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The Crystal Structure of Acetylcholine Iodide

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Acetylcholine iodide [$C_7H_{16}NO_2I$, $M_r = 273{\cdot}1$. Superposition structure: tetragonal, $A = B = 8{\cdot}255$ (1), $c = 31{\cdot}443$ (8) Å, $U = 2143$ Å^3, $Z = 8$, $D_m = 1{\cdot}700$, $D_c = 1{\cdot}693$ g cm^{-3}] crystallizes with a disordered (OD) structure. One MDO structure has been determined from single-crystal X-ray diffractometer data and refined to $R = 0{\cdot}048$ for 2217 reflexions. The environments of all acetylcholine ions are essentially equal. The conformation of the acetylcholine ion is *gauche–gauche*.

Introduction

Acetylcholine iodide crystallizes as colourless rectangular plates. These show no anisotropy when examined in polarized light and preliminary examination by X-ray techniques revealed that the structure is disordered. Choline esters have been found to adopt different conformations in a number of different salts, and different conformers even coexist in some salts. The conformations of the acetylcholine ions in acetylcholine iodide crystals might thus change with the change in environment caused by the disorder; the present investigation was undertaken as a part of conformational studies of choline esters in the solid state.

OD structure

Crystals of acetylcholine iodide showed discrete reflexions for $A = B = 8{\cdot}255$, $c = 31{\cdot}443$ Å and more or less diffuse streaks for $a = b = 16{\cdot}510$, $c = 31{\cdot}443$ Å. Acetylcholine iodide thus crystallizes with a disordered crystal structure of OD type (Dornberger-Schiff, 1966), *i.e.* a structure which consists of ordered, equivalent layers whose mode of stacking is disordered. The conditions limiting possible reflexion may be summarized as (i) discrete reflexions, hkl, for $h = 2H$, $k = 2K$; diffuse streaks, $hk\zeta$, for $h = 2H + 1$, $k = 2K + 1$, where ζ can take any value; (ii) HKl: $H + K + l = 2n$; (iii) hkl: $h + k = 2n$; (iv) hkl: $\pm(h \pm k) + 2l = 4n$; (v) $hk0$: $h = 2n$ ($k = 2n$), where hkl reflexions refer to the cell with dimensions $a = b = 16{\cdot}510$, $c = 31{\cdot}443$ Å.

From reflexion conditions (i) and (ii) it is apparent that the superposition structure, corresponding to the family reflexions, HKl, has $A = B = \frac{1}{2} \times 16{\cdot}510$, $c = 31{\cdot}443$ Å and belongs to space group $I4$, $I\bar{4}$ or $I4/m$. Reflexion condition (v), which is independent of the mode of stacking of the layers, indicates the presence of a and b glide planes in each ordered layer, while reflexion condition (iii) shows that the real structure is C face-centred.

That the streaks were weak and that the maxima on them obeyed reflexion condition (iv) in the form hkl: $\pm(h - k) + 2l = 4n$ indicated that the crystal investigated had a structure closely approaching that of one of the ordered extreme forms (structure of maximum degree of order, MDO). Successive layers in this MDO structure must thus be related by the translation $\mathbf{a}/4 - \mathbf{b}/4 + \mathbf{c}_0$ (or $\mathbf{b}/4 - \mathbf{a}/4 + \mathbf{c}_0$), where $\mathbf{c}_0$ is the unit vector perpendicular to the layers in the direction of non-periodicity and $c_0 = c/2$.

