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## The Structures of Acetylcholine Hydrogen Tartrates\*

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### Abstract

The crystal structures of acetylcholine hydrogen ( $\pm$ )-tartrate,  $C_7H_{16}NO_2^+ \cdot C_4H_5O_6^-$ , and of two polymorphs of acetylcholine hydrogen (+)-tartrate have been determined. Crystals of the racemate are orthorhombic, space group  $Pna2_1$ ,  $a = 11.853$  (2),  $b = 8.615$  (2),  $c = 14.111$  (3) Å,  $Z = 4$ . The two forms of the optically active salt are monoclinic, space group  $P2_1$ ,  $a = 6.198$  (3),  $b = 14.530$  (9),  $c = 8.043$  (4) Å,  $\beta = 97.76$  (1)°,  $Z = 2$ , and  $a = 12.323$  (2),  $b = 8.518$  (2),  $c = 13.453$  (2) Å,  $\beta = 90.45$  (1)°,  $Z = 4$ , respectively. The final  $R$  values are 0.035 (1950 reflections), 0.030 (1426 reflections), and 0.069 (1672 reflections). The hydrogen tartrate ions in all three structures are interlinked *via* hydrogen bonds into infinite chains. The acetylcholine ions are not involved in hydrogen-bond formation in any of the structures, and no distinct contacts between the formally charged groups are found.

\* IUPAC name: (acetoxylethyl)trimethylammonium hydrogen tartrate.

### Introduction

The crystal structures of a series of acetylcholine tartrates and acetylcholine hydrogen tartrates have been investigated. The purpose was to examine interactions between the acetylcholine ion and the environment and to see whether the conformation of the flexible acetylcholine ion is influenced by these interactions. Tartrates and hydrogen tartrates were chosen because one could expect to get a series of six closely related structures (optically active, racemic, and *meso* as tartrate and hydrogen tartrate), in which a great number of potential hydrogen-bond donors are present. The hope was that the structures would constitute a material from which the packing forces could be analysed semiquantitatively, for instance by SCFF calculations. The problem has, however, been complicated by the finding that some of the structures are disordered. This paper describes the crystal structures of three hydrogen tartrates, *i.e.* the racemate, ARABIT, and two forms of the optically active salt, APBIT1 and APBIT2. A preliminary report on these salts was given in the abstract for the Fourth European Crystallo-

graphic Meeting, Oxford (Jensen, 1977). The crystal structures of two acetylcholine tartrates will be described in a subsequent paper (Jensen & Norrestam, 1982).

### Experimental and refinement methods

Acetylcholine hydrogen tartrates were prepared from strictly stoichiometric amounts of the pertinent tartaric acid, silver nitrate, and recrystallized commercial acetylcholine iodide. The tartaric acid was dissolved in water and added to a dispersion of freshly precipitated silver oxide, washed to neutral reaction. Finally, a solution of acetylcholine iodide was added, and after stirring for a few minutes the silver iodide was removed and the water was evaporated. The residue was dried by repeated additions of benzene and ethanol followed by evaporation.

Single crystals of both forms of acetylcholine hydrogen (+)-tartrate, APBIT1 and APBIT2, were obtained from mixtures of benzene, dimethyl formamide, and methanol, in which the freshly prepared uncrystallized compound was dispersed. The two modifications were not found in the same batch. Single crystals of acetylcholine hydrogen ( $\pm$ )-tartrate, ARABIT, were obtained from a dispersion of the uncrystallized compound in a mixture of ethanol and benzene. All attempts to obtain crystalline acetylcholine hydrogen *meso*-tartrate have been unsuccessful.

The geometry and the space groups of the crystals were deduced from Weissenberg and precession photographs. The unit-cell parameters were refined by least-squares techniques from diffractometer-measured  $\theta$  angles (Mo  $K\alpha$  radiation,  $\lambda = 0.7107 \text{ \AA}$ ). The crystals are slightly hygroscopic and those chosen for data collection were sealed in glass capillaries. Table 1 summarizes the unit-cell parameters and conditions

Table 1. Cell parameters and data collection and refinement conditions

	ARABIT	APBIT1	APBIT2
	$C_{11}H_{21}NO_8$	$C_{11}H_{21}NO_8$	$C_{11}H_{21}NO_8$
System	Orthorhombic	Monoclinic	Monoclinic
$a$ (Å)	11.853 (2)	6.198 (3)	12.323 (2)
$b$ (Å)	8.615 (2)	14.530 (9)	8.518 (2)
$c$ (Å)	14.111 (3)	8.043 (4)	13.453 (2)
$\beta$ (°)		97.76 (4)	90.45 (1)
$V$ (Å <sup>3</sup> )	1441	718	1412
$M_r$	295.29	295.29	295.29
$D_x$ (Mg m <sup>-3</sup> ) (floatation)	1.37	1.37	1.39
$D_c$ (Mg m <sup>-3</sup> )	1.36	1.37	1.39
m.p. (K) (hot-stage microscope)	373–376	377–381	370.7–372
Space group	$Pna2_1$	$P2_1$	$P2_1$
$Z$	4	2	4
Crystal size (mm)	0.40 × 0.48 × 0.75	0.22 × 0.56 × 0.60	0.15 × 0.42 × 0.52
Stability	No decline	No decline	Decline approximately 10%. Corrected
Technique	Picker 4-circle diffractometer $\theta/2\theta$ scan	Nonius CAD-4 diffractometer $\omega/2\theta$ scan	Nonius AD-3 diffractometer $\omega$ scan
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.25	1.26	1.28
Range for $\theta$ (°)	$\theta \leq 30.5$	$\theta \leq 28.0$	$\theta \leq 25.0$
Number of independent reflections	2267	1794	2651
Criterion for observed reflections	$I \geq 5.0\sigma(I)$	$I \geq 3.0\sigma(I)$	$I \geq 3.0\sigma(I)$
Number of observed reflections	1950	1426	1672
Atomic scattering factors	As implemented in XRAY 72		
Computer programs	XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)		
Solution	<i>MULTAN</i> (Germain, Main & Woolfson, 1971)		
Refinement method	Full-matrix and block-diagonal least squares on observed $F^2$ 's		
H atoms	Most in calculated positions		
Parameters refined			
Non-hydrogen atoms	Positional and anisotropic thermal		Same, but isotropic thermal for most partial atoms
Hydrogen atoms	Not refined	Positional parameters of hydroxy H refined	Not refined
Weighting scheme	Hughes-type empirical so as to give no trends in $\langle w\Delta^2 \rangle$		
$R$ (obs)	0.035	0.030	0.069
$R_w$ (obs)	0.046	0.036	0.082

