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Structures of Muscarone Iodide and Muscarone Picrate

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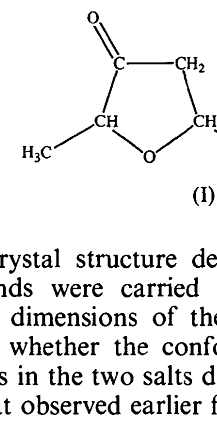
Abstract. (1) (±)-*cis-N,N,N*-Trimethyl(2-methyl-3-oxotetrahydro-5-furyl)methylammonium iodide, $C_9H_{18}NO_2^+.I^-$, $M_r = 299{\cdot}0$, orthorhombic, *Pnam*, $a = 12{\cdot}791\ (2)$, $b = 13{\cdot}097\ (2)$, $c = 7{\cdot}4390\ (9)$ Å, $V = 1246{\cdot}3\ (6)$ Å^3, $Z = 4$, D_x (105 K) = 1·59 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 2·516 mm^{-1}, $F(000) = 592$, $T = 105$ K, m.p. (hot-stage microscope) = 439·0–440·5 K (corrected), $R = 0{\cdot}025$ for 2603 observed reflections $[I \geq 3\sigma(I)]$. The crystal structure is disordered, as each equivalent position can be occupied by either a (+)- or a (−)-muscarone ion. The atoms C4, N7, C9 and H91 are situated on the mirror plane. The space group is different from that previously published for the structure of (±)-muscarone iodide. (2) (±)-*cis-N,N,N*-Trimethyl-(2-methyl-3-oxotetrahydro-5-furyl)methylammonium picrate, $C_9H_{18}NO_2^+.C_6H_2N_3O_7^-$, $M_r = 400{\cdot}3$, triclinic, $P\bar{1}$, $a = 6{\cdot}584\ (3)$, $b = 23{\cdot}127\ (6)$, $c = 11{\cdot}962\ (3)$ Å, $\alpha = 91{\cdot}02\ (2)$, $\beta = 104{\cdot}76\ (3)$, $\gamma = 90{\cdot}37\ (3)°$, $V = 1761\ (2)$ Å^3, $Z = 4$, D_x (105 K) = 1·51 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 0·118 mm^{-1}, $F(000) = 840$, $T = 105$ K, m.p. (hot-stage microscope) = 414–416 K (corrected), $R = 0{\cdot}047$ for 3324 observed reflections $[I \geq 5\sigma(I)]$. The compound crystallizes in the monoclinic space group $P2_1/n$ ($\beta \simeq 105°$) but changes on cooling (105 K) to triclinic $P\bar{1}$ with two muscarone and two picrate ions in the asymmetric unit. Only small conformational differences are seen between the two chemically identical ions in the asymmetric unit. The five-membered rings of the muscarone ions in the two salts have approximately the same overall conformation, but the quaternary ammonium group adopts a *trans* orientation [(O—C—C—N) = ± 157·5 (2)°] in muscarone iodide, while it is in a *gauche* orientation [(O—C—C—N) = ± 68·9 (5) and ± 58·7 (5)°] in muscarone picrate. The conformation of the ring is a distorted twist, $^1T_5$, with a puckering amplitude in the region $\theta_m = 35{\cdot}2$–$38{\cdot}5°$. Crystal packings are stabilized by electrostatic and van der Waals interactions. Charge–charge interactions bring the quaternary ammonium groups close to the iodide ions and the nitro groups of the picrate ions.

Introduction. Muscarone (I) mimics the function of the natural neurotransmitter acetylcholine in the muscarinic as well as in the nicotinic part of the cholinergic nervous system. A high degree of stereospecificity has been observed for many muscarinic agonists, but not for muscarone. It is therefore of interest to compare the conformation of the muscarone ion with that of other more stereospecific muscarinic agonists in order to obtain information on the 'active conformation' of the agonists, when they interact with the receptor site (Frydenvang, 1989).



