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Space Groups of Some *N*-Substituted 2-Halogenoalkylammonium Halides

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The space groups are reported of sixteen salts, one of which is dimorphous. A detailed study was subsequently made of the structure of one of them, 2-bromo-2-*p*-tolylethyldimethylammonium bromide.

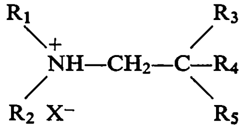
These compounds are of interest medically as adrenomotor antagonists (*e.g.*, Graham, 1962), and it was hoped that this crystallographic study would provide some correlation between molecular conformation and pharmacological activity.

Experimental

In an attempt to obtain better crystals, many of the compounds were recrystallized from analytical reagent grade methanol, ethanol or isopropyl alcohol. The alcohol was previously carefully dried with quicklime, as any water present would hydrolyse the halide to the corresponding alcohol. The densities were measured by

Table 1. *Chemical constitution of compounds described*

General formula:



$$R_1R_2\overset{+}{N}H\,X^-\text{—}CH_2\text{—}C(R_3)(R_4)(R_5)$$

Trivial name	R_1	R_2	R_3	R_4	R_5	X^-
Dibenamine	Benzyl	Benzyl	Cl	H	H	Cl^-
W	Cyclohexyl	Cyclohexyl	Cl	Methyl	H	Cl^-
U	Cyclohexyl	Cyclohexyl	Br	Methyl	H	Br^-
AT3	9-Fluorenyl	Ethyl	I	H	H	I^-
L13	n-Propyl	H	Br	Phenyl	H	Br^-
L17	Benzyl	H	Br	Phenyl	H	Br^-
L42	Methyl	Methyl	Br	Phenyl	Methyl	Br^-
SM	Methyl	Methyl	Br	4-Methylphenyl	H	Br^-
S2	Methyl	Methyl	Br	4-Chlorophenyl	H	Br^-
S4	Methyl	Methyl	Cl	3,4-Dichlorophenyl	H	Cl^-
S14	Methyl	Methyl	Br	3-Bromophenyl	H	Br^-
S15	Methyl	Methyl	Br	3-Chlorophenyl	H	Br^-
S1	Methyl	Methyl	Cl	4-Chlorophenyl	H	Cl^-
LT	Morpholine*		Cl	Phenyl	H	Cl^-
L23	Pyrrolidine*		Br	Phenyl	H	Br^-
R	Piperidine*		Br	Phenethyl	H	Br^-