concerning data collection and structure refinement. Some details for the single structures are given in the following.

Most of the hydrogen atoms of the three structures were included in the refinement in their calculated positions as fixed contributions.

For ARABIT a difference Fourier map calculated at a late stage of the refinements showed the hydrogen atoms of the acetyl group to be disordered. They were therefore included in calculated positions as six half hydrogen atoms. The positions of the three hydrogen atoms bonded to oxygen were deduced from the difference Fourier map.

For APBIT1 the positions of the hydrogen atoms of the acetyl group seemed well defined and they were refined together with the positions of hydrogen atoms bonded to oxygen. The position of the hydrogen atom of the carboxyl group [H(042)] did not, however, refine to a stable position, and the coordinates were finally deduced from a difference Fourier map.

Refinements of the structure of APBIT2 were not uncomplicated and the final result can be taken only as a reasonable model of the real structure. The rather low number of observed reflections (1672 out of 2651 measured within  $\theta \leq 25^\circ$ ) indicated that strong thermal motion or some sort of disorder might be expected. Least-squares refinements of positional and anisotropic thermal parameters for non-hydrogen atoms converged at an  $R$  value of 0.071. At this stage the temperature factor of one oxygen atom was not positive definite, and the temperature factors of a number (but not all) other atoms were extreme, having very low values of  $U_{22}$ . In an attempt to give an explanation for the irregularities, the oxygen atoms most affected were split into two halves and refined with individual isotropic temperature factors. The same procedure was used for C(6B), an atom in one of the crystallographically independent acetylcholine ions. This model converged at an  $R$  value of 0.069, and it was judged that further refinements would give no further information. Hydrogen atoms were introduced as a fixed contribution in spite of the fact that their localization in difference Fourier maps was very uncertain.

### Results and discussion

The final atomic coordinates and thermal parameters are given in Table 2,\* and the bond lengths, valency angles, and selected torsion angles are given in Tables

\* Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36297 (140 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final positional and thermal parameters for non-hydrogen atoms

For atoms refined with isotropic parameters the  $U_{\text{iso}}$  ( $\text{\AA}^2$ ) are given. For all other atoms  $U_{\text{eq}}$  is shown.  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ .

