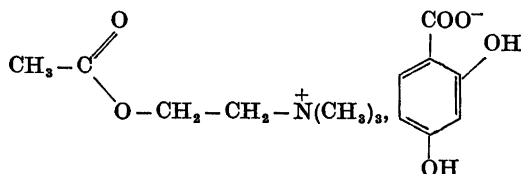# The Crystal Structure of Acetylcholine β-Resorcylate

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Acetylcholine β-resorcylate, $C_{14}H_{21}NO_6$, crystallizes in space group $P2_1/c$ with a unit cell having dimensions $a = 14.562(6)$, $b = 14.109(4)$, $c = 15.096(6)$ Å, and $\beta = 106.90(3)°$. $Z = 8$. The structure was determined by direct methods from diffractometer collected three-dimensional X-ray data and refined by full-matrix least-squares techniques to an R index of 0.078. Layers of β-resorcylate ions alternate with layers of acetylcholine ions. The β-resorcylate ions are linked together in infinite chains by strong hydrogen bonds while no hydrogen bonds involve the acetylcholine ions.

The crystal structure determination of acetylcholine β-resorcylate was taken up as part of conformational studies of choline derivatives in

the solid state. The crystal structures of a large number of salts of choline derivatives are known. Among these the carbamoylcholine salts [1–2] seem to be exceptional, showing an apparently greater flexibility than found for most other choline derivatives. This is in agreement with the PCILO calculations of Pullman and Courière.[3] However, it is noticed, that in all known crystal structures of carbamoylcholine salts the two possible hydrogen bonds $N-H\cdots X$ are actually found, and the possibility is not precluded that the formation of these hydrogen bonds is of importance for the observed conformational changes. Among the salts of other choline derivatives, of which the crystal structures have been determined, only very few

have any possibility of formation of hydrogen bonds. It therefore seems to be of interest to examine salts of choline derivatives with hydroxy acids and other potential hydrogen bond donors, especially in view of the actions of acetylcholine in biological media.

EXPERIMENTAL

Acetylcholine β-resorcylate was prepared from an aqueous solution of acetylcholine chloride and excess of freshly precipitated silver salt of β-resorcylic acid. After stirring for 1 h the precipitate was filtered off, and the solution evaporated *in vacuo*. Colourless prisms of acetylcholine β-resorcylate were obtained by recrystallization from ethanol. The crystals used for the X-ray examination were grown by diffusion at room temperature of dimethoxymethane into a solution of the compound in ethanol containing 5 % water.

Crystal data. Acetylcholine β-resorcylate, $C_{14}H_{21}NO_6$, $M = 299.33$. M.p. 144.5 – 147 °C (decomp.). Monoclinic, $a = 14.562(6)$, $b = 14.109(4)$, $c = 15.096(6)$ Å. $\beta = 106.90°$, $U = 2967.6$ Å^3. $D_m = 1.33$ g cm^{-3}, $Z = 8$, $D_c = 1.34$ g cm^{-3}. Linear absorption coefficient for X-rays [$\lambda(MoK\alpha) = 0.7107$ Å], $\mu = 1.1$ cm^{-1}. $F(000) = 1280$. Systematically absent reflections: $h0l$ when l is odd, $0k0$ when k is odd: space group $P2_1/c$.

The unit-cell parameters were refined by least-squares techniques from the diffractometer-measured θ angles observed for 33 reflections. The crystal density was measured by flotation in a mixture of chlorobenzene and bromobenzene. The melting point was determined on a Leitz hot stage microscope.