* NHR_1R_2

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Table 2. *Space group data*

Name	Molecular formula	Habit	Laue symmetry	Parameters	Densities in gm.cm.$^{-3}$	Space group
DB	$C_{16}H_{19}NCl_2$	Laths, elongated along [001] with (100) prominent	$2/m$	a 9·7 ±1 Å b 12·8 ±1 c 13·0 ±1 β 103±1°	D_m $1{\cdot}2_2$ D_x $1{\cdot}2_6$ (4)*	Monoclinic $P2_1/c$ (14†, b unique)
W	$C_{15}H_{29}NCl_2$	Needles, elongated along [100] with (001) prominent	$2/m$	a 5·45±5 Å b 11·8 ±1 c 20·0 ±2 β 94±1°	D_m $1{\cdot}5_0$ D_x $1{\cdot}5_2$ (4)	Monoclinic $P2_1/c$ (14, b unique)
U	$C_{15}H_{29}NBr_2$	Needles, elongated along [100] with (001) prominent	mmm	a 5·50±5 Å b 24·0 ±2 c 38·5 ±5	D_m $1{\cdot}9_0$ D_x $1{\cdot}9_4$ (16)	Orthorhombic $F2dd$ (43, non-standard setting)
AT3(1)	$C_{17}H_{19}NI_2$	Needles, elongated along [100] with (010) prominent	$2/m$	a 11·05±5 Å b 14·25±5 c 13·50±5 β 122±1°	D_m $1{\cdot}8_6$ D_x $1{\cdot}8_2$ (4)	Monoclinic $P2_1/c$ (14, b unique)
AT3(2)	$C_{17}H_{19}NI_2$	Rhombs	$\bar{1}$	a 8·58±5 Å b 11·93±5 c 22·7 ±1 α 105·0°±1° β 90·5 ±1° γ 108·5°±1°	D_m $1{\cdot}8_6$ D_x $1{\cdot}8_8$ (4)	Triclinic $P1$ (1) or Triclinic $P\bar{1}$ (2)
L13	$C_{11}H_{17}NBr_2$	Laths, elongated along [010] with (001) prominent	mmm	a 10·1 ±1 Å b 10·5 ±1 c 24·9 ±2	D_m $1{\cdot}5_8$ D_x $1{\cdot}6_1$ (8)	Orthorhombic $Pbca$ (61)
L17	$C_{15}H_{17}NBr_2$	Laths, elongated along [100] with (001) prominent	mmm	a 7·00±5 Å b 14·5 ±1 c 15·1 ±1	D_m $1{\cdot}6_0$ D_x $1{\cdot}6_2$ (4)	Orthorhombic $P2_1cn$ (33, non-standard setting) or Orthorhombic $Pmcn$ (62, non-standard setting)
L42	$C_{11}H_{17}NBr_2$	Laths, elongated along [100] with (010) prominent	$2/m$	a 7·45±5 Å b 17·1 ±1 c 9·0 ±1 β 96±1°	D_m $1{\cdot}8_3$ D_x $1{\cdot}8_6$ (4)	Monoclinic $P2_1/n$ (14, non-standard setting; b unique)
SM	$C_{11}H_{17}NBr_2$	Laths, elongated along [100] with (001) prominent	mmm	a 7·10±5 Å b 8·40±5 c 21·8 ±1	D_m $1{\cdot}6_0$ D_x $1{\cdot}6_4$ (4)	Orthorhombic $Pc2_1n$ (33, non-standard setting) or Orthorhombic $Pcmn$ (62, non-standard setting)
S2	$C_{10}H_{14}NBr_2Cl$	Laths, elongated along [100] with (001) prominent	mmm	a 7·10±5 Å b 8·40±5 c 21·8 ±2	D_m $1{\cdot}7_8$ D_x $1{\cdot}7_7$ (4)	Orthorhombic $Pc2_1n$ (33, non-standard setting) or Orthorhombic $Pcmn$ (62, non-standard setting)
S4	$C_{10}H_{13}NCl_4$	Laths, elongated along [100] with (001) prominent	mmm	a 6·95±5 Å b 8·25±5 c 25·6 ±2	D_m $1{\cdot}3_0$ D_x $1{\cdot}3_1$ (4)	Orthorhombic $Pc2_1n$ (33, non-standard setting) or Orthorhombic $Pcmn$ (62, non-standard setting)
S14	$C_{10}H_{14}NBr_3$	Laths, elongated along [010] with (001) prominent	$2/m$	a 8·50±5 Å b 7·35±5 c 21·0 ±2 β 98±1°	D_m $1{\cdot}9_6$ D_x $1{\cdot}9_8$ (4)	Monoclinic $P2_1/c$ (14, b unique)
S15	$C_{10}H_{14}NBr_2Cl$	Laths, elongated along [010] with (001) prominent	$2/m$	a 8·50±5 Å b 7·35±5 c 21·0 ±2 β 98±1°	D_m $1{\cdot}7_0$ D_x $1{\cdot}7_3$ (4)	Monoclinic $P2_1/c$ (14, b unique)

Table 2 (*cont.*)