	$x$	$y$	$z$	$U_{\text{eq}}$ or $U_{\text{iso}}$ ( $\text{\AA}^2$ ) ( $\times 10^2$ )
<b>ARABIT</b>				
C(1)	0.7699 (2)	0.8888 (3)	0.6820 (2)	5.4 (1)
C(2)	0.7171 (2)	0.7455 (2)	0.7197 (2)	4.1 (1)
O(3)	0.7128 (2)	0.7085 (2)	0.8016 (2)	6.3 (1)
O(4)	0.6727 (1)	0.6596 (2)	0.6498 (2)	4.2 (1)
C(5)	0.6203 (2)	0.5158 (2)	0.6772 (2)	4.1 (1)
C(6)	0.5455 (2)	0.4612 (2)	0.5973 (2)	4.0 (1)
N(7)	0.6046 (1)	0.3853 (2)	0.5143 (2)	3.6 (1)
C(8)	0.6920 (2)	0.4896 (3)	0.4718 (2)	5.0 (1)
C(9)	0.6599 (2)	0.2360 (2)	0.5442 (2)	4.7 (1)
C(10)	0.5159 (2)	0.3483 (3)	0.4423 (2)	6.2 (1)
O(011)	0.6105 (1)	0.8538 (2)	0.1490 (2)	4.7 (1)
O(012)	0.5220 (2)	1.0773 (2)	0.1817 (1)	4.4 (1)
C(01)	0.5685 (2)	0.9497 (2)	0.2042 (2)	3.3 (1)
C(02)	0.5723 (2)	0.9103 (2)	0.3100	3.4 (1)
O(02)	0.6307 (2)	0.7703 (2)	0.3239 (2)	5.8 (1)
C(03)	0.4527 (2)	0.8994 (2)	0.3488 (1)	3.1 (1)
O(03)	0.3872 (1)	0.7997 (2)	0.2920 (1)	4.7 (1)
C(04)	0.4524 (1)	0.8429 (2)	0.4514 (1)	3.2 (1)
O(041)	0.3993 (1)	0.7285 (2)	0.4736 (2)	4.7 (1)
O(042)	0.5095 (2)	0.9298 (2)	0.5076 (1)	5.5 (1)
<b>APBIT1</b>				
C(1)	0.5066 (7)	0.1237 (3)	0.8214 (6)	7.6 (3)
C(2)	0.6381 (6)	0.1408 (3)	0.6859 (4)	6.2 (2)
O(3)	0.6552 (9)	0.2114 (2)	0.6167 (6)	16.8 (4)
O(4)	0.7424 (4)	0.0662 (2)	0.6470 (2)	5.0 (1)
C(5)	0.8708 (5)	0.0698 (2)	0.5104 (4)	4.9 (2)
C(6)	0.7422 (4)	0.0390 (2)	0.3477 (3)	4.1 (1)
N(7)	0.6655 (3)	-0.0604 (2)	0.3401 (3)	3.7 (1)
C(8)	0.5016 (5)	-0.0778 (2)	0.4582 (4)	4.9 (2)
C(9)	0.8521 (5)	-0.1262 (2)	0.3741 (4)	5.1 (2)
C(10)	0.5551 (5)	-0.0758 (3)	0.1648 (4)	5.1 (2)
O(011)	0.2252 (3)	0.1028 (2)	0.2355 (2)	4.9 (1)
O(012)	0.0348 (3)	0.1080 (2)	-0.0208 (2)	4.5 (1)
C(01)	0.1338 (4)	0.1442 (2)	0.1130 (3)	3.4 (1)
C(02)	0.1334 (4)	0.2500	0.1167 (3)	3.7 (1)
O(02)	0.2511 (4)	0.2818 (2)	0.2674 (3)	6.5 (2)
C(03)	-0.0990 (4)	0.2862 (2)	0.0956 (3)	3.5 (1)
O(03)	-0.2196 (4)	0.2407 (2)	0.2060 (4)	6.6 (2)
C(04)	-0.1048 (4)	0.3909 (2)	0.1230 (3)	3.3 (1)
O(041)	-0.1963 (3)	0.4212 (2)	0.2361 (2)	5.2 (1)
O(042)	-0.0160 (3)	0.4380 (2)	0.0164 (2)	4.5 (1)
<b>APBIT2</b>				
C(1A)	0.4637 (9)	-0.5178 (15)	0.3896 (9)	6.1 (8)
C(2A)	0.5436 (8)	-0.6227 (11)	0.3387 (9)	4.0 (6)
O(3A)	0.5591 (7)	-0.6309 (10)	0.2531 (6)	6.3 (6)
O(4A)	0.5958 (6)	-0.7138 (10)	0.4073 (6)	5.6 (5)
C(5A)	0.6711 (10)	-0.8281 (11)	0.3714 (8)	4.9 (6)
C(6A)	0.7876 (8)	-0.7777 (11)	0.3843 (7)	4.1 (6)
N(7A)	0.8321 (7)	-0.7979 (9)	0.4873 (6)	3.7 (5)
C(8A)	0.7672 (10)	-0.7128 (14)	0.5643 (8)	5.5 (7)
C(9A)	0.8389 (10)	-0.9675 (13)	0.5154 (9)	5.7 (7)
C(10A)	0.9438 (8)	-0.7298 (7)	0.4867 (9)	6.3 (8)
C(1B)	0.0035 (11)	-0.0650	0.0174 (10)	6.9 (8)
C(2B)	0.1162 (11)	-0.0650 (16)	-0.0215 (8)	5.5 (8)
O(3B)	0.1716 (9)	0.0478 (13)	-0.0344 (7)	8.7 (7)
O(4B)	0.1468 (7)	-0.2151 (11)	-0.0437 (7)	7.6 (6)
C(5B)	0.2513 (18)	-0.234 (3)	-0.0879 (17)	17.1 (18)
C(61B)	0.327 (4)	-0.319 (6)	-0.054 (4)	9.4 (33)
C(62B)	0.339 (4)	-0.260 (4)	-0.025 (2)	4.4 (18)
N(7B)	0.3472 (7)	-0.4065 (10)	0.0383 (6)	4.2 (5)
C(8B)	0.2615 (9)	-0.3943 (12)	0.1158 (8)	5.0 (6)
C(9B)	0.3441 (16)	-0.5677 (17)	-0.009 (4)	12.3 (14)
C(10B)	0.4537 (10)	-0.3858 (19)	0.0813 (10)	4.4 (9)