Data collection. Three-dimensional diffraction data were measured at room temperature (20 – 22 °C) on a Nonius three-circle automatic dif-

Table 1. Atomic parameters with estimated standard deviations, referring to the last significant figure, in parenthesis. Positional parameters are $\times 10^4$. Thermal parameters are $\times 10^2$. The temperature factor is defined by

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*+\cdots)]$$

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(11)	2234(4)	1723(4)	0104(3)	4.0(3)	5.0(3)	3.1(3)	0.3(2)	1.4(2)	−0.2(2)
C(12)	2197(4)	2395(4)	0775(4)	4.1(3)	4.9(3)	3.9(3)	−0.2(3)	0.8(2)	−0.5(3)
C(13)	2200(4)	2100(4)	1665(3)	5.3(3)	4.9(3)	2.6(3)	−0.4(3)	1.1(2)	−0.5(2)
C(14)	2221(4)	1155(4)	1865(4)	4.6(3)	5.6(4)	3.4(3)	0.3(3)	0.7(2)	0.4(3)
C(15)	2258(4)	0477(4)	1209(4)	5.1(3)	4.2(3)	4.7(3)	0.3(3)	1.1(3)	−0.4(3)
C(16)	2262(4)	0772(4)	0334(4)	4.7(3)	5.6(4)	3.7(3)	0.2(3)	1.2(3)	−0.4(3)
C(17)	2262(4)	2037(5)	−0836(4)	4.4(3)	6.5(4)	3.9(3)	0.3(3)	1.0(3)	−0.3(3)
O(171)	2318(3)	1436(3)	−1417(3)	8.9(3)	7.3(3)	4.4(2)	0.0(3)	3.0(2)	−0.7(2)
O(172)	2221(3)	2933(3)	−0990(3)	8.9(3)	6.5(3)	4.4(2)	0.1(2)	3.1(2)	0.9(2)
O(12)	2183(3)	3342(3)	0604(3)	8.5(3)	4.7(2)	4.8(2)	−0.3(2)	2.9(2)	0.1(2)
O(14)	2215(3)	0856(3)	2727(3)	8.7(3)	6.0(3)	3.4(2)	−0.1(2)	1.9(2)	1.1(2)
C(21)	7143(4)	3098(4)	1060(3)	4.0(3)	4.8(3)	2.9(3)	−0.4(2)	1.4(2)	−0.4(2)
C(22)	7330(4)	2476(4)	0403(4)	4.0(3)	3.6(3)	4.0(3)	−0.2(2)	1.6(2)	−0.4(2)
C(23)	7359(4)	2827(4)	−0456(4)	5.1(3)	4.8(3)	3.7(3)	0.2(3)	2.0(3)	−0.2(3)
C(24)	7209(4)	3780(4)	−0652(4)	5.0(3)	4.8(3)	3.1(3)	−0.1(3)	1.4(2)	−0.1(3)
C(25)	7016(4)	4406(4)	−0014(4)	6.1(4)	4.7(3)	3.7(3)	0.2(3)	1.2(3)	−0.2(3)
C(26)	6992(4)	4046(4)	0830(4)	4.9(3)	5.0(3)	3.7(3)	0.0(3)	1.2(3)	−0.5(3)
C(27)	7145(4)	2751(5)	1994(4)	4.6(3)	6.2(4)	3.2(3)	−0.8(3)	1.3(3)	−0.4(3)