If the MDO structure is described in terms of the primitive cell $\mathbf{a} = (\mathbf{a}_c + \mathbf{b}_c)/2$, $\mathbf{b} = (\mathbf{b}_c - \mathbf{a}_c)/2$, $\mathbf{c} = \mathbf{c}_c$, where $\mathbf{a}_c$, $\mathbf{b}_c$ and $\mathbf{c}_c$ refer to the C face-centred cell, the layer symmetry can be formulated

$$P \quad 1 \quad 1 \left(\frac{4}{n}\right) \quad 1 \quad 1.$$

Successive layers are then related by the translation $\mathbf{b}/2 + \mathbf{c}_0$. It is thus apparent that acetylcholine iodide crystallizes as a family of structures characterized by the OD groupoid symbol (Dornberger-Schiff, 1966):

$$\begin{array}{c} P \quad 1 \quad 1 \left(\dfrac{4}{n}\right) \quad 1 \quad 1 \\ \left[\begin{array}{c} 1 \quad 1 \left(\begin{array}{c} \bar{4} \\ 4_4 \\ 2_2 \\ \hline n_{r,s} \end{array}\right) 1 \quad 1 \end{array}\right] \end{array}$$

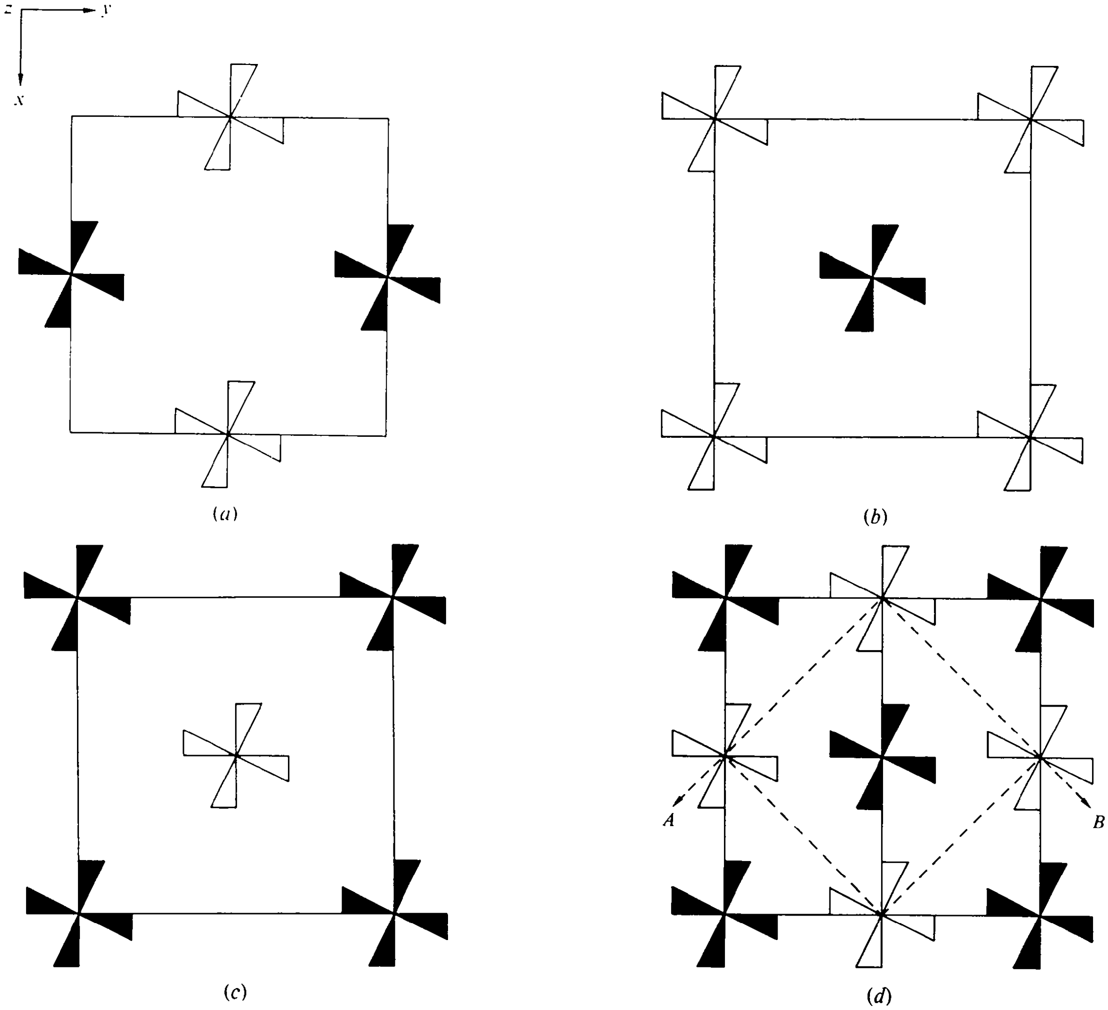

Fig. 1. Schematic representation of the symmetry elements in (*a*) layer L_0, (*b*) layer L_1, (*c*) layer L'_1 and (*d*) the superposition structure. The diagrams refer to the primitive unit cell (a b 11·674, c 31·443 Å). The unit cell of the superposition structure is indicated with dotted lines in (*d*). Notation: (*a*) empty triangles: z, filled triangles: $-z$; (*b*), (*c*) empty triangles: $\frac{1}{2}+z$, filled triangles: $\frac{1}{2}-z$; (*d*) empty triangles: $\pm z$; filled triangles: $\frac{1}{2}\pm z$.

This symbol gives the total symmetry of any pair of consecutive layers, *i.e.* the partial symmetry operations within a layer and those which convert any given layer into the next. These symmetry elements are illustrated in Fig. 1(*a*–*d*).

The two possible MDO structures can be seen to arise from two different sets of values for the components (r,s) of the n glide converting one layer into the next. If $r = 1$ and $s = 0$, the partial symmetry operations converting a given layer, L_0, into the next layer, L_1, are (see Fig. 1*a*, *b*):