Table 2 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ or $U_{\text{iso}}$ ( $\text{\AA}^2$ ) ( $\times 10^3$ )
O(0111C)	0.0397 (10)	-0.8856 (16)	0.2881 (10)	2.6 (4)†
O(0112C)	0.0236 (10)	-0.8858 (17)	0.2544 (10)	2.5 (4)†
O(0121C)	0.1125 (12)	-0.6583 (17)	0.2217 (12)	2.4 (4)†
O(0122C)	0.1169 (12)	-0.6553 (18)	0.2508 (12)	2.6 (4)†
C(01C)	0.1097 (8)	-0.8109 (10)	0.2421 (7)	3.3 (5)
C(02C)	0.2110 (7)	-0.8921 (9)	0.2041 (7)	3.0 (5)
O(021C)	0.2011 (12)	-1.060 (2)	0.2223 (12)	2.7 (5)†
O(022C)	0.1934 (11)	-1.0562 (17)	0.1935 (11)	2.0 (4)†
C(03C)	0.3138 (7)	-0.8446 (9)	0.2595 (7)	2.9 (5)
O(03C)	0.3014 (5)	-0.8560 (8)	0.3625 (5)	4.3 (4)
C(04C)	0.4090 (7)	-0.9459 (12)	0.2214 (7)	3.6 (5)
O(041C)	0.4313 (6)	-0.9438 (10)	0.1340 (5)	5.7 (5)
O(042C)	0.4544 (5)	-1.0262 (9)	0.2912 (5)	4.9 (4)
O(0111D)	0.0376 (14)	-1.290 (2)	0.2697 (13)	3.4 (5)†
O(0112D)	0.0366 (13)	-1.290 (2)	0.2424 (13)	3.1 (5)†
O(0121D)	-0.0594 (12)	-1.5093 (19)	0.2328 (12)	2.2 (4)†
O(0122D)	-0.0567 (12)	-1.5154 (19)	0.2610 (12)	2.6 (4)†
C(01D)	-0.0489 (7)	-1.3591 (10)	0.2517 (6)	2.7 (5)
C(02D)	-0.1542 (8)	-1.2715 (10)	0.2467 (7)	3.3 (5)
O(021D)	-0.1464 (10)	-1.1085 (14)	0.2587 (10)	1.6 (3)†
O(022D)	-0.1262 (12)	-1.1100 (18)	0.2891 (12)	3.5 (4)†
C(03D)	-0.2369 (7)	-1.3400 (10)	0.3201 (8)	3.3 (5)
O(03D)	-0.1900 (5)	-1.3685 (8)	0.4136 (5)	4.2 (4)
C(04D)	-0.3367 (7)	-1.2332 (10)	0.3312 (8)	3.3 (5)
O(041D)	-0.3636 (6)	-1.2014 (9)	0.4151 (6)	5.0 (5)
O(042D)	-0.3869 (5)	-1.1956 (8)	0.2507 (5)	4.4 (4)

*Acetylcholine ions*

Bond lengths found in ARABIT and APBIT1 are very similar, with the exception of the bond lengths in the acetyl group. The difference is caused by the fact that the acetyl group in APBIT1 is affected by the strong thermal motion (or disorder) of the carbonyl oxygen atom. The anisotropic thermal parameters  $U_{11}$ ,  $U_{22}$  and  $U_{33}$  for this atom are 26.2 (5), 5.2 (2), and 19.1 (4)  $\text{\AA}^2$ , respectively. No corrections for this effect have been calculated. Out of the four C–N bonds in the quaternary ammonium group the bond C(6)–N(7) is the longest, a trend which has been found in a number of crystal structures containing the element O–C–C–N(CH<sub>3</sub>) in a *gauche* conformation (*e.g.* Svinning & Sørum, 1975; Jensen, 1975). The valency angles in the quaternary ammonium group also agree with the pattern observed in other crystal structures (Jagner & Jensen, 1977, and references therein). The angle C(6)–N(7)–C(10) is invariably found to be the smallest of the six C–N–C angles [when numbering is chosen so as to give the torsion angle C(5)–C(6)–N(7)–C(10) a value of *ca* 180°]. This conforms with the pattern found for the structure element R–X–C(CH<sub>3</sub>)<sub>3</sub> (de Vos, Schreurs, van Duijneveldt & Kroon, 1980). The difference between the values found for the angle O(4)–C(5)–C(6) in ARABIT and in APBIT1 may be correlated with the conformational differences (Table 5) of the two acetylcholine ions. The angle O(4)–C(5)–C(6) is generally more open in *gauche-gauche* conformers than in *trans-gauche* conformers (Jensen, 1981), where it is again more open than in *trans-trans* conformers (Jensen, 1975, 1979).

3–5. The molecules with the atomic numbering are shown in Fig. 1. Owing to the low accuracy of the parameters determined for APBIT2 no detailed discussion of the geometry of the ions in this structure is relevant.

Table 3. *Bond lengths* ( $\text{\AA}$ )

For APBIT2 the value referring to a partial atom with end-number 1 is always given first.

	ARABIT	APBIT1	APBIT2	
			Ion A	Ion B
C(1)–C(2)	1.483 (3)	1.468 (6)	1.50 (2)	1.49 (2)
C(2)–O(3)	1.200 (4)	1.179 (6)	1.17 (1)	1.19 (2)
C(2)–O(4)	1.341 (3)	1.321 (5)	1.36 (1)	1.37 (2)
O(4)–C(5)	1.439 (3)	1.442 (4)	1.43 (1)	1.43 (2)
C(5)–C(6)	1.510 (4)	1.505 (4)	1.51 (2)	1.27 (6) 1.39 (5)
C(6)–N(7)	1.513 (4)	1.519 (4)	1.50 (1)	1.47 (5) 1.51 (3)
N(7)–C(8)	1.497 (3)	1.503 (4)	1.50 (1)	1.49 (1)
N(7)–C(9)	1.504 (3)	1.497 (4)	1.50 (1)	1.51 (3)
N(7)–C(10)	1.496 (3)	1.499 (4)	1.49 (1)	1.44 (2)
			Ion C	
			Ion D	
C(01)–O(011)	1.240 (3)	1.226 (3)	1.24 (2) 1.25 (2)	1.24 (2) 1.21 (2)
C(01)–O(012)	1.270 (3)	1.278 (3)	1.33 (2) 1.33 (2)	1.31 (2) 1.34 (2)
C(01)–C(02)	1.532 (3)	1.538 (3)	1.52 (1)	1.50 (1)
C(02)–O(02)	1.404 (3)	1.406 (3)	1.46 (2) 1.42 (2)	1.40 (1) 1.53 (2)
C(02)–C(03)	1.523 (3)	1.521 (4)	1.52 (1)	1.54 (1)
C(03)–O(03)	1.408 (2)	1.401 (4)	1.40 (1)	1.40 (1)
C(03)–C(04)	1.527 (2)	1.538 (4)	1.55 (1)	1.54 (1)
C(04)–O(041)	1.211 (2)	1.218 (3)	1.21 (1)	1.21 (1)
C(04)–O(042)	1.284 (2)	1.278 (4)	1.29 (1)	1.28 (1)
O(042)–H(042)	0.88	1.07		

