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A Reinvestigation of the Crystal Structure of Acetylcholine Bromide

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A reinvestigation of the structure of acetylcholine bromide, $[C_7H_{16}O_2N]^+Br^-$, with X-ray diffraction intensities collected from two untwinned crystals has been carried out. The crystals are monoclinic, space group $P2_1/n$, with $a=10.966$ (4), $b=13.729$ (7), $c=7.159$ (4) Å, $\beta=108.18$ (7)°, $Z=4$. The structure was refined by full-matrix least-squares calculations with 1730 observed reflexions, and anisotropic temperature factors for all non-hydrogen atoms. The final R was 0.041. Atomic coordinates, thermal parameters, bond lengths and angles are compared with those from previous work on acetylcholine derivatives.

Introduction

An X-ray investigation of the structure of acetylcholine bromide was first reported by Sørum (1956, 1959). The structure was solved in space group $P2_1$ with two crystallographically different molecules in the asymmetric unit. From physiological considerations Canepa (1964) suggested that one of these molecular forms was incorrect, and Dunitz (1963), observing some unusual systematic absences, suggested that the crystal used was a twinned $P2_1/c$ rather than a single $P2_1$ specimen. Taking this into account, the structure was refined from the previous photographic intensities corrected for twinning by Canepa, Pauling & Sørum (1966), referred to hereafter as CPS, to a final R of 0.10. Because of the importance of acetylcholine as a synaptic transmitter, it seemed worth while to re-examine the structure with diffractometer data obtained from an untwinned crystal. It is also of interest to determine the positions of the H atoms.

Experimental

Crystal data

Crystals were kindly prepared by Dr T. Bruun of The Institute of Organic Chemistry of this University by recrystallization from acetone and HBr of a sample supplied from Koch-Light Laboratories Ltd. They are colourless and slightly hygroscopic. Weissenberg photographs of the $hk0$, $hk1$ and $hk3$ reciprocal-lattice planes showed none of the additional diffraction spots

reported by Sørum (1956). Crystallographic data based on observations for two such untwinned specimens are summarized below.

Acetylcholine bromide, $[C_7H_{16}O_2N]^+Br^-$; F.W. 226.12; monoclinic; $\lambda(Mo\ K\alpha)=0.71069$ Å; $\mu(Mo\ K\alpha)=42.106$ cm^{-1}. $a=10.966$ (4), $b=13.729$ (7), $c=7.159$ (4) Å, $\beta=108.18$ (7)°; $V=1024.2$ Å^3; $Z=4$. Systematic absences: $h0l$: $h+l=2n+1$; $0k0$: $k=2n+1$. Space group $P2_1/n$. $D_c=1.467$ g cm^{-3}.

Another choice of axes giving the space group $P2_1/c$ results in $a=11.069$ Å and $\beta=109.71°$, leaving b and c unchanged. These values may be compared with $a=11.057$, $b=13.690$, $c=7.153$ Å and $\beta=109.65°$ obtained by Hjortås (1966) and $a=11.10$, $b=13.67$, $c=7.18$ Å and $\beta=110°$ obtained by Sørum (1959). The cell dimensions found in the present work are mean values from repeated measurements for two crystals on an automatic diffractometer. The least-squares method was used to fit the settings for 12 high-angle reflexions. The estimated standard deviations are approximately 2.5 times larger than the e.s.d.'s from one measurement.

Data collection and processing

Intensities were collected for two plate-shaped crystals of dimensions $0.3 \times 0.3 \times 0.1$ mm and $0.3 \times 0.2 \times 0.15$ mm for specimen I and II respectively. As the crystals were hygroscopic they were mounted in glass capillaries with c approximately parallel to the φ axis of the goniometer. The crystal faces parallel to c were (110) planes. The intensities were collected on a Picker FACS-1 four-circle automatic diffractometer

with Zr-filtered Mo $K\alpha$ radiation and a scintillation counter. All measured reflexions were of the classes hkl and $\bar{h}kl$. The $\omega/2\theta$ scan mode was applied with a scan rate of $1°$ $\min^{-1}$ in 2θ and a basic scan width of $1\cdot2°$ determined from inspection of the mosaic spread in the crystals. The latter value was corrected for dispersion in order to determine the actual scan width. The counting rate was kept below approximately 10^4 c.p.s. by means of attenuators. The background intensity was measured for 40 s at each end of the scan.