$$\left[\begin{array}{ccccc} 1 & 1 & \left(\begin{array}{c}\bar{4}\\ 4_4\\ 2_2\\ \hline a\end{array}\right) & 1 & 1\end{array}\right]_{0,1}.$$

Repetition of the a glide, *i.e.* the stacking sequence $L_0L_1L_0$ ..., leads to the ordered extreme structure (MDO_1) approached by the crystal investigated. If, on the other hand, $r = 0$ and $s = 1$, the partial symmetry operations converting L_0 into L'_1 are (see Fig. 1*a*, *c*):

$$\left[\begin{array}{ccccc} 1 & 1 & \left(\begin{array}{c}\bar{4}\\ 4_4\\ 2_2\\ \hline b\end{array}\right) & 1 & 1\end{array}\right]_{0,1}.$$

The MDO_2 structure is thus obtained by repetition of the b glide, *i.e.* the stacking sequence $L_0L'_1L_0$.... This structure would give rise to maxima on the streaks corresponding to hkl: $h + l = 2n$ (primitive cell) or $\pm(h + k) + 2l = 4n$ (C-centred cell). In principle each crystal of acetylcholine iodide can exhibit a different stacking sequence and can thus be described in terms of larger or smaller contributions from the different MDO structures.

The fictitious superposition structure $\hat{\rho}(x,y,z)$, which is related to the real structure (primitive cell) by $\hat{\rho}(x,y,z) = \frac{1}{2}[\rho(x,y,z) + \rho(x+\frac{1}{2}, y+\frac{1}{2}, z)]$, is seen to belong to space group $I4/m$ (Fig. 1*d*).

Experimental

Crystal data

$C_7H_{16}NO_2I$, $M_r = 273{\cdot}1$, m.p. 162·3 °C. Superposition structure: tetragonal, $A = B = 8{\cdot}255$ (1), $c = 31{\cdot}443$ (8) Å, $U = 2143$ Å^3, $Z = 8$, $D_m = 1{\cdot}700$ (by flotation), $D_c = 1{\cdot}693$ g cm^{-3}, $\mu[\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å$] = 29{\cdot}0$ cm^{-1}. The unit-cell parameters were refined by least-squares techniques from diffractometer-measured 2θ angles for 37 independent reflexions. The melting point was determined on a Leitz hot-stage microscope.

