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Structures of Acetylcholine Picrate and Methoxycarbonylcholine Picrate Hemihydrate

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Abstract. Acetylcholine picrate, $C_7H_{16}NO_2^+.C_6H_2N_3O_7^-$, $M_r = 374{\cdot}3$, orthorhombic, *Pbca*, at 105 K: $a = 18{\cdot}799\,(4)$, $b = 7{\cdot}726\,(2)$, $c = 22{\cdot}878\,(4)$ Å, $V = 3323\,(2)$ Å^3, $Z = 8$, D_m(295 K, flotation) = 1·44, D_x(105 K) = 1·496 Mg m^{-3}, μ(Mo $K\alpha$) = 0·120 mm^{-1}, $F(000) = 1568$, m.p. (hot-stage microscope) 381–382 K, $R = 0{\cdot}048$ for 1049 observed $[I \geq 3{\cdot}0\sigma(I)]$ reflections. Methoxycarbonylcholine picrate hemihydrate, $C_7H_{16}NO_3^+.C_6H_2N_3O_7^-.\frac{1}{2}H_2O$, $M_r = 399{\cdot}3$, monoclinic, $P2/n$, at 105 K: $a = 11{\cdot}337\,(16)$, $b = 7{\cdot}279\,(2)$, $c = 21{\cdot}424\,(13)$ Å, $\beta = 103{\cdot}01\,(7)°$, $V = 1723\,(4)$ Å^3, $Z = 4$, D_m(295 K, flotation) = 1·49, D_x(105 K) = 1·539 Mg m^{-3}, μ(Mo $K\alpha$) = 0·126 mm^{-1}, $F(000) = 836$, m.p. (hot-stage microscope) 391–391·5 K, $R = 0{\cdot}033$ for 6359 observed $[I \geq 3{\cdot}0\sigma(I)]$ reflections. The acetylcholine ion as well as the methoxycarbonylcholine ion have as first neighbours a great number of oxygen atoms. Contacts to the quaternary ammonium group do not seem to be more important than contacts to the acetyl or methoxycarbonyl moieties. No direct contacts between aromatic rings and quaternary ammonium groups are found.

Introduction. The crystal structure determinations of acetylcholine picrate (ACPICR) and methoxycarbonylcholine picrate hemihydrate (MECOPI) were performed as part of conformational studies of choline derivatives in the solid state. It has earlier been found that the dimensions of choline derivatives change as a function of the actual conformation (Jensen, 1984*a*). A great number of the known crystal structures of choline esters and other choline derivatives are of low accuracy. This is caused by strong thermal motion or disorder in the crystals, and in order to minimize thermal effects and to obtain more precise geometrical data low-temperature studies have been performed. A preliminary account of other crystal structures in the series has been presented (Jensen, 1984*b*). The methoxycarbonylcholine ion has earlier been observed in the unusual fully extended conformation (Jensen, 1979), while more folded conformations of the ethoxycarbonylcholine ion were found (Jensen, 1981). Ethoxycarbonylcholine picrate hemihydrate was prepared and shown (films) to be isomorphic with methoxycarbonylcholine picrate hemihydrate. No further studies of these crystals are planned.