For specimen I 2084 reflexions, excluding 113 systematically extinct and 471 unobserved $(I \le 2\sigma)$, were measured and used in the determination and first refinement of the structure. The reflexions 002 and 080 were selected as standards and measured after every 30 reflexions. The maximum value of 2θ was $60°$. For specimen II 1378 reflexions, excluding 75 systematically extinct and 200 unobserved, were measured, with 002, 080 and 112 as standards; the maximum value of 2θ was $50°$. The intensities of the standards diminished 3–4 % during the data collection.

The data were corrected for Lorentz and polarization factors by the program $XPROG\$$ (Borgen & Mestvedt, 1969). Correction for slight variations of the intensities of the standard reflexions was made relative to a polynomial of the nth degree determined by least-squares fit to the sum of the standards, and carried out by means of the program $STARD$ (Sivertsen, 1972a). The intensities were later corrected for absorption by a nonanalytical method (Coppens, 1970).

In the final stages of refinement the two sets of data were averaged as follows:

$$\bar{F}_H = (F_{\mathrm{I},H}/\sigma_{\mathrm{I},H}^2 + F_{\mathrm{II},H}/K\sigma_{\mathrm{II},H}^2)/[\sigma_{\mathrm{I},H}^{-2} + (K\sigma_{\mathrm{II},H})^{-2}],$$

$$\sigma(\bar{F}_H) = [\sigma_{\mathrm{I},H}^{-2} + (K\sigma_{\mathrm{II},H})^{-2}]^{-1/2},$$

$$K = \sum_H F_{\mathrm{I},H}/\sum_H F_{\mathrm{II},H},$$

by the program $FSTAT1$ (Sivertsen, 1972b). H denotes the reflexions hkl common to both sets of data, comprising 1378 reflexions. In addition 352 reflexions

measured for crystal I only were included. The scale factors were refined independently for these two groups of data.

Determination and refinement of the structure

The position of the Br atom was found from a sharpened origin-removed vector map. With initial values of the scale and temperature factors from a Wilson plot, a full-matrix least-squares refinement resulted in an R of $0\cdot34$ $(R = [\|F_o| - K|F_c\||]/\sum|F_o|)$, the function minimized being $\sum w(F_o - KF_c)^2$. The positions of the other non-hydrogen atoms were found from a difference map. Subsequent cycles of refinement with isotropic temperature factor and unit weight reduced R to $0\cdot133$, and the following refinement with anisotropic temperature factor gave $R = 0\cdot081$. Alternating difference maps and refinement revealed reasonable positions for all the H atoms and gave $R = 0\cdot066$. At this stage the absorption correction was introduced, the absorption coefficient A^* ranging from $2\cdot13$ to $2\cdot90$, and $F_{\mathrm{corr}} = (A^*)^{1/2}F_o$. R decreased to $0\cdot060$. Because of unreasonable bond lengths and angles, the positions of H(21), H(22), H(42), H(43), H(61) and H(62), as indicated in Fig. 1, were calculated from the tetrahedral angle and a C–H distance of 1 Å. Refinement of all parameters gave $R = 0\cdot055$. Weights equal to $w = (\sigma^2 + cF_o^2)^{-1/2}$ were introduced ascribing c the value of $0\cdot0003$ from the condition that $w(|F_o| - |F_c|)^2$ should be constant within intervals of increasing $|F_o|$. R remained unchanged whereas $R_w = [\sum w(|F_o| - K|F_c|)^2/\sum w F_o^2]^{1/2}$, the sums being taken over all reflexions, was $0\cdot044$. The reflexions in the range $50° < 2\theta \le 60°$, being measured for crystal I only, and all very weak, were removed, giving the final R based on data from crystal I as $0\cdot042$, while $R_w = 0\cdot039$. No significant shifts in bond lengths and angles were observed. Inclusion of the data from specimen II, as mentioned above, gave $R = 0\cdot041$ and $R_w = 0\cdot038$, c in the weight factor expression now being $0\cdot00025$. The shifts in the last cycle of least-squares refinement were less than $0\cdot2\sigma$. The unobserved reflex-