While the dimensions found for ion *A* of APBIT2 are in fair agreement with the expected values, those calculated for ion *B* are clearly unreliable. This is not surprising as the thermal parameters indicate that most, or all atoms in ion *B* are affected by disorder, but only C(6*B*) has been treated as two partial atoms. The overall conformation of ion *B* is approximately the same as that of ion *A*. In APBIT2 as well as in APBIT1 the acetylcholine ions are found in a *gauche-gauche* conformation, but it is worth noting that the chirality of the acetylcholine ions in APBIT2 is different from that

found in APBIT1, although both structures are hydrogen (+)-tartrates.

#### Hydrogen tartrate ions

In the structures of ARABIT and APBIT1 the hydrogen atom of the carboxyl group is bonded to O(042). The dimensions (Table 3) of the carboxylate group in the two structures are clearly affected by the hydrogen bonding, resulting in great differences in the C—O bond lengths of the groups. The same pattern is found in the structure of APBIT2, and as direct

Table 4. Valency angles (°)

For APBIT2 the value referring to a partial atom with end-number 1 is always given first.

	ARABIT	APBIT1	APBIT2	
			Ion <i>A</i>	Ion <i>B</i>
C(1)—C(2)—O(3)	125.8 (2)	126.3 (4)	127 (1)	126 (1)
C(1)—C(2)—O(4)	111.2 (2)	112.1 (3)	110 (1)	110 (1)
O(3)—C(2)—O(4)	123.0 (2)	121.6 (4)	124 (1)	124 (1)
C(2)—O(4)—C(5)	116.6 (2)	119.3 (3)	118 (1)	116 (1)
O(4)—C(5)—C(6)	108.7 (2)	111.7 (2)	113 (1)	125 (3) 118 (2)
C(5)—C(6)—N(7)	116.2 (2)	116.3 (2)	115 (1)	135 (4) 122 (3)
C(6)—N(7)—C(8)	111.8 (2)	111.7 (2)	113 (1)	116 (2) 107 (2)
C(6)—N(7)—C(9)	110.7 (2)	111.7 (2)	111 (1)	96 (3) 120 (2)
C(6)—N(7)—C(10)	107.0 (2)	106.3 (2)	106 (1)	115 (2) 100 (2)
C(8)—N(7)—C(9)	108.9 (2)	110.4 (2)	109 (1)	110 (1)
C(8)—N(7)—C(10)	110.0 (2)	107.9 (2)	108 (1)	111 (1)
C(9)—N(7)—C(10)	108.3 (2)	108.7 (3)	109 (1)	107 (1)
			Ion <i>C</i>	Ion <i>D</i>
O(011)—C(01)—O(012)	126.4 (3)	126.3 (3)	129 (1) 123 (1)	126 (1) 124 (1)
O(011)—C(01)—C(02)	116.9 (2)	118.5 (2)	121 (1) 121 (1)	121 (1) 120 (1)
O(012)—C(01)—C(02)	116.6 (2)	115.2 (2)	111 (1) 115 (1)	113 (1) 116 (1)
C(01)—C(02)—O(02)	109.9 (2)	110.1 (2)	109 (1) 111 (1)	115 (1) 104 (1)
C(01)—C(02)—C(03)	109.7 (2)	110.3 (2)	113 (1)	111 (1)
O(02)—C(02)—C(03)	110.8 (2)	110.8 (2)	104 (1) 116 (1)	110 (1) 105 (1)
C(02)—C(03)—O(03)	110.3 (1)	110.1 (2)	112 (1)	112 (1)
C(02)—C(03)—C(04)	111.3 (1)	111.5 (2)	109 (1)	112 (1)
O(03)—C(03)—C(04)	110.1 (1)	110.6 (2)	112 (1)	110 (1)
C(03)—C(04)—O(041)	120.4 (2)	119.1 (3)	120 (1)	117 (1)
C(03)—C(04)—O(042)	113.5 (1)	114.4 (2)	112 (1)	116 (1)
O(041)—C(04)—O(042)	126.1 (2)	126.4 (3)	128 (1)	127 (1)

Table 5. Torsion angles (°)

For APBIT2 the value referring to a partial atom with end-number 1 is always given first.