Experimental. The title compounds were prepared by mixing aqueous ethanolic solutions of acetylcholine iodide and methoxycarbonylcholine iodide (Jensen, 1979), respectively, with an aqueous ethanolic solution of picric acid. Single crystals from aqueous ethanol. Enraf–Nonius CAD-4 diffractometer and low-temperature device, graphite-monochromated Mo $K\alpha$ radiation [λ(Mo $K\alpha$) = 0·71073 Å]. Temperature recorded with a thermocouple, variation within 1 K. Cell parameters and orientation matrix for ACPICR from 18 reflections ($10 \leq \theta \leq 18°$) and for MECOPI from 22 reflections ($17 \leq \theta \leq 21°$). No corrections for absorption or secondary extinction. Three intensity control reflections measured every 10000 s; no systematic variation. ω–2θ scan. For ACPICR: crystal size 0·15 × 0·2 × 0·3 mm, $\theta_{\max} = 25°$, range of hkl $-22 \leq h \leq 19$, $0 \leq k \leq 9$, $0 \leq l \leq 26$. 2921 unique reflections, 1872 unobserved. $R_{\rm int} = 0{\cdot}05$. For MECOPI: crystal size 0·35 × 0·4 × 0·4 mm, $\theta_{\max} = 37°$, range of hkl $-11 \leq h \leq 19$, $0 \leq k \leq 12$, $-36 \leq l \leq 34$. 8748 unique reflections, 2389 unobserved. $R_{\rm int} = 0{\cdot}013$. Non-hydrogen atoms localized by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms found in difference maps. Structure refinement (positional parameters for all atoms, anisotropic thermal parameters for non-hydrogen atoms) by least squares minimizing $\sum w(|F_o| - k|F_c|)^2$, $w = 1$ for ACPICR and Hughes-type for MECOPI, $wR = 0{\cdot}042$. All calculations by means of *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Atomic scattering factors as implemented in *XRAY*76. For both structures, features in final difference Fourier map $\leq \pm 0{\cdot}5$ e Å^{-3}.

Discussion. The final atomic coordinates and thermal parameters are given in Table 1.* Bond lengths, valency angles, selected torsion angles and interplanar angles are given in Table 2. The ions with the atomic

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions, dimensions involving H atoms and deviations from planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44655 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional and equivalent isotropic thermal parameters for non-hydrogen atoms*

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2 × 10^2)
ACPICR				
C(1)	0·0400 (4)	0·2090 (8)	0·0204 (3)	3·4