Table 1. *Final atomic parameters of acetylcholine bromide*

The positional parameters of the non-hydrogen atoms have been multiplied by 10^4, and those for the hydrogen atoms by 10^3. Thermal parameters, U_{ij} ($\times 10^4$), as given here, are defined by:

$$\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)].$$

Estimated standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br$^-$	2857·8 (3)	6179·2 (3)	6458·1 (6)	458 (3)	630 (3)	570 (3)	132 (2)	227 (2)	64 (2)
N	5052 (2)	3478 (2)	7560 (4)	306 (14)	341 (13)	429 (16)	−10 (11)	143 (13)	−18 (12)
O(1)	5071 (2)	1387 (2)	5590 (4)	432 (13)	463 (13)	528 (15)	−13 (10)	187 (13)	−93 (11)
O(2)	7126 (3)	1002 (2)	6030 (4)	514 (17)	770 (18)	610 (17)	248 (14)	219 (15)	51 (15)
C(1)	4234 (4)	3462 (3)	5452 (6)	401 (20)	527 (22)	482 (23)	5 (19)	65 (19)	4 (19)
C(2)	4217 (4)	3485 (3)	8864 (7)	439 (21)	457 (21)	680 (29)	−21 (18)	326 (23)	−62 (20)
C(3)	5837 (4)	4395 (3)	7926 (7)	474 (23)	423 (21)	529 (26)	−96 (17)	196 (23)	−59 (18)
C(4)	5983 (3)	2633 (2)	8065 (6)	339 (19)	437 (18)	385 (20)	48 (14)	138 (18)	−7 (15)
C(5)	5409 (4)	1633 (3)	7662 (5)	478 (21)	438 (19)	490 (22)	6 (17)	255 (19)	−3 (17)
C(6)	6059 (4)	1101 (2)	4953 (6)	535 (23)	347 (17)	540 (22)	68 (16)	261 (20)	12 (16)
C(7)	5633 (5)	968 (3)	2783 (7)	754 (33)	610 (27)	541 (26)	−5 (23)	233 (26)	−119 (21)

Table 1 (cont.)

	x	y	z	$B \times 10$ (Å²)
H(11)	372 (3)	293 (2)	522 (5)	36 (8)
H(12)	479 (3)	343 (2)	469 (5)	30 (6)
H(13)	368 (4)	404 (3)	517 (6)	50 (9)
H(21)	372 (3)	293 (3)	862 (6)	42 (8)
H(22)	479 (4)	351 (3)	26 (8)	63 (11)
H(23)	371 (4)	407 (3)	857 (6)	47 (9)
H(31)	634 (3)	436 (2)	712 (4)	21 (6)
H(32)	634 (3)	440 (2)	926 (5)	30 (7)
H(33)	518 (3)	494 (3)	758 (4)	39 (8)
H(41)	657 (3)	274 (2)	738 (5)	28 (6)
H(42)	641 (3)	271 (2)	941 (5)	22 (6)
H(51)	462 (3)	155 (2)	797 (5)	25 (6)
H(52)	607 (3)	114 (2)	845 (5)	27 (6)
H(71)	474 (5)	87 (3)	221 (8)	73 (13)
H(72)	609 (4)	44 (3)	233 (7)	67 (11)
H(73)	583 (4)	159 (4)	223 (7)	77 (13)

ions were given zero weight throughout the refinement. Scattering factors for Br⁻, C, N and O were those given by Doyle & Turner (1968), and for H by Stewart, Davidson & Simpson (1965). Anomalous dispersion correction was applied for Br⁻, the $\Delta f'$ and $\Delta f''$ values being those given by Cromer & Liberman (1970). All calculations were made by means of the X-RAY72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).*