O(271)	6932(4)	3302(3)	2543(3)	10.1(4)	7.1(3)	4.0(2)	1.0(3)	3.6(2)	0.1(2)
O(272)	7388(3)	1876(3)	2177(3)	9.2(3)	5.1(3)	4.4(2)	0.1(2)	3.0(2)	0.6(2)
O(22)	7484(3)	1542(3)	0586(3)	8.7(3)	3.8(2)	4.8(2)	0.4(2)	2.7(2)	0.4(2)
O(24)	7232(3)	4144(3)	−1479(3)	9.6(3)	5.0(2)	4.1(2)	0.4(2)	3.2(2)	0.6(2)
C(31)	4600(5)	3500(5)	−0424(5)	7.4(5)	8.5(5)	5.2(4)	0.2(4)	2.3(3)	−0.5(4)
C(32)	4637(4)	2957(5)	0436(5)	4.8(4)	6.6(5)	5.7(4)	0.5(3)	1.7(3)	−1.5(3)
O(33)	4716(4)	2108(4)	0526(3)	9.6(4)	5.9(3)	7.9(3)	0.8(3)	3.8(3)	−1.5(3)
O(34)	4566(3)	3532(3)	1123(3)	6.8(3)	5.9(3)	5.0(2)	0.1(2)	2.2(2)	−0.9(2)
C(35)	4559(5)	3070(4)	1976(4)	7.0(4)	5.3(4)	5.5(4)	−0.2(3)	2.5(3)	−0.6(3)
C(36)	4108(4)	3741(4)	2515(4)	4.9(3)	5.8(4)	5.0(3)	−0.6(3)	1.6(3)	−0.7(3)
N(37)	4777(3)	4470(3)	3109(3)	4.7(3)	5.1(3)	3.9(2)	0.3(2)	1.4(2)	0.1(2)
C(38)	5193(5)	5106(5)	2524(5)	8.5(5)	6.1(4)	5.0(4)	−1.4(4)	2.6(4)	0.6(3)
C(39)	5581(5)	4016(5)	3842(4)	5.7(4)	7.4(4)	4.1(3)	0.6(3)	0.7(3)	0.8(3)
C(310)	4177(5)	5050(5)	3571(5)	6.8(4)	7.1(5)	6.1(4)	1.2(4)	2.4(3)	−1.2(4)
C(41)	9718(5)	3575(6)	5182(5)	7.3(5)	9.9(6)	7.7(5)	0.6(4)	3.5(4)	1.3(5)
C(42)	9708(5)	3090(6)	4312(6)	5.2(4)	7.9(5)	8.8(5)	0.2(4)	2.9(4)	2.5(5)
O(43)	9704(5)	2249(6)	4201(5)	12.3(5)	8.2(4)	12.5(5)	0.7(4)	5.4(4)	1.8(4)
O(44)	9701(4)	3707(4)	3638(3)	10.2(4)	8.3(4)	6.3(3)	−2.4(3)	2.1(3)	1.1(3)
C(45)	9687(8)	3275(7)	2744(6)	17.1(10)	8.9(6)	6.7(5)	−4.4(6)	2.0(6)	0.2(5)
C(46)	9419(7)	3919(7)	2040(7)	14.2(8)	9.6(7)	9.3(7)	−3.4(6)	3.4(6)	−0.2(6)
N(47)	10107(4)	4685(4)	1885(4)	5.7(3)	6.3(3)	6.0(3)	0.4(3)	2.6(3)	0.1(3)
C(48)	10426(6)	5292(6)	2712(6)	11.3(7)	7.6(5)	7.7(5)	−2.9(5)	2.2(5)	−1.2(4)
C(49)	10915(6)	4326(8)	1580(6)	8.1(6)	19.1(10)	9.6(7)	5.8(6)	4.4(5)	2.6(7)
C(410)	9454(6)	5239(7)	1101(6)	8.6(6)	14.1(8)	7.0(5)	5.0(6)	1.6(4)	1.7(5)