Acetylcholine iodide (Fluka) was recrystallized by slow evaporation of an ethanolic solution containing about 10% water. The crystals grow as colourless rectangular plates, most of which show no anisotropy when examined in polarized light.

Preliminary X-ray investigations were performed for a number of crystals showing different patterns for the non-family reflexions. Finally a crystal 0·2 × 0·2 × 0·1 mm was mounted along **b** and the intensities of the family (HKl) and of the non-family reflexions at the reciprocal-lattice points corresponding to the MDO_1 structure were measured on a Nonius three-circle automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the ω scan technique. One standard reflexion was measured after every 40 reflexions. Data were collected in the range $2{\cdot}5 \le \theta \le 25{\cdot}0°$. The background–peak–background method was used for all reflexions as the intensity of the streaks was extremely low for the crystal used. Of the 2914 reflexions measured, 2217 (1605 family and 612 non-family) had $I_{\text{net}} \ge 3{\cdot}0\sigma(I)$, where $\sigma(I)$ is the standard deviation from counting statistics, and were regarded as observed. The non-family reflexions were given a separate scale factor. Because of instrumental difficulties during the data collection, the family reflexions were divided into two scale groups. No correction was applied for absorption.

Determination and refinement of the structure

The main features of the superposition structure were solved by the heavy-atom method from the family reflexions only. The Patterson map showed the I^- ions in two fourfold special positions. The approximate positions of the atoms of the acetylcholine ion, some of them superimposed on each other, could be deduced from an electron density map phased on the contributions from the I^- ions. Isotropic refinement of the superposition structure gave an R of 0·08 for the family reflexions.

Packing considerations together with the conditions limiting possible reflexions gave the clue to the solution of the MDO structure. Of the sixteen equivalent positions in space group $I4/m$, eight constitute a layer around $z = 0$ (and the remaining eight a layer around $z = \frac{1}{2}$). Only four of the eight positions in a layer can be occupied in a given unit ($A = B = 8{\cdot}255$ Å). For instance, occupation of x,y,z precludes occupation of $x,y,\bar{z}$, as the z value of one C atom is very close to zero. The four positions unoccupied in one unit will be occupied in the neighbouring unit. The 16 equipoints within a layer (based on the unit with $a = b = 16{\cdot}51$ Å) are then $(0,0,0;\ \frac{1}{2},\frac{1}{2},0) + (\pm x,\pm y,z;\ \frac{1}{2}\pm y,\ \mp x,\ -z;\ \pm y,\mp x,z;\ \pm x,\ \frac{1}{2}\pm y,\ -z)$ and the adjacent layer of the MDO structure is obtained by the translation $(\frac{1}{4},-\frac{1}{4},\frac{1}{2})$ of these equipoints. Difference maps indicated that the

Table 1. *Final positional and thermal* (Å^2 × 10^2) *parameters with estimated standard deviations referring to the last figure in parentheses*

The coordinates refer to the unit cell with dimensions $a = b = 16{\cdot}510$, $c = 31{\cdot}443$ Å.

	x	y	z	$U_{11} = U_{22}$	U_{33}
$I^-(11)$	0·0	0·0	0·10051 (4)	4·10 (5)	5·35 (6)
$I^-(12)$	0·5	0·0	0·09239 (4)	4·01 (5)	4·96 (6)
$I^-(21)$	0·0	0·0	0·27070 (3)	5·16 (6)	4·39 (6)
$I^-(22)$	0·5	0·0	0·26801 (3)	5·20 (6)	4·76 (6)