Results and discussion

Fractional coordinates and thermal parameters are given in Table 1, and a projection of the molecule with bond lengths and angles is shown in Fig. 1. Fig. 2 shows the molecular packing. A comparison of bond lengths and angles for five different works on acetylcholine is given in Table 2.

Thermal motion

A least-squares rigid-body analysis of the molecule (Schomaker & Trueblood, 1968) gave $\langle U_{ij,c} - U_{ij,o} \rangle = 0.0057$ Å² where $\langle \rangle$ denotes the mean value. $U_{ij,c}$ are the vibrational parameters calculated from the $\mathbf{L}$, ω and $\mathbf{s}$ tensors, and $U_{ij,o}$ are the observed vibrational parameters. The standard deviations are $\langle \sigma(U_{ij,c}) \rangle = 0.0068$ and $\langle \sigma(U_{ij,o}) \rangle = 0.0017$. The translational motion is approximately 0.2 Å and nearly isotropic. The librational motions are 1.9, 4.2 and 2.4° relative to the axes through the molecular centre of gravity and par-

allel to $\mathbf{b} \times \mathbf{c}^*$, $\mathbf{b}$ and $\mathbf{c}^*$ respectively. A correction of bond lengths (Cruickshank, 1956) gave shifts of ~ 0.005 Å. As this is within the standard deviations of the bond lengths, it has not been included in the values given in Table 2. The 'minimum correction' of Busing & Levy (1964) gave shifts of ~ 0.002 Å. The programs used for these calculations were TERMVIB2 and KORREKS (Evensen, 1970) and RIDEX (Svinning, 1974).

Bond lengths and angles

As to the results given for comparison in Table 2, it should be noted that the values obtained by Marzotto, Graziani, Bombieri & Forsellini (1974) for bis(acetylcholine)tetrabromodioxouranium refer to a disordered structure, while CPS's results were based on photographic data for a twinned crystal. The most significant

Table 2. *Molecular parameters of acetylcholine from five different works*

E.s.d.'s for the column headed SS are given in parentheses. E.s.d.'s for the columns HS and MS are (1) for bond lengths and (1) for angles. For values in the column MGBF the e.s.d.'s are from (4) to (8) for the bond lengths and from (2) to (5) for the angles. Bond lengths are in Å, angles in degrees.

	CPS*	HS†	MS‡	MGBF§	SS‖
R	0·10	0·071	0·088	0·087	0·041
N——C(1)	1·50	1·50	1·49	1·49	1·496 (5)
N——C(2)	1·52	1·49	1·49	1·50	1·498 (6)
N——C(3)	1·52	1·52	1·51	1·52	1·502 (4)
N——C(4)	1·54	1·49	1·52	1·54¶	1·513 (4)
C(4)—C(5)	1·52	1·47	1·47	1·50¶	1·500 (5)
C(5)—O(1)	1·50	1·45	1·43	1·48¶	1·452 (5)
C(6)—O(1)	1·32	1·38	1·38	1·36	1·358 (5)
C(6)—O(2)	1·25	1·18	1·20	1·22	1·192 (4)
C(6)—C(7)	1·55	1·49	1·51	1·50	1·487 (6)
N——O(1)	3·29	3·26	3·13	3·14	3·201 (4)
C(1)—O(1)	3·02	3·17	3·00	2·96	2·985 (5)
H(11)-O(1)					2·56 (3)
C(1)—N——C(2)	106	109	111	103	109·8 (3)
C(1)—N——C(3)		111	110	109	108·6 (3)
C(1)—N——C(4)	111	111	109	111¶	112·2 (3)
C(2)—N——C(3)	109	108	107	108	108·3 (3)
C(2)—N——C(4)		111	112	111¶	110·7 (3)
C(3)—N——C(4)	109	107	108	112¶	107·1 (2)
N——C(4)-C(5)	118	119	119	112¶	116·4 (3)
C(4)—C(5)-O(1)	113	111	109	103¶	111·6 (3)
C(5)—O(1)-C(6)	115	115	115	121¶	115·7 (3)
O(1)—C(6)-C(7)	110	108	111	113	111·3 (3)
O(1)—C(6)-O(2)	124	123	121	118	122·8 (4)
C(7)—C(6)-O(2)	126	129	128	128	125·9 (4)