fractometer using graphite monochromated MoKα radiation. The ω scan technique with a scan speed of 1.2° min⁻¹ was employed, and the scan angle was 1.2°. Background counts were taken for half the scanning time at each of the scan range limits. One standard reflection was measured after each 25 reflections. All the data were measured from a single crystal of irregular shape. The approximate dimensions were $0.20 \times 0.36 \times 0.48$ mm. The crystal was mounted with [001] along the ϕ-axis of the goniostat. Out of the 5435 reflections measured in the range $2.5° \leq \theta \leq 25°$, 2509 had $I_{net} \geq 2.5 \ \sigma(I)$, where $\sigma(I)$ is the standard deviation from counting

statistics. These were regarded as observed reflections. Lorentz and polarization corrections were applied, but no absorption corrections were made owing to the low absorption coefficient.

Structure determination and refinement. The structure was solved by direct methods in a straight forward way using the programs of the X-RAY system.[4] In an *E*-map based on 299 *E(hkl)*'s with $|E(hkl)| \geq 1.7$ the 29 highest peaks were found in positions corresponding to the heavier atoms of the two β-resorcylate ions and to seven atoms [C(31) − N(37)] of one of the acetylcholine ions. Seven more of the higher peaks were found at correct atomic positions [corresponding to C(38) − C(310) and C(41) − O(44)]. From an electron density map calculated using the phases from the contributions of the above mentioned 29 atoms the positions of the remaining 13 atoms in the asymmetric unit could be deduced. Individual atomic parameters of all 42 carbon, nitrogen, and oxygen atoms were refined using the full-matrix least-squares method. Owing to the great number of variables the refinements were performed in a few big blocks. A three-dimensional difference synthesis calculated at the stage of convergence of the refinement using individual isotropic temperature factors $(R \sim 0.14)$ showed maxima at the calculated positions for 19 of the 42 hydrogen atoms, namely the hydrogen atoms bonded to the benzene rings and 13 of the 16 hydrogen atoms of one of the acetylcholine ions, III. The 19 hydrogen atoms were introduced in the refinement as a fixed contribution in the calculated positions and with arbitrary temperature factors. After refinement of the heavier atoms using individual anisotropic temperature factors a difference synthesis based only on reflections for which sin $\theta/\lambda \leq 0.35$ was examined, but from this only the positions of the four OH-hydrogen atoms could further be postulated. Nevertheless all 42 hydrogen atoms were now introduced as a fixed contribution in the refinement, in an attempt to reduce the very strong "thermal motion" observed (*cf.* Table 1). The three hydrogen atoms of each of

Table 2. Atomic parameters used for the hydrogen atoms. Positional parameters are $\times 10^4$. Thermal parameters are $\times 10^2$.

Atom	x/a	y/b	z/c	U	P.P.	Atom	x/a	y/b	z/c	U	P.P.
H(13)	2177	2577	2147	5.1		H(391)	5304	3626	4244	7.6	
H(15)	2285	−0214	1362	5.1		H(392)	5962	3625	3533	7.6	
H(16)	2269	0284	−0141	5.1		H(393)	6015	4512	4234	7.6	
H(12)	2200	3450	0000	7.6		H(3101)	3659	5365	3095	7.6	
H(14)	2200	1370	3200	7.6		H(3102)	3916	4624	3963	7.6	
						H(3103)	4628	5524	3964	7.6	
H(23)	7507	2384	−0920	5.1							
H(25)	6898	5094	−0160	5.1		H(4113)	9138	3333	5339	10.1	0.5
H(26)	6836	4490	1281	5.1		H(4123)	10309	3357	5644	10.1	0.5
H(22)	7350	1430	1240	7.6		H(4133)	9698	4282	5256	10.1	0.5
H(24)	7350	3820	−1960	7.6		H(4114)	10303	3978	5380	10.1	0.5
						H(4124)	9131	3994	5056	10.1	0.5
H(3113)	5182	3340	−0595	7.6	0.5	H(4134)	9707	3123	5680	10.1	0.5
H(3123)	4014	3242	−0913	7.6	0.5	H(451)	10420	3075	2821	10.1	
H(3133)	4522	4211	−0511	7.6	0.5	H(452)	9334	2667	2658	10.1	
H(3114)	3957	3854	−0630	7.6	0.5	H(461)	9152	3582	1391	10.1	
H(3124)	5123	3975	−0300	7.6	0.5	H(462)	8807	4293	2086	10.1	
H(3134)	4630	3086	−0952	7.6	0.5	H(481)	9860	5636	2794	10.1	
H(351)	4161	2484	1836	7.6		H(482)	10731	4894	3247	10.1	
H(352)	5222	2912	2357	7.6		H(483)	10905	5782	2629	10.1	
H(361)	3589	4094	2058	7.6		H(491)	11235	3770	2032	10.1	
H(362)	3839	3356	2928	7.6		H(492)	10615	3937	0954	10.1	
H(381)	5576	4707	2200	7.6		H(493)	11376	4735	1498	10.1	
H(382)	4672	5437	2051	7.6		H(4101)	9209	4862	0524	10.1	
H(383)	5637	5587	2916	7.6		H(4102)	8911	5546	1268	10.1	
						H(4103)	9938	5734	1030	10.1	

Table 3. Least squares planes. The equations of the planes are in direct (unit cell) space. Distances (Å) to atoms defining the plane are marked with an asterisk.