(I)

The crystal structure determinations of the title compounds were carried out in order to obtain accurate dimensions of the muscarone ion and to examine whether the conformations of the muscarone ions in the two salts differ from each other and from that observed earlier for (±)-muscarone iodide (Pauling & Petcher, 1972). This has until now been the only salt of muscarone studied crystallographically, but no atomic coordinates were published.

Experimental. (±)-*Muscarone iodide*. The compound was kindly donated by Dr Marco De Amici (Istituto Chimico Farmaceutico, Universita di Milano, Italy). Single crystals were obtained by vapour diffusion of dimethoxymethane into a solution of acetone. Crystal size 0·34 × 0·20 × 0·26 mm. Intensity data were sampled on an Enraf–Nonius CAD-4 diffractometer equipped with a low-temperature device and graphite-monochromated Mo $K\alpha$ radiation. The temperature (105 K) was recorded with a thermocouple, variation within 1 K. Cell parameters and the orientation matrix were determined from 25 reflections ($19{\cdot}43 \leq \theta \leq 23{\cdot}21°$). *CRYSTL* was used to define crystal shape and dimensions and *ABSCOR* was used for the absorption correction (Coppens, Leiserowitz & Rabinovich, 1965). Maximum and

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minimum correction values were 0·6625 and 0·5691. Three intensity control reflections were measured every 10^4 s, no systematic variation was observed. $\omega/2\theta$ scan, $\theta_{\max} = 40°$, range of *hkl*: $-10 \leq h \leq 13$, $0 \leq k \leq 23$, $0 \leq l \leq 23$. 4063 unique reflections, 1460 unobserved [$I < 3\sigma(I)$]. $R_{\rm int} = 0{\cdot}035$ (on $F_{\rm obs}$). Calculations were first performed in space group $Pna2_1$ and later in *Pnam*. The iodide was localized by the heavy-atom method. The other non-H atoms were localized by direct methods (*DIRDIF*). H atoms were calculated by *HYDRO* and most of them were identified in the $\Delta\rho$ map. Structure refinement (positional parameters for all atoms, except H11, H12 and H13, anisotropic thermal parameters for non-H atoms, and temperature factors fixed for H atoms) carried out by least-squares minimizations of $\sum w(|F_o| - k|F_c|)^2$, $1/w = |\sigma^2(I) + (0{\cdot}02I)^2|/I$. In space group *Pnam*, final $R = 0{\cdot}025$, $wR = 0{\cdot}024$, $S = 1{\cdot}19$, $(\Delta/\sigma) \leq 0{\cdot}65$. Maximum and minimum heights in final $\Delta\rho$ map were 0·9 and $-1{\cdot}1$ e Å^{-3} (about 0·5 Å from iodide). Atomic scattering factors for C, H, N, O and iodide were used as implemented in the *SDP* package (Frenz, 1982), which was used for all calculations (including *CRYSTL*, *ABSCOR*, *DIRDIF* and *HYDRO* calculations).

(±)-*Muscarone picrate*. The compound was prepared from (±)-muscarone iodide and picric acid dissolved in hot ethanol. Single crystal was obtained by slow cooling of a hot ethanol solution. Crystal size 0·10 × 0·18 × 0·45 mm. Intensity data were collected as for (±)-muscarone iodide. Cell parameters and the orientation matrix were determined from 24 reflections ($12{\cdot}84 \leq \theta \leq 19{\cdot}73°$). No correction for absorption was performed. Three intensity control reflections were measured every 10^4 s, and due to decay (−9·8% in 122 h) corrections were made. $\omega/2\theta$ scan, $\theta_{\max} = 27°$, range of *hkl*: $0 \leq h \leq 8$, $-27 \leq k \leq 27$, $-14 \leq l \leq 13$. 7686 unique reflections, 4362 unobserved [$I < 5\sigma(I)$]. $R_{\rm int} = 0{\cdot}028$ (on $F_{\rm obs}$). All non-H atoms were localized by direct methods (*MULTAN*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) followed by $\Delta\rho$ maps. H atoms were calculated by *HYDRO* and identified in the $\Delta\rho$ map. Structure refinement (positional parameters and anisotropic thermal parameters for non-H atoms, H fixed completely) performed by least-squares minimizations of $\sum w(|F_o| - k|F_c|)^2$, $1/w = |\sigma^2(I) + (0{\cdot}04I)^2|/I$. Final $R = 0{\cdot}047$, $wR = 0{\cdot}062$, $S = 2{\cdot}01$, $(\Delta/\sigma) \leq 0{\cdot}05$. Maximum and minimum heights in final $\Delta\rho$ maps were 0·4 and $-0{\cdot}3$ e Å^{-3}. Atomic scattering factors for uncharged atoms were used as implemented in the *SDP* package (Frenz, 1982), which was used for all calculations (including the *MULTAN* and *HYDRO* calculations).