* Canepa, Pauling & Sørum (1966): bromide.
† Herdklotz & Sass (1970): chloride.
‡ Mahajan & Sass (1974): perchlorate.
§ Marzotto, Graziani, Bombieri & Forsellini (1974): bis-tetrabromodioxouranium.
‖ Present work.
¶ Mean values for a disordered structure.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30891 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Least-squares planes of the acetylcholine molecule*

x, y, z are orthogonal axes of length 1 Å parallel to $\mathbf{a}$, $\mathbf{a} \times \mathbf{b}$ and $\mathbf{a} \times \mathbf{c}$.

I	C(5)–O(1)–C(6)–O(2)–C(7)	$0·2727x + 0·9504y - 0·1498z = 2·4634$
II	C(3)–N–C(4)–C(5)	$-0·3499x - 0·0060y + 0·9368z = 3·4175$
III	O(1)–C(5)–C(1)–N	$0·9631x + 0·2266y - 0·1456z = 3·9319$

Table 3 (*cont.*)

Deviations (Å) from least-squares planes

	I	II	III
N		0·021	0·112
O(1)	−0·046		0·100
O(2)	−0·005		
C(1)			−0·095
C(3)		−0·026	
C(4)		0·032	
C(5)	0·039	−0·028	−0·117
C(6)	−0·020		
C(7)	0·033		

difference between the bond lengths for acetylcholine chloride (Herdklotz & Sass, 1970) and those from the present work is 0·03 Å (~2σ) for C(4)–C(5). The same applies also to a comparison with the structure of acetylcholine perchlorate (Mahajan & Sass, 1974).

The strained N–(CH₃) bonds have a mean value of 1·499 Å compared with the usual value of 1·479 Å (Kennard *et al.*, 1972) for a four-covalent N–C bond. The C(5)–O(1), C(6)–O(1) and C(6)–O(2) lengths of 1·452, 1·358 and 1·192 Å respectively, correspond to normal single, partial double and double bonds. The last value is slightly shorter than that expected for a C=O double bond, *i.e.* 1·23 Å, but in good agreement with values obtained by Jones & Karle (1974), *i.e.* 1·188 Å for 19*R*-methoxy-5,19-methyleneoxido-17β-acetoxy-5β-androstan-3-one and by Oberhänsli, Wagner & Isler (1974), *i.e.* 1·183 Å in vitamin-A acetate. The shortening of the C(4)–C(5) and C(6)–C(7) lengths may be due to the presence of one and two neighbouring partial double bonds respectively. The largest deviation of the bond lengths in the acetyl group from those of Jones & Karle (1974) is 0·036 Å for C(6)–C(7) and from those of Oberhänsli *et al.* (1974) 0·031 Å for C(6)–O(1), the angles at C(6) agreeing to within 0·6°. The mean value of the tetrahedral angles not involving H atoms is 112·48°, and of the C–H lengths 0·96 (4) Å.