Plane I	$13.8613x + 0.4643y + 0.2239z = 3.1780$
Plane II	$13.2396x + 2.4566y + 1.4735z = 10.3725$
Plane III	$13.7909x + 1.3358y + 0.2758z = 6.8000$
Plane IV	$13.9762x - 0.0328y - 0.1564z = 13.4899$

I		II	
C(11)	0.001*	C(21)	0.002*
C(12)	− 0.005*	C(22)	− 0.001*
C(13)	0.006*	C(23)	− 0.002*
C(14)	− 0.004*	C(24)	0.005*
C(15)	0.000*	C(25)	− 0.004*
C(16)	0.001*	C(26)	0.001*
C(17)	0.034	C(27)	0.056
O(171)	0.070	O(271)	− 0.009
O(172)	0.015	O(272)	0.190
O(12)	0.016	O(22)	0.002
O(14)	− 0.007	O(24)	0.002

III		IV	
C(31)	− 0.000*	C(41)	− 0.000*
C(32)	0.001*	C(42)	0.001*
O(33)	− 0.001*	O(43)	− 0.000*
O(34)	− 0.000*	O(44)	− 0.000*
C(35)	− 0.048	C(45)	− 0.005
C(36)	− 0.565	C(46)	− 0.371
N(37)	0.471	N(47)	0.591
C(38)	1.114	C(48)	1.022
C(39)	1.539	C(49)	1.726
C(310)	− 0.267	C(410)	− 0.311

the two acetyl groups were introduced as two times six atoms with occupancy-factor 0.5. On convergence of the refinement using anisotropic temperature factors the R-value was 0.078. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where weights were taken as a unity. A weight analysis showed this not to be too unsatisfactory and in view of the limited amount of data and the expence in computer time further refinement was judged not to be justified. In all calculations the contribution from unobserved reflections were included in the refinement, when $|F_c| \geq |F_o|$. All the atoms were treated as uncharged, and the form factors were taken from *International Tables for X-Ray Crystallography.*[5] The calculations were performed on a GIER computer and an IBM 360/75 computer using *INDIFF,*[6] a local version of *The N.R.C. 2A Picker Data Reduction Program,*[7] *The X-Ray System,*[4] and *ORTEP.*[8]

The observed and calculated structure factor data are available from the author upon request.

The final atomic parameters of carbon, nitrogen and oxygen atoms are listed in Table 1. In Table 2 the parameters used for the hydrogen atoms are given. Bond lengths and angles are shown in Fig. 1. The parameters of a number of planes calculated through parts of the ions are given in Table 3.