	x	y	z	U
C(1)	0·1574 (6)	0·0810 (6)	0·0016 (4)	6·3 (2)
C(2)	0·1870 (6)	0·1220 (6)	0·0403 (3)	5·0 (2)
O(3)	0·1636 (5)	0·1852 (5)	0·0547 (2)	6·8 (2)
O(4)	0·2459 (4)	0·0779 (4)	0·0602 (2)	4·5 (2)
C(5)	0·2787 (6)	0·1121 (7)	0·0984 (3)	5·0 (3)
C(6)	0·2261 (6)	0·0931 (6)	0·1361 (3)	4·4 (2)
N(7)	0·2450 (5)	0·0140 (5)	0·1593 (2)	3·6 (2)
C(8)	0·2460 (7)	−0·0547 (7)	0·1280 (3)	5·0 (3)
C(9)	0·3252 (7)	0·0194 (7)	0·1828 (3)	5·0 (2)
C(10)	0·1804 (7)	0·0031 (7)	0·1919 (3)	5·4 (3)
H(11)	0·186	0·050	−0·0183	
H(12)	0·112	0·043	0·0097	
H(13)	0·134	0·135	−0·0132	
H(51)	0·334	0·089	0·1033	
H(52)	0·282	0·172	0·0949	
H(61)	0·232	0·138	0·1569	
H(62)	0·169	0·090	0·1260	
H(81)	0·192	−0·060	0·1139	
H(82)	0·288	−0·045	0·1058	
H(83)	0·258	−0·107	0·1431	
H(91)	0·370	0·030	0·1616	
H(92)	0·323	0·064	0·2039	
H(93)	0·338	−0·033	0·1979	
H(101)	0·180	0·050	0·2124	
H(102)	0·126	−0·000	0·1779	
H(103)	0·192	−0·048	0·2072	

positions of the I^- ions were affected by the disorder, and four independent I^- ions had to be introduced in the calculations. After refinement of the MDO structure with the non-family reflexions only, the positions of all H atoms could be deduced from a difference map based on all observed reflexions for which $\sin \theta/\lambda \leq 0{\cdot}35$ Å^{-1}. The final full-matrix least-squares refinement based on all observed reflexions included three scale factors (two for the family and one for the non-family reflexions), and the positional parameters for all non-hydrogen atoms, the individual isotropic thermal parameters for the C, N and O atoms and individual anisotropic thermal parameters for the I^- ions, while the H atoms were introduced as a fixed contribution ($U - 0{\cdot}051$ Å^2). The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\{1 + |(F_o - B)/A|^2\}$, $A = B = 250$. ($28 \leq F_o \leq 1652$.) The final R values for the two groups of family reflexions were 0·034 and 0·042, while R for the non-family reflexions was 0·101. From an analysis of the whole data set it can be seen that R for the non-family reflexions is high because the intensities of very many of them are low. No significant differences were found between the final relative values of the three scale factors and the relative values judged from the intensities measured for the standard reflexion. Scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for all other atoms were those listed in *International Tables for X-ray Crystallography* (1974). All atoms except I^- were treated as uncharged. The calculations were performed on an IBM 360/75 computer with a local version of the *NRC2A* Picker data-reduction program (Ahmed, 1968), with the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), and with *ORTEP* II (Johnson, 1971).

The final atomic parameters are presented in Table 1.*

Description of the structure

The bond lengths and angles of the acetylcholine ion are shown in Fig. 2 and are in agreement, within the limits of accuracy, with corresponding values listed by Svinning & Sørum (1975) for a number of acetylcholine salts. The torsion angles are listed in Table 2. For all the choline ester salts of which the crystal structures are known, the torsion angle C(1)–C(2)–O(4)–C(5) is approximately 180°, and the conformation found around C(6)–N(7) is staggered. The torsion angles C(2)–O(4)–C(5)–C(6) and O(4)–C(5)–C(6)–N(7) found in crystal structures of choline esters, unsubstituted at C(5) and C(6), are summarized in Fig. 3. The data for all ions, except some of the unmodified and modified carbamoylcholine ions, clearly cluster around two main conformations, often called *trans–gauche* and *gauche–gauche*; the acetylcholine ions in the crystals of acetylcholine iodide are seen to belong to the latter group.