Discussion. The final atomic coordinates and displacement parameters for the title compounds are given in Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. The ions with the atomic numbering are shown in Figs. 1(*a*)–1(*f*).

(±)-*Muscarone iodide*. The space group for muscarone iodide can be either $Pna2_1$ or *Pnam*, based on the systematic absences. There are four molecules in the unit cell, and $Pna2_1$ was expected to be correct, as it was used for the description of the previously published structure of (±)-muscarone iodide (Pauling & Petcher, 1972). A model in the space group $Pna2_1$ could be refined to an *R* value of 0·028, but the conformation of the muscarone ion was clearly unreasonable: one torsion angle in the five-membered ring was >50°, which is much larger than expected (Cremer & Pople, 1975), and the geometry around the carbonyl group was nonplanar. Some of the atoms in the ring were moved to the opposite side of the 'pseudo mirror plane' ($z = 0{\cdot}5$) in an attempt to achieve a reasonable geometry. The *z* coordinate of the O atom in the ring, O11, had to be fixed to prevent it from moving back to the pseudo mirror plane during refinements and thereby give some unrealistic bond lengths (*e.g.* C2—O11 > 1·50 Å). As the results of the refinements seemed unsatisfactory, a disordered model in the space group *Pnam* was refined. The unit cell contains four formula units, and each equivalent position can thus be occupied by either a (+)- or a (−)-muscarone ion (Fig. 1*b*). The iodide ion and some of the atoms in the muscarone ion (I, C4, N7, C9, H91) are situated on the mirror plane. C9 is one of the methyl groups of the quaternary ammonium group. The two remaining methyl groups of this group are found at each side of the mirror plane, so that the position C8 is always occupied. The atomic coordinates of C8 are however average values of the coordinates of real atoms, and this is reflected in the displacement parameters of C8. In one of the enantiomers the C8 position is occupied by a C atom, for which the torsion angle C5—C6—N7—C is ~180° and in the other enantiomer the atom, which is involved in a torsion angle C5—C6—N7—C ~60°, is found at the position called C8 (*cf.* Fig. 1*b*). Refinements of this model gave geometrically satisfactory results. The final *R* value is 0·025.

The published structure of (±)-muscarone iodide is not compared in detail with this structure at

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* Lists of structure factors, anisotropic displacement parameters, H-atom positions, selected non-bonded distances and angles, deviations from planes and angles between planes, and a figure showing the numbering of the five-membered ring according to Rao, Westhof & Sundaralingam (1981) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54293 (83 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0199]

Table 1. *Final atomic coordinates and thermal parameters* (B_{eq}) *for non-*H *atoms* (*with e.s.d.'s in parentheses*)