RESULTS AND DISCUSSION

The structure is built up of alternating negatively and positively charged puckered layers roughly parallel to (100) and with an *inter*layer distance of approximately $x/4$, *cf.* Fig. 2. Layers consisting of both of the crystallographically independent β-resorcylate ions I and II are found about $x \sim 1/4$ and $x \sim 3/4$. A layer consisting of acetylcholine ions III only is found about $x \sim \frac{1}{2}$, and a layer of acetylcholine ions IV is situated about $x \sim 1.0$. The layers are held together by a great number of relatively weak *inter*ionic contacts. The resorcylate ions within each layer are linked together in infinite chains in the c direction by strong hydrogen bonds $O(x4) - H \cdots O(x72)$. Chains consisting of β-resorcylate ions I alternative with chains con-
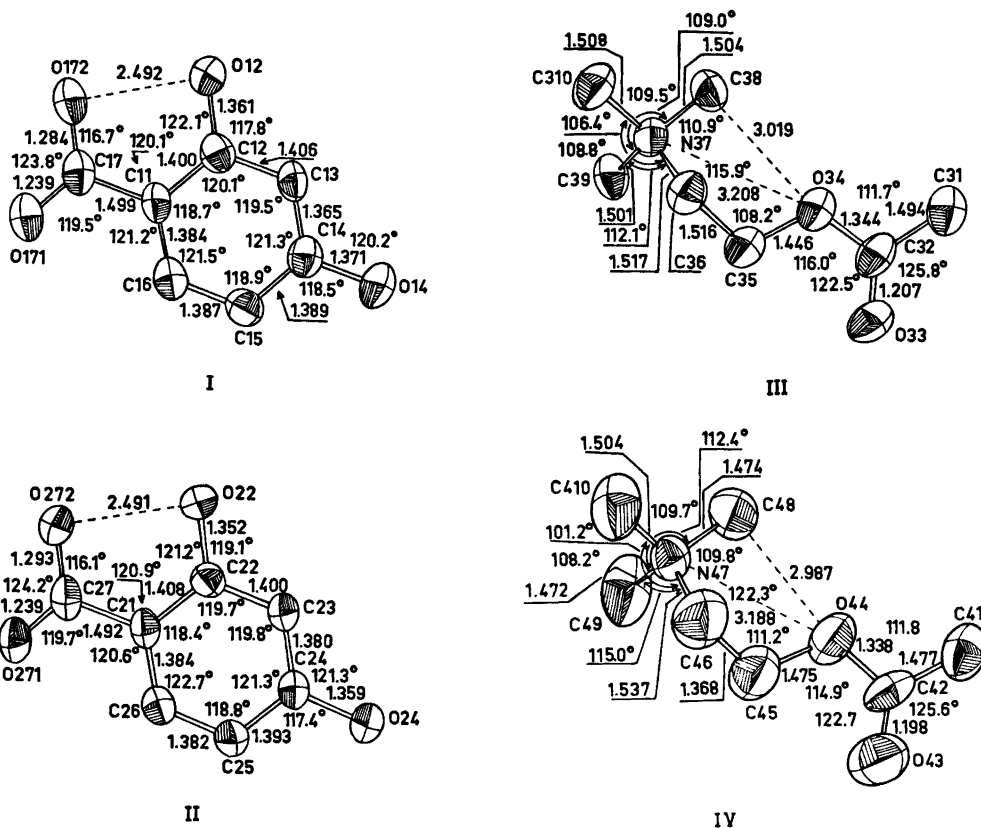
Fig. 1. Numbering system, bond distances and bond angles of β-resorcylate ion I, β-resorcylate ion II, acetylcholine ion III, and acetylcholine ion IV. All ions are viewed along the a*-axis. The *intra*ionic hydrogen bonds of the β-resorcylate ions are indicated, and so are the distances O(x4)···N(x7) and O(x4)···C(x8) of the acetylcholine ions. The estimated standard deviations in bonds and angles are 0.008 Å and 0.5°, respectively, for dimensions of the β-resorcylate ions, while the corresponding figures for dimensions of the acetylcholine ions are in the range 0.008 − 0.013 Å and 0.4 − 0.8°, respectively.

sisting of β-resorcylate ions II. The O(x4)··· O(x72) distance is 2.580 Å when x = 1, and 2.550 Å when x = 2. No close contacts are found between the chains. The angle between (100) and the ring plane of β-resorcylate ion I is 2.1°, while the corresponding angle for β-resorcylate ion II is 11.5°. The angle between the ring planes I and II is 9.5°.

Within the layer consisting of acetylcholine ions III only very few contacts between the ions are observed, *cf.* Fig. 3a. The angle between the best plane through the atoms C(31), C(32), O(33) and O(34) and the ring plane of resorcylate ion I is 3.6°, and the corresponding angle to the ring plane of resorcylate ion II is 6.5°. The five

atoms C(31) to C(35) are squeezed in between the resorcylate ions $I_{(x,y,z)}$ and $II_{(x,y,z)}$. The distances of the five atoms to the planes of the two rings are in the range 3.3 to 3.5 Å, the shorter *inter*atomic distances being of this magnitude too. A number of rather weak contacts are seen between the cationic head of the acetylcholine ion III and atoms, mostly oxygen atoms, of resorcylate ions in the two adjacent layers, *cf.* Fig. 3a.