Name	Molecular formula	Habit	Laue symmetry	Parameters	Densities in gm.cm.$^{-3}$	Space group
S1	$C_{10}H_{14}NCl_3$	Laths, elongated along [100] with (010) prominent	2/*m*	*a* 7·00 ± 5 Å *b* 37·5 ± 5 *c* 9·6 ± 1 *β* 92 ± 1°	D_m 1·3$_5$ D_x 1·3$_4$ (8)	Monoclinic *B*2$_1$ or Monoclinic *B*2$_1$/*m*
LT	$C_{12}H_{17}NOCl_2$	Laths, elongated along [100] with (010) prominent	2/*m*	*a* 7·00 ± 5 Å *b* 38·0 ± 5 *c* 9·6 ± 1 *β* 92 ± 1°	D_m 1·3$_7$ D_x 1·3$_6$ (8)	Monoclinic *B*2$_1$ or Monoclinic *B*2$_1$/*m*
L23	$C_{12}H_{17}NBr_2$	Laths, elongated along [100] with (001) prominent	*mmm*	*a* 7·35 ± 5 Å *b* 8·60 ± 5 *c* 10·4 ± 1	D_m 1·64 D_x 1·64 (2)	Orthorhombic *Pm*2$_1$*n* or *P*2$_1$*mn* (31) or Orthorhombic *Pmmn* (59)
R	$C_{15}H_{23}NBr_2$	Laths, elongated along [100] with (001) prominent	2/*m*	*a* 6·15 ± 5 Å *b* 24·0 ± 2 *c* 11·6 ± 1 *β* 108 ± 1°	D_m 1·6$_0$ D_x 1·6$_1$ (4)	Monoclinic *P*2$_1$/*c* (14, *b* unique)

* This denotes the value of Z, the number of molecules per unit cell for which D_x has been calculated.
† This denotes the number assigned to the space group in the International Tables on Crystallography.

flotation (Wulff & Heigl, 1931), with a mixture of benzene and carbon tetrachloride for crystals of densities in the range 1·0 to 1·6 g.cm^{-3}, or a mixture of carbon tetrachloride and bromoform for densities between 1·6 and 2·0 g.cm^{-3}. The densities were also calculated by means of the relation $D_x = ZMf/V$, where Z is the number of molecules per unit cell, M is the molecular weight of the compound, f is the mass of one gram atom and V is the volume of the unit cell.

Crystallographic data were derived from oscillation and Weissenberg photographs taken with Cu *Kα* radiation. For one compound only (the triclinic variety of AT3) precession photographs taken with Mo *Kα* radiation were used.

The chemical constitution and trivial names of the compounds studied are given in Table 1, and their crystallographic properties are recorded in Table 2.

Discussion

The compounds W and U are chemically similar, the Cl of W being replaced by Br in U. Both have a short axis of 5·5 Å in the unit cell, but the *b* and *c* axes of U are almost exactly twice those of W. This suggests that the conformation of the molecules is similar, but that the difference in molecular size produces different packing of the molecules in the *bc* plane and consequently different space groups.

The only iodo compound for which data are reported is AT3, two crystalline modifications of which were obtained. One of them yielded the only triclinic space group discovered amongst these substances; all the remainder were either monoclinic or orthorhombic.

Table 3 gives a list of certain features of nine chemically similar compounds of this group which may with advantage be compared.

Table 3. *Comparison of unit-cell dimensions*

Z is the number of molecules per unit cell.
In all these compounds, X is the halogen occurring both covalently bound in the *β* position with respect to the N atom and as the free anion. In some compounds, further halogen atoms occur elsewhere in the molecule.

Compound	Approximate cell dimensions (Å)	*Z*	X	
SM	7 × 8·5 × 21	4	Br	probably isomorphous
S2	7 × 8·5 × 21	4	Br	
S14	7 × 8·5 × 21	4	Br	probably isomorphous
S15	7 × 8·5 × 21	4	Br	
L42	7 × 9 × 17	4	Br	
L23	7 × 8·5 × 10	2	Br	
LT	7 × 9·5 × 40	8	Cl	probably not isomorphous
S1	7 × 9·5 × 40	8	Cl	
S4	7 × 8·5 × 26	4	Cl	

SM and S2, and S14 and S15 are probably isomorphous pairs, since not only do the members of each pair have identical parameters and space groups, but the patterns of the intensities of the X-ray reflexions as shown by Weissenberg photographs are also similar. The close chemical resemblance of each pair will probably allow of the formation of solid solutions and overgrowths, but this has not been checked. LT and S1, however, can hardly be truly isomorphous, although their parameters and space groups are identical, since chemically and in the pattern of their X-ray reflexions they are quite different.