C(2)	0·0705 (3)	0·1635 (6)	0·0783 (2)	2·6
O(3)	0·1202 (2)	0·2345 (5)	0·1011 (2)	3·2
O(4)	0·0356 (2)	0·0294 (4)	0·1031 (1)	2·5
C(5)	0·0593 (3)	−0·0165 (7)	0·1615 (2)	2·4
C(6)	0·1274 (3)	−0·1197 (6)	0·1619 (2)	2·3
N(7)	0·1206 (2)	−0·3107 (5)	0·1477 (2)	2·1
C(8)	0·0854 (3)	−0·3380 (7)	0·0895 (2)	2·5
C(9)	0·0793 (3)	−0·4045 (7)	0·1941 (2)	2·4
C(10)	0·1947 (3)	−0·3851 (7)	0·1458 (2)	2·6
C(21)	0·2828 (3)	0·1927 (6)	−0·1758 (2)	2·2
C(22)	0·3294 (3)	0·1171 (7)	−0·1320 (2)	2·5
C(23)	0·3066 (3)	0·0387 (7)	−0·0820 (2)	2·7
C(24)	0·2349 (3)	0·0210 (6)	−0·0721 (2)	2·6
C(25)	0·1847 (3)	0·0812 (7)	−0·1119 (2)	2·6
C(26)	0·2076 (3)	0·1605 (7)	−0·1616 (2)	2·1
O(21)	0·3024 (2)	0·2805 (5)	−0·2180 (1)	3·4
N(22)	0·4064 (2)	0·1256 (6)	−0·1409 (2)	4·1
O(221)	0·4301 (2)	0·1717 (8)	−0·1877 (3)	10·6
O(222)	0·4452 (2)	0·0799 (7)	−0·1018 (2)	6·0
N(24)	0·2110 (3)	−0·0634 (6)	−0·0196 (2)	4·0
O(241)	0·2553 (3)	−0·1085 (6)	0·0175 (2)	5·8
O(242)	0·1462 (3)	−0·0885 (6)	−0·0140 (2)	5·3
N(26)	0·1534 (2)	0·2199 (6)	−0·2026 (2)	2·9
O(261)	0·0929 (2)	0·2430 (6)	−0·1836 (2)	4·8
O(262)	0·1692 (2)	0·2409 (6)	−0·2537 (2)	4·6
MECOPI				
C(11)	0·65331 (9)	0·6356 (1)	0·53070 (4)	2·27
O(1)	0·67581 (5)	0·7591 (1)	0·48193 (3)	1·60
C(2)	0·60739 (7)	0·7274 (1)	0·42366 (4)	1·41
O(3)	0·53688 (6)	0·6032 (1)	0·40819 (3)	1·97
O(4)	0·63237 (5)	0·8590 (1)	0·38489 (3)	1·53
C(5)	0·57149 (7)	0·8375 (1)	0·31814 (4)	1·49
C(6)	0·60339 (7)	1·0022 (1)	0·28225 (4)	1·40
N(7)	0·52400 (6)	1·1691 (1)	0·28195 (3)	1·21
C(8)	0·51247 (9)	1·2213 (1)	0·34798 (4)	2·02
C(9)	0·40082 (7)	1·1343 (1)	0·24033 (4)	1·76
C(10)	0·58000 (8)	1·3270 (1)	0·25386 (4)	1·71
C(21)	0·08407 (7)	0·7339 (1)	0·38256 (4)	1·35
C(22)	0·17983 (6)	0·8143 (1)	0·43251 (4)	1·37
C(23)	0·17183 (7)	0·8408 (1)	0·49510 (4)	1·33
C(24)	0·06611 (7)	0·7901 (1)	0·51372 (3)	1·23
C(25)	−0·03149 (6)	0·7138 (1)	0·46998 (3)	1·16
C(26)	−0·02297 (6)	0·6919 (1)	0·40759 (3)	1·10
O(21)	0·09256 (6)	0·6981 (1)	0·32706 (3)	2·14
N(22)	0·29276 (6)	0·8718 (1)	0·41665 (4)	1·79
O(221)	0·29100 (7)	0·9178 (1)	0·36108 (4)	3·27
O(222)	0·38506 (6)	0·8742 (1)	0·45975 (4)	2·37
N(24)	0·05467 (7)	0·8199 (1)	0·57832 (3)	1·53
O(241)	0·13805 (7)	0·8982 (1)	0·61614 (3)	2·21
O(242)	−0·03815 (6)	0·7661 (1)	0·59397 (3)	2·31
N(26)	−0·13087 (6)	0·6226 (1)	0·36407 (3)	1·22
O(261)	−0·19489 (5)	0·5111 (1)	0·38504 (3)	1·66
O(262)	−0·15578 (6)	0·6794 (1)	0·30880 (3)	1·97
O(8)	0·25	0·5418 (2)	0·25	3·93