	ARABIT	APBIT1	APBIT2	
			Ion <i>A</i>	Ion <i>B</i>
C(1)—C(2)—O(4)—C(5)	±179.1 (2)	177.0 (3)	177 (1)	176 (1)
C(2)—O(4)—C(5)—C(6)	±162.6 (2)	−93.6 (3)	103 (1)	124 (4) 92 (3)
O(4)—C(5)—C(6)—N(7)	±78.0 (2)	−63.6 (3)	79 (1)	−10 (8) 63 (4)
C(5)—C(6)—N(7)—C(8)	∓56.7 (2)	66.0 (3)	−57 (1)	−1 (7) −69 (3)
C(5)—C(6)—N(7)—C(9)	±65.0 (2)	−58.2 (3)	66 (1)	114 (6) 58 (4)
C(5)—C(6)—N(7)—C(10)	∓177.2 (2)	−176.6 (2)	−175 (1)	−133 (5) 175 (3)
			Ion <i>C</i>	Ion <i>D</i>
C(01)—C(02)—C(03)—C(04)	±173.8 (1)	172.2 (2)	175 (1)	169 (1)
O(02)—C(02)—C(03)—O(03)	∓70.3 (2)	−73.1 (3)	−68 (1) −80 (1)	−84 (1) −66 (1)

localization of hydrogen atoms was prohibited by the low accuracy of the structure it is impossible to establish some groups as carboxylate groups and others as carboxyl groups. The dimensions and conformations of the hydrogen tartrate ions in ARABIT and APBIT1 are very similar to those previously found for the ion (Carlström, 1973). As indicated in Table 6, each carboxyl or carboxylate group forms a plane. The deviations of the  $\alpha$ -hydroxyl oxygen atoms from these planes are small. Also, the hydroxyl hydrogen atoms were found in the planes in positions suggesting the existence of *intraionic* hydrogen bonds (Table 7) to those oxygen atoms of the carboxyl(ate) groups which are bonded to carbon *via* the shorter C—O bond.

The disorder in the hydrogen tartrate ions of APBIT2 has been simulated, as indicated above, by splitting each of three oxygen atoms at one end of each of the two hydrogen tartrate ions into two. The typical distance between two halves is 0.4–0.5 Å. The numbering has been chosen so as to give maximum coplanarity to the atoms O(011*n*), O(012*n*), C(01), and

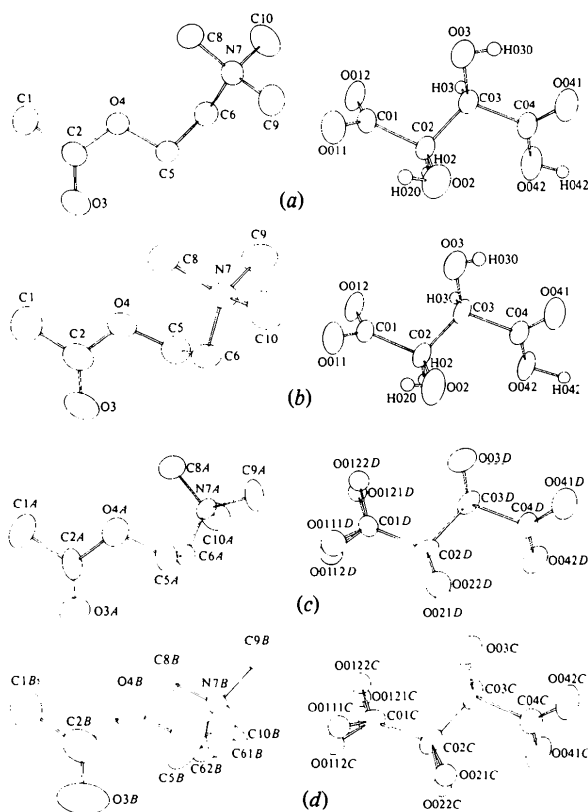


Fig. 1. Acetylcholine ions and hydrogen tartrate ions as found in (a) ARABIT, (b) APBIT1, and (c), (d) APBIT2. Atoms are represented by their thermal ellipsoids drawn at the 50% probability level. For clarity hydrogen atoms of acetylcholine ions have been omitted. Drawings were produced by ORTEP (Johnson, 1971).

Table 6. *Least-squares planes through the carboxyl and carboxylate groups and distances of pertinent atoms from the planes*

Significant deviations out of the plane were not found for ARABIT and APBIT1. The maximum deviation calculated for APBIT2 was 0.04 Å. For APBIT2 values referring to planes involving partial atoms with end-number 1 are given first. Numbers in parentheses refer to distances to atoms having an end-number different from that of the atoms in the plane. Atoms marked ' are those hydrogen bonded to the carboxylate group.

E.s.d.'s are  $\leq 0.01$  Å for ARABIT and APBIT1 and  $\leq 0.02$  Å for APBIT2.

The calculated e.s.d.'s for angles between planes are  $< 3^\circ$ .

Plane I C(01), C(02), O(011), O(012)	$\Delta O(02)$	$\Delta O(042)'$	$\Delta H(042)'$
ARABIT	0.07	0.55	0.36
APBIT1	0.04	0.15	0.03
		$\Delta O(012n)'$	
APBIT2, ion C	0.10 (0.47)	0.62 0.29	
	0.01 (0.39)	1.01 0.64	
APBIT2, ion D	0.09 (0.27)	0.23 0.14	
	0.72 (0.31)	0.60 0.21	

Plane II C(03), C(04), O(041), O(042)	$\Delta O(03)$	$\Delta O(012)'$	$\Delta H(042)$
ARABIT	0.01	0.71	0.22
APBIT1	0.13	0.18	0.14
		$\Delta O(042)'$	
APBIT2, ion C	0.06	0.06	
APBIT2, ion D	0.06	0.02	

Angle plane I—plane II ( $^\circ$ )

ARABIT	64
APBIT1	61
APBIT2, ion C	55 77
APBIT2, ion D	74 87

Angle between carboxyl(ate) groups, connected *via* a hydrogen bond ( $^\circ$ )

ARABIT	62
APBIT1	61
APBIT2, disordered	42, 24, 27, 20
APBIT2, ordered	14

C(02),  $n = 1, 2$ . Physically this corresponds to roughly a rotation of the carboxyl(ate) groups around the C—C bond of about  $20^\circ$ . The bond lengths, angles and torsion angles calculated for this model are in fair agreement with expected values and give no reason for supposing that the model does not represent reality reasonably well.