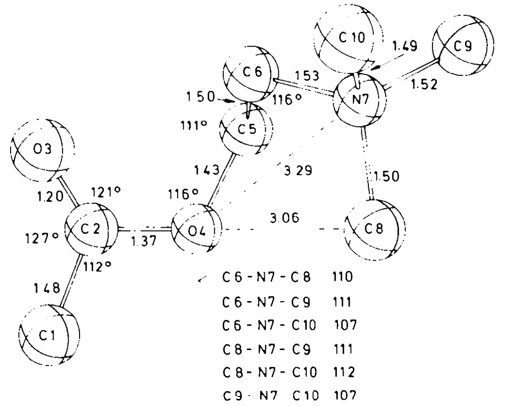

Fig. 2. Bond lengths (Å) and angles (°) together with the numbering used. The estimated standard deviations on bond lengths and angles are about 0·01 Å and 0·8° respectively.

The positions of the H atoms bonded to C(1) were postulated from a difference map, while the positions of all other H atoms were calculated. The three torsion angles O(4)–C(2)–C(1)–H(1x)(x = 1 → 3), are −36, −158 and 87° for acetylcholine iodide and −21, −147 and 95° for acetylcholine bromide (Svinning & Sørum, 1975). Although the structures of a great many acetylcholine salts have been examined by X-ray techniques, the positions of all H atoms have been published only for acetylcholine bromide. Only a few of the data sets obtained from acetylcholine salts have been of high quality and this correlates with the fact that the values of the thermal parameters are often found to be high. These high values may in some cases be interpreted as a result of statistical disorder, as in acetylcholine resorcylate (Jensen, 1975*b*) and acetylcholine (+)-bitartrate (Jensen, unpublished), in which one of the two crystallographically independent acetylcholine ions seems to be affected by disorder, and in bis(acetylcholine)tetrabromodioxouranium(VI) (Marzotto, Graziani, Bombieri & Forsellini, 1974), in which

Table 2. *Selected torsion angles*

C(1)–C(2)–O(4)–C(5)	180 (1)°
C(2)–O(4)–C(5)–C(6)	±83 (1)
O(4)–C(5)–C(6)–N(7)	±89 (1)
C(5)–C(6)–N(7)–C(8)	∓53 (1)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32561 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