The situation within the layer consisting of acetylcholine ions IV is very similar to that described for the layer of acetylcholine ions III. Only few contacts between the acetylcholine ions are found, *cf.* Fig. 3b. The angle between
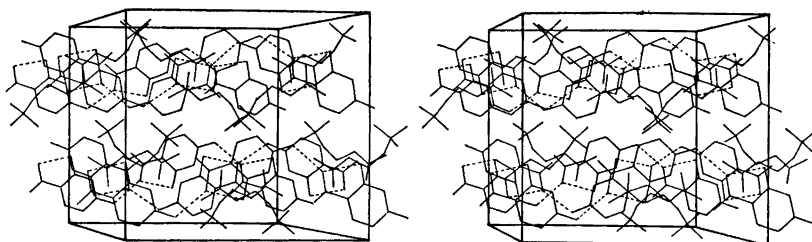
Fig. 2. Stereo diagram illustrating the packing. The *b*-axis is ↑, the *c*-axis is →, and *a** is pointing into the paper. Hydrogen bonds are drawn with broken lines.
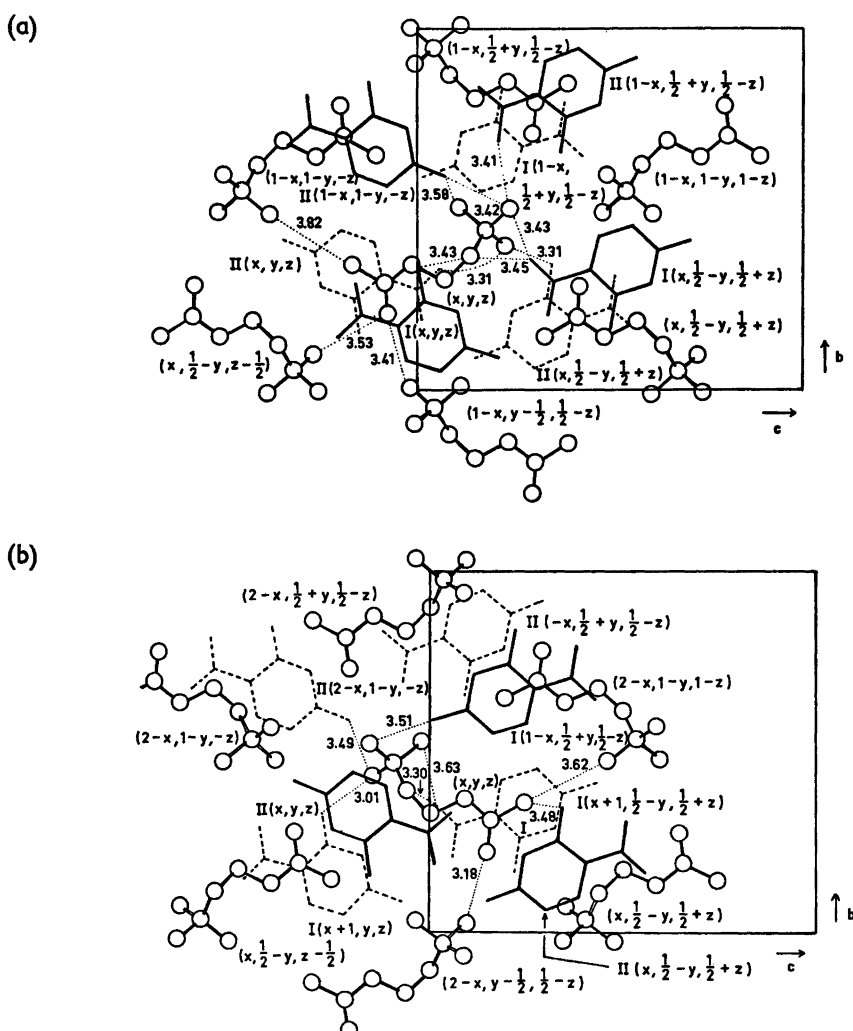
(a)