### Packing

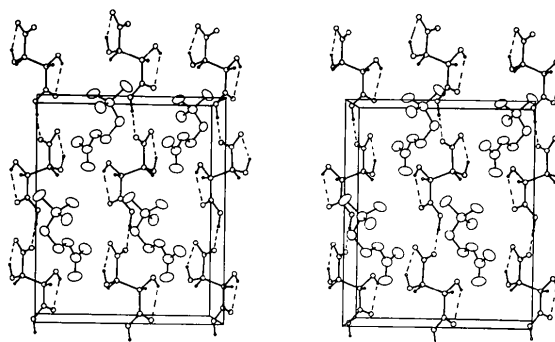
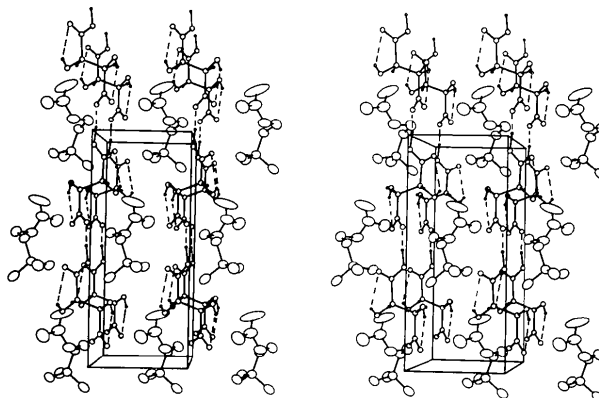
In the structures of ARABIT and of APBIT1 (Figs. 2 and 3), the hydrogen tartrate ions are connected in

Table 7. Distances of possible interactions of the type  $X-H \cdots Y$  (Å)

I. Contacts between carboxyl(ate) groups		
ARABIT	O(042) $\cdots$ O(012) $(1-x, 2-y, \frac{1}{2}+z)$	2.486 (2)
APBIT1	O(042) $\cdots$ O(012) $(-x, \frac{1}{2}+y, -z)$	2.473 (4)
APBIT2	O(042C) $\cdots$ O(042D) $(x+1, y, z)$	2.49 (1)
	O(0121C) $\cdots$ O(0121D) $(x, y+1, z)$	2.48 (2)
	O(0122C) $\cdots$ O(0121D) $(x, y+1, z)$	2.51 (2)
	O(0121C) $\cdots$ O(0122D) $(x, y+1, z)$	2.48 (2)
	O(0122C) $\cdots$ O(0122D) $(x, y+1, z)$	2.45 (2)
II. Contacts between hydroxy groups and carboxyl(ate) groups in neighbouring ions		
APBIT2	O(021C) $\cdots$ O(0111D) $(x, y, z)$	2.89 (2)
	O(021C) $\cdots$ O(0112D) $(x, y, z)$	2.83 (2)
	O(022C) $\cdots$ O(0111D) $(x, y, z)$	2.96 (2)
	O(022C) $\cdots$ O(0112D) $(x, y, z)$	2.85 (2)
	O(021D) $\cdots$ O(0111C) $(x, y, z)$	3.00 (2)
	O(021D) $\cdots$ O(0112C) $(x, y, z)$	2.83 (2)
	O(022D) $\cdots$ O(0111C) $(x, y, z)$	2.80 (2)
	O(022D) $\cdots$ O(0112C) $(x, y, z)$	2.70 (2)
III. Intraionic contacts		
ARABIT	O(02) $\cdots$ O(011)	2.582 (4)
	O(03) $\cdots$ O(041)	2.639 (3)
APBIT1	O(02) $\cdots$ O(011)	2.616 (4)
	O(03) $\cdots$ O(041)	2.636 (4)
APBIT2	O(021C) $\cdots$ O(0111C)	2.64 (2)
	[O(022C) $\cdots$ O(0111C)	2.71 (2)]
	O(022C) $\cdots$ O(0112C)	2.68 (2)
	[O(021C) $\cdots$ O(0112C)	2.68 (2)]
	O(03C) $\cdots$ O(042C)	2.57 (1)
	O(021D) $\cdots$ O(0111D)	2.75 (2)
	[O(022D) $\cdots$ O(0111D)	2.55 (2)]
	O(022D) $\cdots$ O(0112D)	2.61 (2)
	[O(021D) $\cdots$ O(0112D)	2.75 (2)]
	O(03D) $\cdots$ O(041D)	2.57 (1)

infinite chains *via* hydrogen bonds between carboxyl and carboxylate groups. The angles between the planes of hydrogen-bonded groups in the two structures are very similar (Table 6). The hydroxyl groups do not form *interionic* hydrogen bonds, and the chains have only few and inferior contacts shorter than the sum of the van der Waals radii to neighbouring ions. This also means that strong contacts to acetylcholine ions are absent. No hydrogen bonds to the oxygen atoms of the acetylcholine ions exist and direct contacts between the formally charged groups in the structures seem to play no major role. It seems as if the conformational variation observed for the acetylcholine ion from one crystal structure to another is caused less by specific packing forces exerting pressure on the ion than by the tendency of the flexible ion to occupy the available space, choosing the most appropriate of nearly equi-energetic conformers.