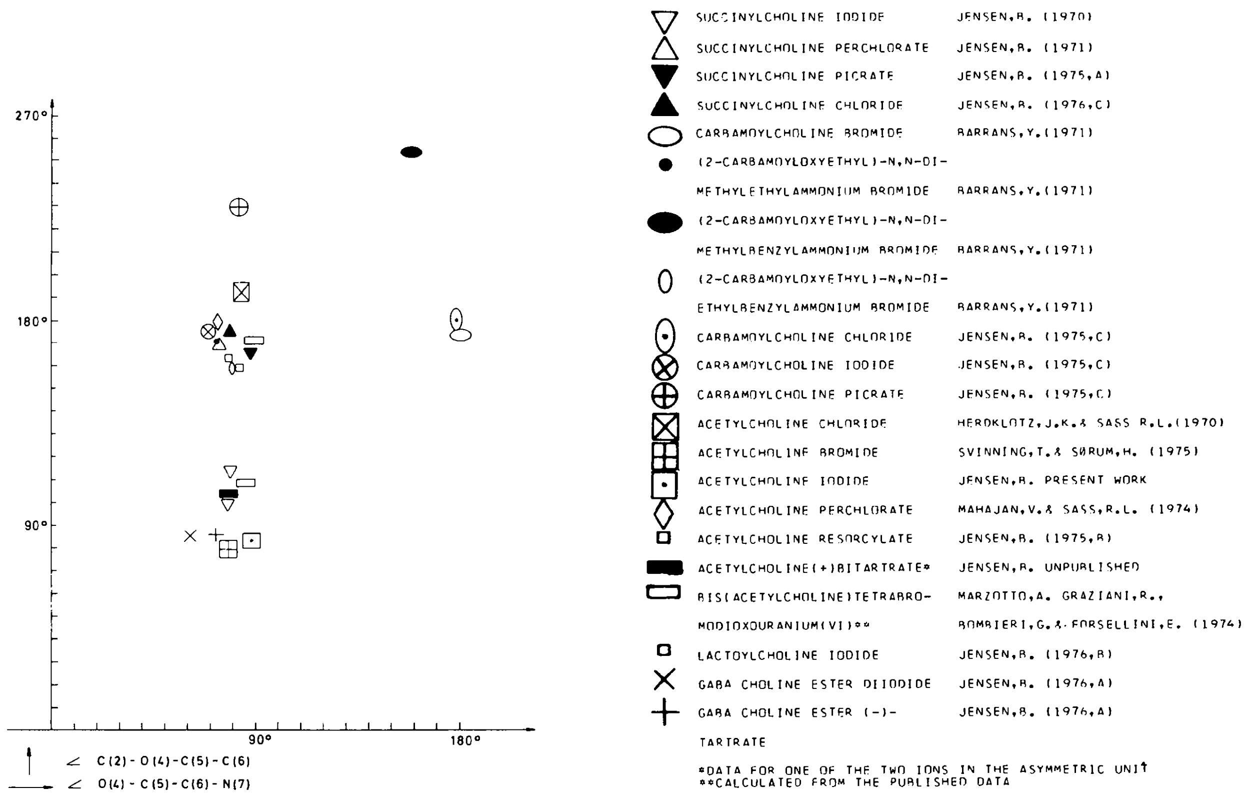

Fig. 3. The torsion angles C(2)–O(4)–C(5)–C(6) and O(4)–C(5)–C(6)–N(7) in structures of choline esters, unsubstituted at C(5) and C(6). [Note: The correct reference to succinylcholine chloride is Jensen (1977).]

two different conformers, one *trans–gauche* and one *gauche–gauche*, coexist in the crystals. Only in acetylcholine iodide, however, has an ordered disorder been found. The surroundings of all acetylcholine ions are essentially equal, the main difference being the contact to $I^-(2x)$, which for half of the ions is $C(6)\cdots I^-(21)$, 3·93 (1) Å, and for the other half $C(6)\cdots I^-(22)$, 3·99 (1) Å.

Non-bonded contacts less than or equal to the sum of the van der Waals radii (Pauling, 1960) are listed in Table 3. A close contact, 3·09 (1) Å, is observed between C(8) of the quaternary ammonium group and the carbonyl O(3) of a neighbouring acetylcholine ion. Similar contacts have been found in many of the crystal structures listed in Fig. 3. Within the layers the surroundings of the I^- ions have fourfold symmetry. As can be seen from Fig. 4 and Table 3 the environments of $I^-(11)$ and $I^-(12)$ are rather different; the difference between their positions in the **c** direction is 0·255 (3) Å. A much smaller, but highly significant, difference is found between the corresponding positions of $I^-(21)$ and $I^-(22)$, namely 0·085 (3) Å. The distances from $I^-(21)$ to the four surrounding C(10) methyl groups are 3·88 (1) while the distances from $I^-(22)$ to the four surrounding C(9) methyl groups are 3·95 (1) Å. $I^-(21)$

Table 3. *Non-bonded distances* (Å) *less than* 4·2 Å ($I^-\cdots C$), 4·0 Å ($C\cdots C$) *and* 3·4 Å ($O\cdots C$)

The equipoints refer to the unit cell with dimensions $a=b=16{\cdot}510$, $c=31{\cdot}443$ Å.