L42 has a somewhat shorter *c* axis than SM *etc.* because it has no other atom or group substituted on to the benzene ring; S4 has a slightly longer *c* axis because unlike SM *etc.* it has two halogen atoms substituted on to the benzene ring.

It is virtually certain that there are strong similarities in the conformation and packing of all these molecules listed in Table 3. All have axes of approximately 7 Å and 9 Å with a c axis of 10, 20 or 40 Å depending upon whether there are 2, 4 or 8 molecules per unit cell, respectively. For those in monoclinic space groups, the β angle is never far from 90°.

L17 also has an axis of 7 Å but it is chemically quite different from the other compounds discussed above, and consequently its b and c axes are different.

The author is indebted to Mr R. G. Howells of the Department of Physics, University College, Cardiff, and to Professor D. Rogers of the Department of Chemical Crystallography, Imperial College, London for their advice, guidance and encouragement during the performance of this work.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1968). B**24**, 595

The crystal structure of tris-(2-dimethylaminoethyl)amine nickel(II) and copper(II) bromides.

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(*Received* 19 *October* 1967)

The crystal structures of Ni(Me$_6$tren)Br$_2$ and Cu(Me$_6$tren)Br$_2$ [Me$_6$tren = N{CH$_2$CH$_2$N(CH$_3$)$_2$}$_3$] have been determined by three-dimensional X-ray analysis and refined to final R values of 7·7% and 6·2% respectively. Crystals of the two complexes are cubic, space group $P2_13$, $a = 12{\cdot}123 \pm 0{\cdot}002$ and $a = 12{\cdot}137 \pm 0{\cdot}003$ Å for the nickel(II) and copper(II) compounds respectively, with four formula units per unit cell. The two structures consist of M(Me$_6$tren)Br$^+$ and Br$^-$ ions arranged in a distorted NaCl type arrangement. The coordination polyhedron about the metal atoms is a trigonal bipyramid with C_3 crystallographic symmetry. The structure is essentially identical with that of the corresponding cobalt compound.

Ciampolini & Nardi (1966*a*,*b*) have reported the preparation and the chemical properties of a series of five-coordinated high-spin complexes with general formula

$$\mathrm{M^{II}(Me_6tren)X_2},$$

where M$^{\mathrm{II}}$ = Cr, Mn, Fe, Co, Ni, Cu, Zn and Me$_6$tren = tris-(2-dimethylaminoethyl)amine, N{CH$_2$CH$_2$N(CH$_3$)$_2$}$_3$ and X = Cl, Br, I, NO$_3$ and ClO$_4$.

As a part of an X-ray structural investigation on the isomorphous series of the complex bromides, we have already reported in detail the structure of the cobalt(II) complex (Di Vaira & Orioli, 1967). We wish now to report the results of the X-ray analysis of the nickel(II) and copper(II) complexes. Since the experimental procedure has closely followed the lines of the structure determination of the cobalt(II) analogue only some significant different points will be mentioned here.

Crystals of the two compounds, kindly supplied by Dr Ciampolini, are tetrahedral in shape and belong to the space group $P2_13$. Cell dimensions, determined from Weissenberg photographs with the NaCl rotation pattern superimposed, are: $a = 12{\cdot}123 \pm 0{\cdot}002$ Å for the nickel(II) complex and $a = 12{\cdot}137 \pm 0{\cdot}003$ Å for the copper(II) complex; $Z = 4$. For Cu $K\alpha$ radiation $\mu = 73{\cdot}8$ and $75{\cdot}6$ cm^{-1} for the nickel(II) and copper(II) complexes respectively. The crystals selected for data collection had the shape of regular tetrahedra with edge about 0·25 mm.

A total of 443 independent reflexions were measured for the nickel(II) compound and 540 for the copper(II) compound.

Initial parameters for the atoms were taken from the last isotropic least-squares cycle of the structure of the cobalt(II) complex. After a few cycles of least-squares refinement with anisotropic temperature factors the final R values were 0·077 and 0·062 for the nickel(II) and copper(II) complexes respectively. Reduction of the intensities, structure factor calculations and least-squares refinement were performed at the C.N.U.C.E. in Pisa with programs written or adapted for the IBM 7090 by Stewart (1964). Table 1 reports the