numbering are shown in Fig. 1. The dimensions of the acetylcholine ion and of the methoxycarbonylcholine ion found in the present low-temperature studies confirm the patterns previously observed in a large number of less accurate room temperature studies of acetylcholine salts and analogues (Jensen, 1984*a*). The C(5)—C(6) bond is about 0·02 Å shorter than a normal C_{sp^3}—C_{sp^3} bond owing to the substitution with O and the quaternary ammonium N (Allinger, Schäfer, Siam, Klimkowski & Van Alsenoy, 1985). The magnitude of the angle O(4)—C(5)—C(6) can vary by more than 10° as a function of the conformation of the choline ester, being as small as 100° when both of the torsion angles C(2)—O(4)—C(5)—C(6) and O(4)—C(5)—C(6)—N(7) are 180° (Jensen, 1979) and about

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

X(1) is C(1) in ACPICR and O(1) in MECOPI. Interplanar angles for the picrate ions are also given.

	ACPICR	MECOPI
C(11)—O(1)		1·444 (1)
X(1)—C(2)	1·486 (8)	1·333 (1)
C(2)—O(3)	1·203 (7)	1·203 (1)
C(2)—O(4)	1·351 (6)	1·339 (1)
O(4)—C(5)	1·452 (5)	1·450 (1)
C(5)—C(6)	1·508 (8)	1·511 (1)
C(6)—N(7)	1·516 (6)	1·511 (1)
N(7)—C(8)	1·502 (7)	1·499 (1)
N(7)—C(9)	1·502 (7)	1·500 (2)
N(7)—C(10)	1·508 (7)	1·503 (2)
C(21)—C(22)	1·454 (7)	1·464 (2)
C(22)—C(23)	1·364 (7)	1·378 (2)
C(23)—C(24)	1·374 (8)	1·395 (2)
C(24)—C(25)	1·391 (7)	1·394 (2)
C(25)—C(26)	1·361 (7)	1·371 (1)
C(26)—C(21)	1·472 (8)	1·465 (2)
C(21)—O(21)	1·236 (6)	1·242 (1)
C(22)—N(22)	1·463 (7)	1·458 (2)
N(22)—O(221)	1·213 (8)	1·233 (1)
N(22)—O(222)	1·207 (6)	1·230 (2)
C(24)—N(24)	1·439 (7)	1·435 (1)
N(24)—O(241)	1·239 (7)	1·237 (1)
N(24)—O(242)	1·240 (8)	1·238 (2)
C(26)—N(26)	1·459 (7)	1·451 (2)
N(26)—O(261)	1·231 (6)	1·239 (1)
N(26)—O(262)	1·217 (6)	1·226 (1)
C(11)—O(1)—C(2)		114·21 (7)
X(1)—C(2)—O(3)	125·4 (5)	126·74 (8)
X(1)—C(2)—O(4)	111·6 (5)	107·32 (7)
O(3)—C(2)—O(4)	123·0 (4)	125·94 (8)
C(2)—O(4)—C(5)	115·1 (4)	114·49 (7)
O(4)—C(5)—C(6)	113·3 (4)	107·52 (6)
C(5)—C(6)—N(7)	116·2 (4)	115·42 (6)
C(6)—N(7)—C(8)	111·3 (4)	112·23 (6)
C(6)—N(7)—C(9)	111·2 (4)	109·92 (8)
C(6)—N(7)—C(10)	107·4 (4)	108·16 (7)
C(8)—N(7)—C(9)	109·3 (4)	109·68 (6)
C(8)—N(7)—C(10)	109·2 (4)	108·58 (7)
C(9)—N(7)—C(10)	108·3 (4)	108·17 (8)
C(21)—C(22)—C(23)	124·6 (5)	124·54 (9)
C(22)—C(23)—C(24)	119·4 (5)	119·35 (7)
C(23)—C(24)—C(25)	121·6 (5)	121·06 (9)
C(24)—C(25)—C(26)	118·8 (5)	118·83 (8)
C(25)—C(26)—C(21)	124·3 (5)	125·35 (6)
C(26)—C(21)—C(22)	111·0 (4)	110·8 (1)
O(21)—C(21)—C(22)	125·4 (5)	125·39 (9)
O(21)—C(21)—C(26)	123·5 (5)	123·76 (7)
C(21)—C(22)—N(22)	118·8 (4)	119·34 (9)
C(23)—C(22)—N(22)	116·6 (5)	116·12 (7)
C(22)—N(22)—O(221)	120·0 (4)	118·62 (7)
C(22)—N(22)—O(222)	118·8 (4)	118·2 (1)
O(221)—N(22)—O(222)	121·2 (4)	123·18 (9)
C(23)—C(24)—N(24)	119·3 (5)	120·37 (7)
C(25)—C(24)—N(24)	119·1 (5)	121·06 (9)
C(24)—N(24)—O(241)	119·3 (5)	118·66 (9)
C(24)—N(24)—O(242)	117·6 (5)	118·70 (7)
O(241)—N(24)—O(242)	123·1 (5)	122·6 (1)
C(25)—C(26)—N(26)	117·3 (5)	115·63 (8)
C(21)—C(26)—N(26)	118·4 (4)	119·0 (1)
C(26)—N(26)—O(261)	117·6 (4)	118·22 (9)
C(26)—N(26)—O(262)	119·3 (4)	118·74 (7)
O(261)—N(26)—O(262)	123·1 (4)	123·03 (8)
C(11)—O(1)—C(2)—O(4)		∓175·9 (1)
X(1)—C(2)—O(4)—C(5)	±176·4 (4)	∓175·8 (1)
C(2)—O(4)—C(5)—C(6)	±78·1 (5)	∓176·6 (1)
O(4)—C(5)—C(6)—N(7)	±78·8 (5)	±85·9 (1)
C(5)—C(6)—N(7)—C(8)	∓56·1 (5)	∓51·2 (1)
C(5)—C(6)—N(7)—C(9)	±66·1 (5)	±71·1 (1)
C(5)—C(6)—N(7)—C(10)	∓175·6 (4)	∓171·0 (1)