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}	Occupancy
Muscarone iodide					
I	0·18088 (1)	0·14357 (1)	−0·250	1·695 (2)	0·5
C1	1·0969 (2)	0·3939 (2)	0·2726 (7)	2·61 (6)	0·5
C2	0·9956 (2)	0·3949 (3)	0·1696 (5)	1·85 (5)	0·5
C3	0·9238 (2)	0·3064 (2)	0·2166 (4)	1·69 (6)	0·5
C4	0·8146 (2)	0·3483 (2)	0·250	1·83 (3)	0·5
C5	0·8262 (2)	0·4601 (2)	0·1872 (4)	1·36 (4)	0·5
C6	0·7716 (2)	0·5375 (2)	0·3061 (4)	1·45 (4)	0·5
N7	0·6582 (1)	0·5584 (2)	0·250	1·67 (3)	0·5
C8	0·6314 (2)	0·6191 (2)	0·0880 (3)	3·13 (4)	1·0
C9	0·5942 (2)	0·4619 (2)	0·250	1·77 (4)	0·5
O11	0·9359 (1)	0·4834 (1)	0·2142 (3)	1·73 (5)	0·5
O12	0·9509 (2)	0·2187 (1)	0·2309 (4)	2·03 (3)	0·5
Muscarone picrate					
C1	−0·3228 (7)	0·6740 (2)	0·1055 (5)	2·9 (1)	
C2	−0·2976 (7)	0·7332 (2)	0·1604 (4)	2·2 (1)	
C3	−0·1356 (6)	0·7354 (2)	0·2775 (4)	1·93 (9)	
C4	0·0216 (7)	0·7823 (2)	0·2717 (4)	2·2 (1)	
C5	−0·0864 (7)	0·8147 (2)	0·1646 (4)	1·84 (9)	
C6	0·0655 (6)	0·8410 (2)	0·1046 (4)	1·72 (9)	
N7	−0·0277 (5)	0·8790 (2)	0·0033 (3)	1·33 (7)	
C8	−0·1537 (7)	0·8441 (2)	−0·0980 (4)	1·85 (9)	
C9	−0·1632 (7)	0·9247 (2)	0·0338 (4)	2·3 (1)	
C10	0·1537 (7)	0·9077 (2)	−0·0302 (4)	2·04 (9)	
O11	−0·2158 (4)	0·7724 (1)	0·0908 (2)	2·01 (6)	
O12	−0·1382 (5)	0·7052 (1)	0·3576 (3)	2·74 (7)	
C01	0·9520 (7)	0·2048 (2)	0·3903 (4)	2·8 (1)	
C02	0·8381 (7)	0·2555 (2)	0·3287 (4)	2·3 (1)	
C03	0·6615 (7)	0·2391 (2)	0·2226 (4)	1·79 (9)	
C04	0·4705 (7)	0·2703 (2)	0·2376 (4)	2·7 (1)	
C05	0·5597 (6)	0·3153 (2)	0·3301 (4)	1·80 (9)	
C06	0·4127 (7)	0·3347 (2)	0·3984 (4)	1·95 (9)	
N07	0·4992 (5)	0·3765 (1)	0·4970 (3)	1·32 (7)	
C08	0·6223 (7)	0·3450 (2)	0·6017 (4)	2·04 (9)	
C09	0·6391 (7)	0·4214 (2)	0·4662 (4)	2·4 (1)	
C010	0·3169 (7)	0·4063 (2)	0·5275 (4)	2·2 (1)	
O011	0·7399 (4)	0·2877 (1)	0·4023 (2)	1·89 (6)	
O012	0·6772 (5)	0·2083 (2)	0·1434 (3)	3·03 (8)	
C21	0·0986 (6)	0·5795 (2)	0·8342 (3)	1·41 (8)	
C22	0·1370 (6)	0·5172 (2)	0·8368 (3)	1·31 (8)	
C23	0·2163 (6)	0·4861 (2)	0·9344 (3)	1·27 (8)	
C24	0·2674 (6)	0·5147 (2)	1·0416 (3)	1·31 (8)	
C25	0·2313 (6)	0·5736 (2)	1·0502 (3)	1·37 (8)	
C26	0·1482 (6)	0·6041 (2)	0·9526 (4)	1·57 (8)	
O21	0·0352 (5)	0·6072 (1)	0·7455 (3)	2·27 (7)	
N22	0·0817 (5)	0·4835 (2)	0·7287 (3)	1·71 (7)	
O221	0·0732 (5)	0·5067 (2)	0·6375 (2)	2·65 (7)	
O222	0·0398 (5)	0·4315 (1)	0·7343 (3)	2·68 (7)	
N24	0·3526 (5)	0·4825 (2)	1·1440 (3)	1·61 (7)	
O241	0·3930 (5)	0·5087 (2)	1·2383 (2)	2·56 (7)	
O242	0·3815 (4)	0·4305 (1)	1·1348 (3)	1·98 (6)	
N26	0·1090 (5)	0·6653 (2)	0·9708 (3)	2·18 (8)	
O261	−0·0040 (6)	0·6920 (2)	0·8926 (3)	3·59 (8)	
O262	0·1899 (5)	0·6873 (2)	1·0671 (3)	3·79 (9)	
C31	0·5880 (6)	0·0677 (2)	0·3190 (3)	1·59 (9)	
C32	0·6423 (6)	−0·0061 (2)	0·3338 (3)	1·26 (8)	
C33	0·7278 (6)	0·0212 (2)	0·4372 (3)	1·32 (8)	
C34	0·7651 (6)	−0·0100 (2)	0·5381 (3)	1·15 (8)	
C35	0·7107 (5)	−0·0683 (2)	0·5352 (3)	1·22 (8)	
C36	0·6277 (6)	−0·0957 (2)	0·4310 (4)	1·41 (8)	
O31	0·5056 (4)	−0·0920 (1)	0·2255 (2)	2·12 (7)	
N32	0·5963 (5)	0·0308 (2)	0·2316 (3)	1·85 (8)	
O321	0·5836 (5)	0·0088 (1)	0·1370 (2)	2·41 (7)	
O322	0·5737 (5)	0·0829 (1)	0·2472 (3)	2·84 (7)	
N34	0·8534 (5)	0·0190 (2)	0·6472 (3)	1·61 (7)	
O341	0·8801 (5)	−0·0100 (1)	0·7363 (2)	2·23 (7)	
O342	0·8975 (4)	0·0708 (1)	0·6483 (2)	1·83 (6)	
N36	0·5676 (5)	−0·1558 (2)	0·4345 (3)	2·09 (8)	
O361	0·5722 (5)	−0·1883 (1)	0·3539 (3)	3·37 (8)	
O362	0·5141 (5)	−0·1721 (1)	0·5203 (3)	3·22 (8)	