Molecular structure and packing

There are some differences in the values of the important intramolecular atomic distances N–O(1) and C(1)–O(1), the most significant being that between the value of 2·985 Å of this work and the value 3·17 Å obtained for acetylcholine chloride by Herdklotz & Sass for C(1)–O(1). Both distances are in this work found to be a little shorter than those reported by CPS. The nature of the C–H···O 'hydrogen bond' proposed by CPS is discussed in some detail by Donohue (1968). The parameters involved in that connexion are the distance O(1)–H(11) of 2·56 Å, the angles O(1)–H(11)–C(1) of 110° and O(1)–C(1)–H(11) of 53°. The torsional angles in the ring structure N–C(1)–H(11)–O(1)–C(5)–C(4)–N are, in the same order, found to be 65, 66, 76, 57, 78 and 56° respectively, the ring being of the chair conformation. The torsional angles of the chain are in Table 4 compared with the corresponding angles of acetylcholine chloride and acetylcholine perchlorate, and confirm the *gauche–gauche* conformation as stated

by CPS. The equations of least-squares planes, as suggested by CPS, and the deviations of the atoms from these planes are given in Table 3. The deviations are fairly small for planes I and II, but considerably larger for plane III. It may, however, be shown by the method of Stout & Jensen (1968) that none of the groups of atoms is planar even at a significance level of 0·5%.
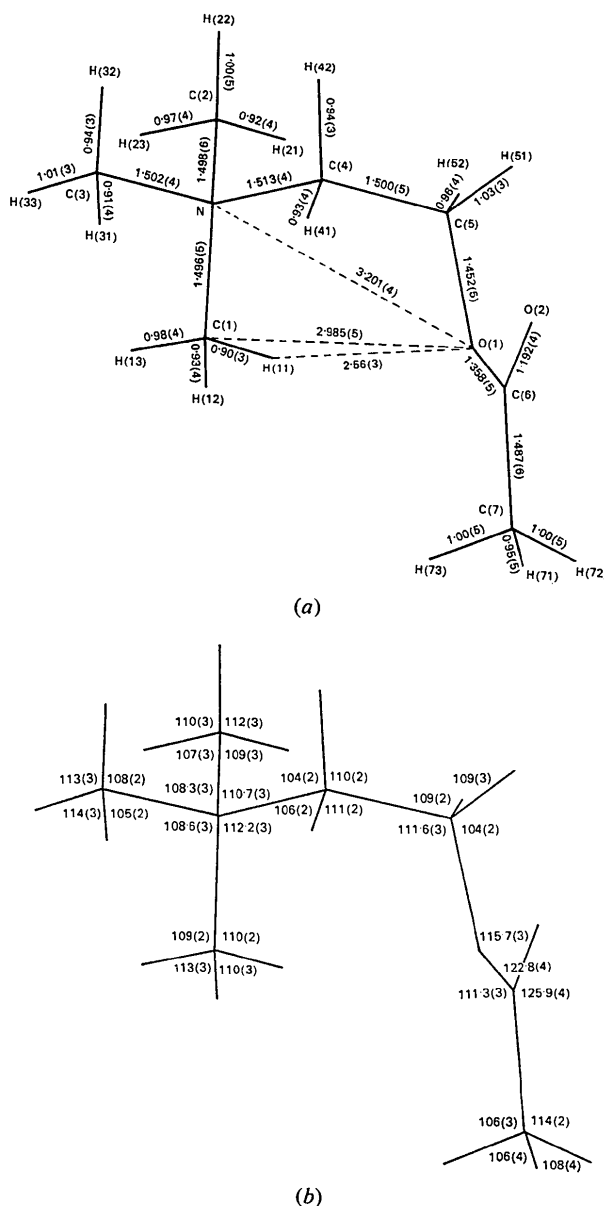

Fig. 1. The acetylcholine molecule as viewed along the *a* axis. Bond lengths are in Å, angles in °. Estimated standard deviations are in parentheses. C(1)–N–C(2) 109·8 (3), C(3)–N–C(4) 107·1 (2), N–C(1)–H(12) 107 (2), H(11)–C(1)–H(13) 107 (3), N–C(2)–H(22) 108 (3), H(21)–C(2)–H(23) 112 (3), N–C(3)–H(33) 104 (2), H(31)–C(3)–H(32) 111 (3), N–C(4)–C(5) 116·4 (3), H(41)–C(4)–H(42) 109 (3), C(4)–C(5)–H(51) 115 (2), O(1)–C(5)–H(52) 109 (2), C(6)–C(7)–H(71) 115 (4), H(72)–C(7)–H(73) 108 (4).