Plane I	C(21), C(22), C(23), C(24), C(25), C(26)
Plane II	C(22), N(22), O(221), O(222)
Plane IV	C(24), N(24), O(241), O(242)
Plane VI	C(26), N(26), O(261), O(262)

	ACPICR	MECOPI
∠ Plane I–II (°)	9·1	43·2
Plane I–IV (°)	4·7	4·3
Plane I–VI (°)	22·0	34·7

113° when the mentioned torsion angles are ~80° (*gauche*) as in ACPICR. This type of interdependence between bond angle and torsion angles is well known for acetals and related compounds (Szarek & Horton, 1979).

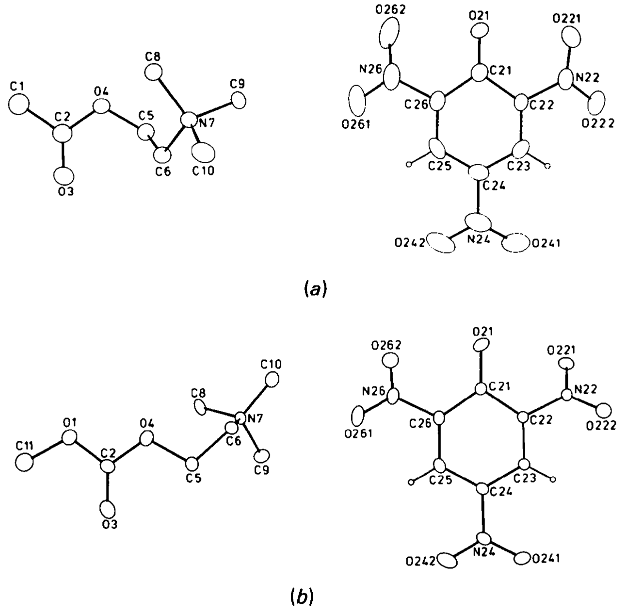
The dimensions of the picrate ion of ACPICR show no significant deviations from the corresponding more accurate dimensions of the picrate ion of MECOPI. The benzene rings are distorted and C(22), C(21) and C(26) deviate up to 0·02 Å in alternating directions from the best plane through the ring. Furthermore, O(21), N(22) and N(26) deviate from the benzene-ring plane, and the crowding is thereby relieved.* This corresponds to what is normally seen in a large number of picrate ions retrieved from the Cambridge Structural Database [Allen *et al.* (1979) (1986 release)].

Table 3. *Selected non-bonded distances* (Å)

ACPICR			
C(6)···O(21^{i})	3·292 (6)	C(10)···O(3^{ii})	3·413 (7)
C(9)···O(21^{i})	3·148 (6)	C(8)···O(242)	3·260 (7)
C(10)···O(21^{i})	3·220 (5)	C(8)···O(222^{iii})	3·243 (7)
C(8)···O(3^{ii})	3·378 (7)	C(1)···O(222^{iv})	3·050 (8)
C(9)···O(3^{ii})	3·591 (7)	C(2)···O(222^{iv})	3·125 (7)
MECOPI			
C(8)···O(3^{i})	3·051 (1)	C(6)···O(21^{v})	3·602 (2)
C(9)···O(8^{i})	3·453 (2)	C(9)···O(21^{v})	3·496 (2)
C(6)···O(241^{ii})	3·314 (4)	C(9)···O(221^{v})	3·131 (3)
C(6)···O(241^{iii})	3·738 (2)	C(5)···O(262^{v})	3·287 (2)
C(10)···O(241^{iii})	3·564 (2)	C(6)···O(262^{v})	3·194 (2)
C(9)···O(242^{iii})	3·437 (2)	C(2)···O(261^{vi})	3·004 (3)
C(10)···O(242^{iii})	3·453 (3)	C(2)···O(222)	2·995 (4)
C(10)···O(21^{iv})	3·550 (2)	O(3)···O(222)	2·988 (2)
C(10)···O(262^{iv})	3·105 (2)	N(24)···O(261^{vii})	2·896 (2)
C(5)···O(21^{v})	3·400 (3)		

Symmetry codes, ACPICR: (i) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (ii) $x, y-1, z$; (iii) $x-\frac{1}{2}, -\frac{1}{2}-y, -z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, -z$.