(b)

Fig. 3. Projection along *a** of (a) the packing around acetylcholine-ion III and (b) the packing around acetylcholine-ion IV.

the best plane through the atoms C(41), C(42), O(43), and O(44) and the ring plane of resorcylate ion $I_{(x+1, \frac{1}{2}-y, \frac{1}{2}+z)}$ is 2.3°. The distances of the five atoms C(41) to C(45) to the plane of the above mentioned adjacent ring are all ≥ 3.5 Å. No resorcylate ion is found directly on top of the atoms of the ester group of acetylcholine ion IV. A number of contacts between the cationic head and resorcylate ions in the adjacent layers are observed. One of them, $C(49)\cdots O(14)_{(x+1, y, z)}$ is remarkably short, 3.01 Å. The shortest contacts to C(45) are $C(45)\cdots C(27)_{(x, y, z)}$ 3.62 Å, and $C(45)\cdots O(171)_{(x+1, \frac{1}{2}-y, \frac{1}{2}+z)}$, 3.69 Å.

The β-resorcylate ions. As visualized in Fig. 1 the dimensions of the two resorcylate ions I and II are very similar, and no significant differences between corresponding figures are found. As in the crystal structure of salicylic acid [9] and of nicotinyl salicylate [10] there is a strong hydrogen bond between the *ortho*-hydroxyl and a carboxylate oxygen atom. The distance $O(x2)\cdots O(x72)$ is 2.49 Å. The corresponding distances in salicylic acid and in nicotinyl salicylate are 2.620 and 2.544 Å, respectively. The carbon — oxygen distances $C(x7)-O(x71)$ and $C(x7)-O(x72)$, 1.239 and 1.284 Å for x = 1, and 1.239 and 1.293 Å for x = 2, are significantly different. This difference is associated to the fact that O(x72) is acceptor for two strong hydrogen bonds, while no hydrogen bond involve O(x71). The distance $C(x2)-O(x2)$, 1.361 Å and 1.352 Å for the ions I and II, respectively, is of the same magnitude as the corresponding bond (1.358 Å) in salicylic acid, and it thus seems doubtful whether the shortening of the corresponding bond (1.318 Å) observed in the salicylate ion [10] can be ascribed to an effect of the strength of the *intra*ionic hydrogen bond. The carboxylate group is out of the plane of the benzene ring by 2 and 6° for resorcylate ion I and II, respectively. These figures do not describe a torsion around the bond $C(x1)-C(x7)$, *cf.* Table 3.

The acetylcholine ions. Rather pronounced differences are observed between the dimensions of the two crystallographically independent acetylcholine ions III and IV, *cf.* Fig. 1. Due to the extremely large "thermal motion" of acetylcholine ion IV these differences can, however, not be interpreted as significant differences in real bond lengths and angles. The bond lengths and angles of acetylcholine ion III are not significantly different from those found by

Table 4. Torsion angles (°) of the acetylcholine ions III and IV.

	III x = 3	IV x = 4
C(x1) — C(x2) — O(x4) — C(x5)	± 178	180
C(x2) — O(x4) — C(x5) — C(x6)	± 159	± 163
O(x4) — C(x5) — C(x6) — N(x7)	± 84	± 77
C(x5) — C(x6) — N(x7) — C(x8)	± 61	± 60

Herdklotz and Sass [11] in the crystal structure of acetylcholine chloride. The conformations of both of the acetylcholine ions are approximately the same and equal to that found in crystals of acetylcholine chloride, while differences from the conformation found by Canepa, Pauling and Sörum [12] are observed. The pertinent torsion angles are listed in Table 4. The distances $O(x4)\cdots N(x7)$ and $O(x4)\cdots C(x8)$ are 3.21 and 3.02 Å when x = 3 and 3.19 and 2.99 Å when x = 4.

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