Table 4. *Torsional angles in the chain of acetylcholine* (°)

	Bromide	Chloride	Perchlorate
C(3)–N——C(4)–C(5)	175·49	171·4	168·3
N——C(4)–C(5)–O(1)	78·44	84·7	73·7
C(4)–C(5)–O(1)–C(6)	78·90	−166·9	179·8
C(5)–O(1)–C(6)–O(2)	4·10	5·2	0·8

The molecules in acetylcholine bromide are packed in layers normal to **b**. There are four important intermolecular contacts between successive layers, one $Br^- \cdots H(72)$ and three between O(2) and $CH_3(3)$. Within the same layer there are, as may be seen from Table 5, some fairly short contacts of the types $Br^- \cdots H$, $C \cdots O$, $C \cdots H$ and $O \cdots H$.

Table 5. *Intermolecular distances* (Å) *less than* 0·2 Å + *sum of van der Waals radii**

The symmetry transformations of the second atom are:

i	x	y	$z+1$	vii	$x+\frac{1}{2}$	$-y+\frac{1}{2}$	$z+\frac{1}{2}$
iv	$-x+1$	$-y+1$	$-z+2$	viii	$x+\frac{1}{2}$	$-y+\frac{1}{2}$	$z-\frac{1}{2}$
v	$-x+1$	$-y+1$	$-z+1$	xii	$-x+1\frac{1}{2}$	$y-\frac{1}{2}$	$-z+1\frac{1}{2}$

H(12)	v	Br⁻	2·99		O(2)	viii	C(2)	2·83
H(22)	iv	Br⁻	2·93		O(2)	xii	C(3)	3·06
H(31)	v	Br⁻	3·05		O(2)	viii	H(23)	2·83
H(32)	iv	Br⁻	3·02		O(2)	xii	H(31)	2·88
H(42)	iv	Br⁻	3·20		O(2)	xii	H(33)	2·81
H(72)	viii	Br⁻	3·13		C(4)	vii	H(11)	3·02
O(2)	vii	C(1)	3·37		C(5)	i	H(73)	3·16

* Kitaigorodskii (1961, 1973).

This work has been carried out as part of the requirements for a degree (T.S.) of this University.

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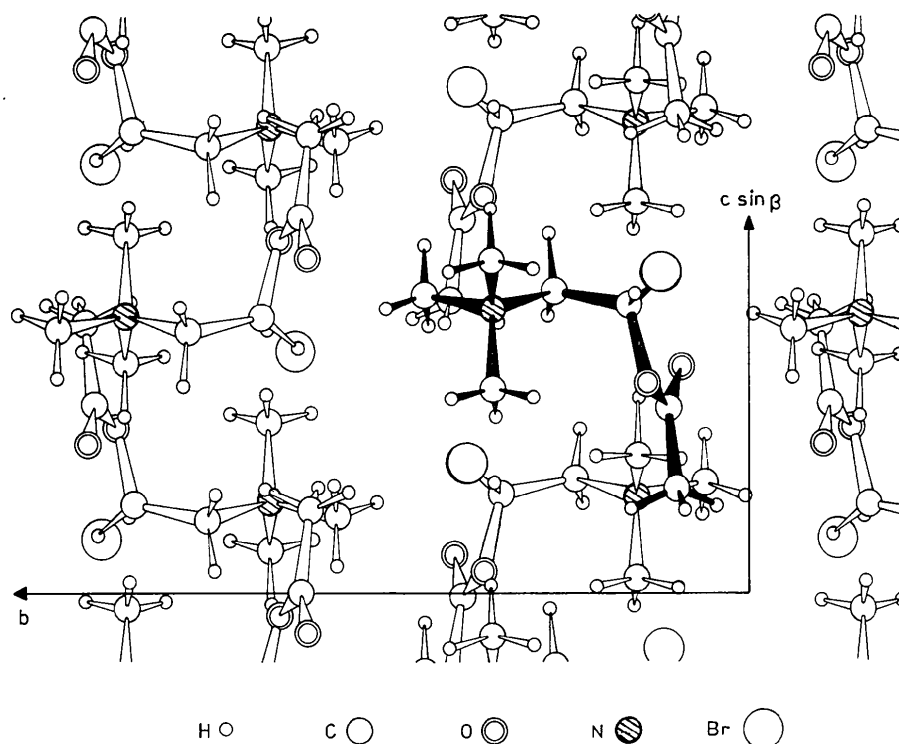
H ○   C ◯   O ◎   N ⊛   Br ◯