Symmetry codes, MECOPI: (i) $x, y+1, z$; (ii) $1-x, 2-y, 1-z$; (iii) $\frac{1}{2}+x, 2-y, -\frac{1}{2}+z$; (iv) $\frac{1}{2}-x, 1+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, y, \frac{1}{2}-z$; (vi) $x+1, y, z$; (vii) $-x, 1-y, 1-z$.



(*a*)

(*b*)

Fig. 1. A view of (*a*) the acetylcholine ion and the picrate ion of ACPICR and (*b*) the methoxycarbonylcholine ion and the picrate ion of MECOPI. H atoms have been omitted in order to improve clarity. Atoms are represented by thermal ellipsoids drawn by use of *ORTEP*II (Johnson, 1976) at the 50% probability level.

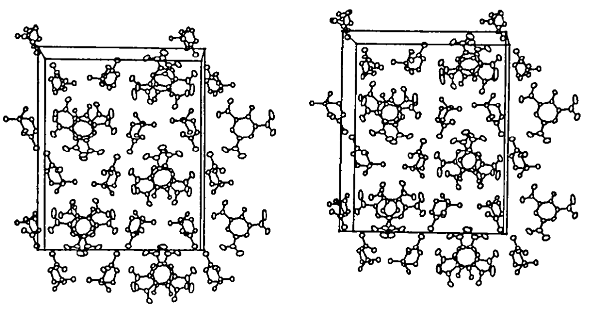


Fig. 2. Stereoview of the packing of ACPICR. *x* is horizontal, *z* is downwards.

The thermal vibrations are generally small for most of the atoms except for those of the nitro groups. In particular, one nitro group in ACPICR [N(22), O(221), O(222)] is strongly vibrating (or slightly disordered). This may correlate with the low percentage of observed reflections measured for ACPICR.

Packing

ACPICR. A stereo view of the packing of ACPICR is shown in Fig. 2. The picrate ions are stacked in columns along the shortest (*b*) axis, the angle between the *ac* plane and the best plane through the six-membered ring being 28·6°. The distance between the planes of adjacent rings is about 3·4 Å. The acetylcholine ions are found between the columns, and nearly all first-neighbour contacts from the quaternary ammonium ion involve oxygen atoms (*cf* Table 3). The shortest contacts [3·050 (8) and 3·125 (7) Å] are, however, found between the acetyl carbon atoms C(1) and C(2) and O(222) ($x-\frac{1}{2}, \frac{1}{2}-y, -z$).

MECOPI. A stereoview of the packing of MECOPI is shown in Fig. 3. Also in this structure are the picrate ions stacked along the *b* axis, and the angle between the ring plane and the *ac* plane is 23·6°. The shortest distance between planes of adjacent rings is here only 3·3 Å. There is, however, no overlap between the rings and the only short contact [2·896 (2) Å] between picrate ions is N(24)···O(261) ($-x, 1-y, 1-z$). The water molecule, which is situated on a twofold axis, forms hydrogen bonds to the two phenolate oxygen atoms. The distances O(8)···O(21) and H(8)···O(21) are 2·921 (2) and 2·11 (2) Å, respectively, and the angle O(8)—H(8)···O(21) is 155 (1)°. The methoxycarbonylcholine ion is surrounded by a number of oxygen atoms (*cf* Table 3). The closest contact to an

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* See deposition footnote.

atom in the quaternary ammonium group is C(8)···O(3) ($x, y+1, z$), 3·051 (1) Å. The carbonyl atom C(2) is involved in two close contacts to O atoms in nitro groups: C(2)···O(261) ($x+1, y, z$) 3·004 (3) and C(2)···O(222) (x, y, z) 2·995 (4) Å. The two O atoms approach the methoxycarbonylcholine ion from each side and in a region attracting negative charge (*cf* Fig. 4). The same type of contact was observed in crystals of ethoxycarbonylcholine iodide (Jensen, 1981).