(*a*) Contacts within the layer

$C(8)\cdots C(5)[\frac{1}{2}-y, x-\frac{1}{2}, x]$	3·73 (1)
$C(8)\cdots O(3)[y, -x, z]$	3·09 (1)
$C(8)\cdots C(6)[y, -x, z]$	3·80 (2)

$I^-(11)\cdots C(2^{i})$	4·15 (1)	$I^-(12)\cdots C(1^{ii})$	4·15 (1)
$I^-(11)\cdots C(6^{i})$	4·19 (1)	$I^-(12)\cdots C(5^{i})$	4·10 (1)
$I^-(11)\cdots C(10^{i})$	4·14 (1)	$I^-(12)\cdots C(9^{i})$	4·06 (1)
$I^-(21)\cdots C(10^{i})$	3·88 (1)	$I^-(22)\cdots C(9^{i})$	3·95 (1)

(*b*) Contacts between atoms in adjacent layers

$I^-(21)\cdots C(6^{iii})$	3·93 (1)	$I^-(22)\cdots C(6^{iv})$	3·99 (1)
$C(10)\cdots C(10^{v})$	4·00 (1)		

Symmetry code

(i) $x,y,z;\ y,-x,z;\ -x,-y,z;\ -y,x,z$
(ii) $\frac{1}{2}-x, -y, -z;\ \frac{1}{2}-y, x, -z;\ \frac{1}{2}+x, y, -z;\ \frac{1}{2}+y, -x, -z$
(iii) $-\frac{1}{4}+x, -\frac{1}{4}+y, \frac{1}{2}-z;\ \frac{1}{4}-x, \frac{1}{4}-y, \frac{1}{2}-z$
or $\frac{1}{4}-y, -\frac{1}{4}+x, \frac{1}{2}-z;\ -\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{2}-z$
(iv) $\frac{3}{4}-y, x-\frac{1}{4}, \frac{1}{2}-z;\ \frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{2}-z$
or $\frac{1}{4}+x, -\frac{1}{4}+y, \frac{1}{2}-z;\ \frac{3}{4}-x, \frac{1}{4}-y, \frac{1}{2}-z$
(v) $\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{2}-z$; or $\frac{1}{4}-y, -\frac{1}{4}+x, \frac{1}{2}-z$

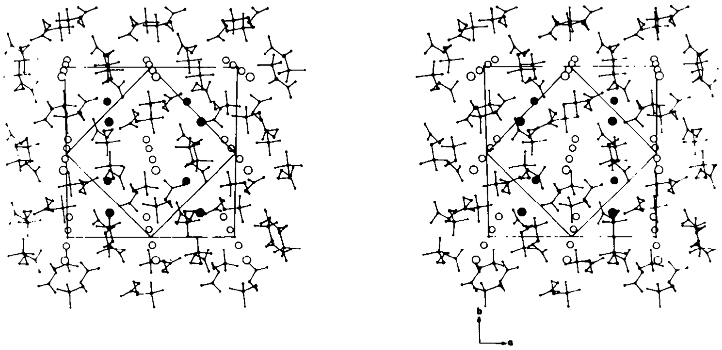

Fig. 4. A stereoview of a layer. The large square indicates the unit cell with $a = b = 16{\cdot}510$ Å. The I^- ions depicted as empty circles are parts of the layer, while those depicted as filled circles are $I^-(21)$ or $I^-(22)$ from adjacent layers.

and $I^-(22)$ each form *two* contacts to C(6) methylene C atoms in the adjacent layers, the distances $I^-(21)\cdots C(6)$ and $I^-(22)\cdots C(6)$ being 3·93 (1) and 3·99 (1) Å respectively. Thus for each of $I^-(21)$ and $I^-(22)$ the distances to the six nearest neighbours are nearly equal. No $I^-\cdots I^-$ contacts shorter than $I^-(11)\cdots I^-(21)$, 5·351 (3) Å, are observed.

The only close contacts between the layers are the above-mentioned $I^-(2x)\cdots C(6)$ contacts and a $C(10)\cdots C(10)$ contact, 4·00 (1) Å. These are all established whether the translation between the layers is $\mathbf{a}/4 - \mathbf{b}/4 + \mathbf{c}/2$ or $\mathbf{a}/4 + \mathbf{b}/4 + \mathbf{c}/2$. It is thus surprising that a crystal like the one examined, in which one kind of interlayer translation dominates completely, can ever be formed.

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