Fig. 2. Molecular packing of acetylcholine bromide as viewed along the *a* axis.

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Comparison of the Results of Two Independent Analyses of the Ethylchlorophyllide A Dihydrate Crystal Structure

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The results of the authors' crystal structure analysis of ethylchlorophyllide A dihydrate are compared with those obtained by Chow, Serlin & Strouse [*J. Amer. Chem. Soc.* In the press]. The agreement between the two sets of positional parameters (except those of the Mg atom) is excellent, as judged by a normal probability plot analysis. However, there appear to be significant differences between the vibrational parameters. Some problems connected with the choice of origin in polar space groups are mentioned.

In the course of a systematic study of chlorophyll derivatives we have determined the crystal structure of ethylchlorophyllide A dihydrate (Fig. 1). The same crystal structure has recently been described elsewhere (Strouse, 1974; Chow, Serlin & Strouse, 1975, here-after CSS). The opportunity to compare the results of two independent structure analyses, based on experimental data measured under different conditions, does not often occur for a molecule of this complexity. The results of such a comparison may therefore be of interest.

Table 1. *Comparison of measurement conditions and some crystallographic data for the two analyses*

	This analysis	Chow, Serlin & Strouse (1975)
Crystals grown from	acetone/water	acetone/water
Diffractometer	Hilger–Watts Y290	Syntex $P\bar{1}$
Size of crystal specimen used for data collection	$0\cdot4 \times 0\cdot3 \times 0\cdot07$ mm	$0\cdot12 \times 0\cdot12 \times 0\cdot05$ mm
Crystallographic data (cell constants from diffractometer measurements	$a = 8\cdot87$ (1) Å	$a = 8\cdot852$ (1) Å
	$c = 38\cdot05$ (3)	$b = 38\cdot087$ (5)
	space group $P3_1$	space group $P3_1$
Radiation used (monochromatized)	Mo $K\alpha$, $\lambda = 0\cdot71069$ Å	Cu $K\alpha$, $\lambda = 1\cdot5405$ Å
	$\mu = 1\cdot14$ cm^{-1}	$\mu = 9\cdot65$ cm^{-1}
Scan mode	ω	$\omega/2\theta$
Approximate $\sin\theta/\lambda$ limit	$0\cdot55$ Å^{-1}	$0\cdot63$ Å^{-1}
Number of reflexions included in refinement	2185	1919
Absorption correction	No	Yes
Number of parameters refined in the last cycles	325	452
Function minimized in least-squares refinement $\sum\omega\|\|F_o\| - \|F_c\|\|^2$ where	$\omega = \exp(r \sin^2\theta/\lambda^2)$ $r = 6$ Å^2	$\omega = 1/\sigma^2$ (F_o)
Final R	$0\cdot048$	$0\cdot05$