). *J. Chem. Phys.* **27**, 200.
GABE, E. J. (1961). *Acta Cryst.* **14**, 1296.
JELLINEK, F. (1958). *Acta Cryst.* **11**, 626.
KARTHA, G., AHMED, F. R. & BARNES, W. H. (1960). *Acta Cryst.* **13**, 525.
MEYERS, A. I. (1961). Private communication.
PIMENTAL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond.* Freeman.
RAMAN, S., REDDY, J. & LIPSCOMB, W. N. (1963). *Acta Cryst,* **16**, 364.
RERAT, P. C. (1960). *Acta Cryst.* **13**, 459.
SENKO, M. E. & TEMPLETON, D. H. (1960). *Acta Cryst.* **13**, 281.
WASER, J. (1951). *Rev. Sci. Instrum.* **22**, 567.

Notes and News

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Radiation Hazards Associated with X-ray Diffraction Techniques

In the April issue of this journal an article on the above topic was published under the sponsorship of the Commission on Crystallographic Apparatus of the International Union of Crystallography (*Acta Cryst.* (1963), **16**, 324). Reprints of this article can be obtained from the author, Dr E. G. Steward, Northampton College of Advanced Technology, St. John Street, London, E. C. 1, England, or from the General Secretary of the Union, Dr D. W. Smits, Mathematisch Instituut, University of Groningen, Reitdiepskade 4, Groningen, The Netherlands.