In the structure of APBIT2, Fig. 4, the hydrogen tartrate ions are also connected in infinite chains *via* hydrogen bonds between carboxylate groups. The crystallographically independent hydrogen tartrate ions alternate in each chain. The planes of hydrogen-bonded

Fig. 2. Stereoview of the packing of ARABIT.  $x$  is  $\rightarrow$ ,  $z$  is  $\downarrow$ . *Intra- and interionic* hydrogen bonds are indicated by broken lines.Fig. 3. Stereoview of the packing of APBIT1,  $x$  is  $\rightarrow$ ,  $y$  is  $\uparrow$ . *Intra- and interionic* hydrogen bonds are indicated by broken lines.

groups are, in the ordered as well as in the disordered region, approximately parallel (Table 6), in contrast to the pattern found in the two other acetylcholine hydrogen tartrate structures. The distances between hydrogen-bonded atoms are virtually unaffected by the disorder and no conclusions can be drawn concerning the possible interdependence of the disordered groups. The chains are linked to parallel chains *via* pairs of hydrogen bonds from the disordered hydroxyl groups to disordered carboxyl(ate) groups. Although the O—O distances involved in these hydrogen bonds are affected by the disorder, all calculated distances (Table 7) are within the range normally accepted for hydrogen-bonded oxygen atoms. The more ordered hydroxyl groups do not form *interionic* hydrogen bonds. It can be noticed that the possible *intraionic* hydrogen bond involves O(041) in the hydrogen tartrate ion *D*, in similarity with the situation found for ARABIT and APBIT1, but involves O(042) in the other. O(042) of both ions of APBIT2 is the oxygen atom involved in the chain-forming hydrogen bond and the one with the longer C—O bond.

The described *interionic* hydrogen bonds between the hydrogen tartrate ions link them into an open network (Fig. 4). The acetylcholine ions are found in the holes of this network. The ester group of ion *A* is

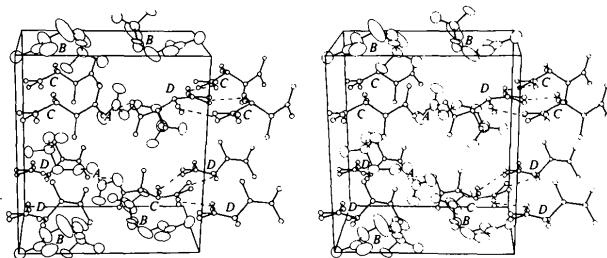


Fig. 4. Stereoview of the packing of APBIT2.  $x$  is  $\rightarrow$ ,  $z$  is  $\downarrow$ . Only the interionic hydrogen bonds are indicated.

squeezed between neighbouring carboxyl(ate) groups in the more ordered region ( $x \approx \frac{1}{2}$ ). The best plane through the atoms C(1A)–C(5A) is nearly parallel with the planes of the adjacent carboxyl(ate) groups. Contacts much shorter than the sum of the van der Waals radii are not found between these planar groups. Also, the best plane through the ester groups of acetylcholine ion *B* is approximately parallel with the carboxyl(ate) groups of two adjacent hydrogen tartrate ions, but the ester group is not squeezed between its neighbours in the same way. The packing of the planar groups around ions *A* and *B* does not seem to be specially favourable, when correlated with the electrostatic potential of the ester group (Johansen, Rettrup & Jensen, 1980). Ion *B* has closer contacts to single atoms in adjacent ions than found for ion *A* (Table 8). Distances to corresponding partial atoms are rather different, and it therefore seems quite reasonable that the acetylcholine ion *B* is found to be strongly affected by the disorder.

While it is possible to explain why acetylcholine ion *B*, and not *A*, is affected by the disorder, it is much harder to understand why the structure is disordered. Apart from the above-mentioned short contacts to atoms of ion *B*, no other extraordinarily short interionic distances are found. The density of the crystals of APBIT2 is slightly higher than those found for the other two acetylcholine hydrogen tartrates (Table 1), but the greatest deviations of atoms from their average positions are still found in the APBIT2 structure. It is far from unusual to find acetylcholine ions which show strong thermal motions (or disorder) (Jagner & Jensen, 1977, and references therein). This may be correlated with the well established flexibility of

Table 8. Selected distances (Å) between ion *B* and the two neighbouring hydrogen tartrate ions in APBIT2

C(2 <i>B</i> )–O(022 <i>C</i> ) ( $x, y + 1, z$ )	3.04 (2)
C(2 <i>B</i> )–O(021 <i>C</i> ) ( $x, y + 1, z$ )	3.44 (2)
C(2 <i>B</i> )–O(0121 <i>D</i> ) ( $-x, 1\frac{1}{2} + y, -z$ )	2.96 (2)
C(2 <i>B</i> )–O(0122 <i>D</i> ) ( $-x, 1\frac{1}{2} + y, -z$ )	3.33 (2)
O(3 <i>B</i> )–O(0121 <i>D</i> ) ( $-x, 1\frac{1}{2} + y, -z$ )	3.04 (2)
O(3 <i>B</i> )–O(0122 <i>D</i> ) ( $-x, 1\frac{1}{2} + y, -z$ )	3.39 (2)

the ion (e.g. Pullman, 1977), which means that it takes only very little energy to change the conformation of the ion. But the question why the present disordered structure is more favourable than a corresponding ordered structure has not been answered.

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