Crystals of ethoxycarbonylcholine picrate hemihydrate (ETCOPI) were, as earlier mentioned, found to be isomorphic with MECOPI. The cell dimensions at room temperature (film data) are for MECOPI $a = 11{\cdot}46$, $b = 7{\cdot}45$, $c = 21{\cdot}35$ Å, $\beta = 103°$ and for ETCOPI $a = 11{\cdot}83$, $b = 7{\cdot}57$, $c = 21{\cdot}09$ Å, $\beta = 103°$. Only little rearrangement is needed to allow for a methyl group [C(12)] attached to C(11) of MECOPI, if the torsion angle C(2)—O(1)—C(11)—C(12) is ~ 180°. Then C(12), calculated from MECOPI coordinates and dimensions, has only one close contact, C(12)···O(242) ($x+1, y, z$), 2·73 Å. As a increases going from MECOPI to ETCOPI it is assumed that this *trans* arrangement exists in ETCOPI crystals.

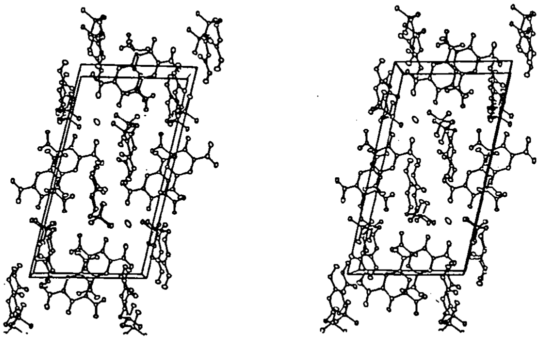

Fig. 3. Stereoview of the packing of MECOPI. x is horizontal, z is downwards.

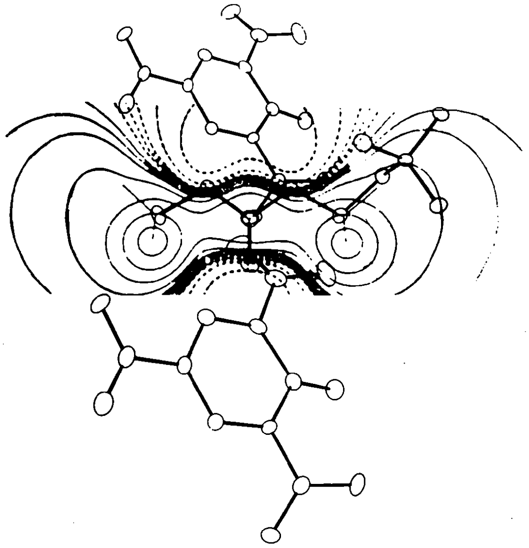

Fig. 4. A methoxycarbonylcholine ion and the two picrate ions having close contacts to the carbonyl C atom. The ester moiety of the methoxycarbonylcholine ion is merging with the corresponding atoms of dimethyl carbonate, for which the electrostatic potential (Johansen, Rettrup & Jensen, 1980) is shown. The potential is that found in a plane $3a$ (~1·6 Å) above (and below) the plane of the ester atoms, and it represents fairly well the potential, which meets the approaching O atoms. Dashed lines indicate negative regions. First contours are ±4·2 kJ mol^{-1}; neighbouring contours differ by a factor of 2.

Contacts from the quaternary ammonium group in choline esters and related molecules to halogenide ions and other counter ions have attracted appreciable interest in recent years (Barrett, Roberts, Burgen & Clore, 1983; Kokkinidis, 1981; Gieren & Kokkinidis, 1981; Rosenfield & Murray-Rust, 1982; Jensen, 1984*a*).

It is possible to indicate preferred positions of halogenide ions relative to the quaternary ammonium group in crystals. The positions of O atoms relative to the quaternary ammonium head do, however, seem to be much more scattered and a possible preference for one type of position is not demonstrated in crystals. This is easy to understand, as the O atoms are generally attached to other molecular fragments. Therefore, their positions will be very dependent on the overall packing, in contrast to the situation for halogenide ions, which are able to move more freely. Association of acetylcholine with aromatic molecules in aqueous solution has been studied by ^{1}H NMR spectroscopic methods (Minch, Sevenair & Henling, 1979), and it was concluded that the quaternary ammonium group was likely to be in van der Waals contact with the aromatic ring and to be positioned with the N atom directly over the ring. Furthermore, in the binding of acetylcholine to a macrocyclic molecule of the speleand type hydrophobic contacts to aromatic rings are supposed to be of importance (Dhaenens, Lacombe, Lehn & Vigneron, 1984). The absence of this kind of contact in the present crystal structures is in agreement with expectations, as nitro groups were found to diminish the influence of the aromatic system on the NMR signals of the ammonium group (Minch *et al.*, 1979). A preliminary examination of crystal structures (Frydenvang, 1988), in which the fragment O—C—C—N$^+R_3$ as well as an aromatic ring system are present, has revealed that the described contact between aromatic rings and the quaternary ammonium group is seldom a striking element in the solid state. Close contacts between the bulky quaternary ammonium group and the flat aromatic ring may be unfavourable for an effective overall crystal packing.

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Structure of Furlone Yellow, $C_{30}H_{24}N_6O_3$

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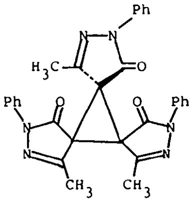
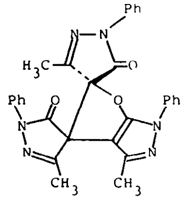
Abstract. Spiro([1,9]dimethyl[3,7]diphenyl[1,3]dioxepino[5,4-*d*:6,7-*d*′]dipyrazole-5,4′-[3]methyl[1]phenylpyrazol[5]one), $M_r = 516{\cdot}6$, monoclinic, $P2_1/c$ (No. 14), $a = 7{\cdot}106\,(2)$, $b = 17{\cdot}691\,(3)$, $c = 21{\cdot}691\,(4)$ Å, $\beta = 105{\cdot}64\,(2)°$, $V = 2625{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}307$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 1080$, $T = 296$ K, final $R = 0{\cdot}031$ for 1094 unique observed reflections. In contrast to former assignments made in solution the compound was found to consist of a heterocyclic seven-membered ring system with 1,3-dioxepin (1,3-dioxacycloheptadiene) structure.

Introduction. 'Furlone yellow' (m.p. 428–429 K), a trimer of 3-methyl-1-phenyl-2-pyrazolin-5-one, was first prepared by Westöö (1953), who assigned the compound the structure *B* possessing a dihydrofuran ring.

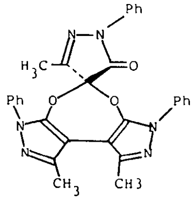
Investigations carried out in solution by ^{1}H and ^{13}C NMR spectroscopy (Mann, Hennig, Wilde, Hauptmann, Behrendt & Kretschmer, 1979) showed the compound to have C_s symmetry, and DNMR measurements were in accordance with the structure *A*, possessing a three-membered ring. In solution, structure *A* was found to be in equilibrium with the non-symmetric isomer *B* proposed by Westöö (1953). However, the NMR data would also be in accordance with the structure *C*. To resolve this ambiguity, we undertook an X-ray diffraction study and in the present paper report the crystal and molecular structure of this quite unusual compound.



(*A*)



(*B*)



(*C*)

Experimental. Pale yellow crystals synthesized by addition of 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one to the oxidized dimer of 3-methyl-1-phenyl-2-pyrazolin-5-one ('pyrazolone-blue') (Westöö, 1953), $0{\cdot}20 \times 0{\cdot}20 \times 0{\cdot}15$ mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, ω–2θ method, lattice parameters from 25 reflections with $4 < \theta < 11°$, two standard reflections measured every hour, no loss of intensity, 2549 reflections (h: 0→6, k: −16→0, l: −20→20) with $\theta < 20°$, 2549 independent, 1094 with $I > 3\sigma(I)$, Lp correction, empirical absorption correction (Walker &

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