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

	Iodide	Picrate C1—O12	Picrate C01—O012
C1—C2	1·505 (5)	1·499 (7)	1·497 (7)
C2—C3	1·520 (4)	1·529 (6)	1·528 (5)
C2—O11	1·427 (4)	1·434 (6)	1·421 (6)
C3—C4	1·521 (4)	1·509 (6)	1·502 (7)
C3—O12	1·206 (3)	1·200 (6)	1·200 (6)
C4—C5	1·545 (3)	1·512 (6)	1·508 (6)
C5—O11	1·450 (3)	1·428 (5)	1·438 (5)
C5—C6	1·516 (4)	1·503 (7)	1·484 (7)
C6—N7	1·534 (3)	1·512 (5)	1·504 (5)
N7—C8	1·484 (2)	1·501 (5)	1·509 (5)
N7—C9	1·506 (3)	1·486 (6)	1·497 (6)
N7—C10	1·484 (2)*	1·506 (6)	1·507 (6)
		X = 2	*X* = 3
C*X*1—C*X*2		1·464 (6)	1·463 (6)
C*X*1—O*X*1		1·230 (5)	1·236 (5)
C*X*1—C*X*6		1·473 (6)	1·462 (6)
C*X*2—C*X*3		1·372 (5)	1·363 (5)
C*X*2—N*X*2		1·460 (5)	1·471 (5)
C*X*3—C*X*4		1·394 (5)	1·387 (6)
C*X*4—C*X*5		1·391 (6)	1·390 (6)
C*X*4—N*X*4		1·435 (5)	1·438 (5)
C*X*5—C*X*6		1·368 (6)	1·369 (5)
C*X*6—N*X*6		1·462 (6)	1·446 (6)
N*X*2—O*X*21		1·213 (5)	1·215 (5)
N*X*2—O*X*22		1·240 (5)	1·233 (5)
N*X*4—O*X*41		1·238 (4)	1·245 (5)
N*X*4—O*X*42		1·226 (5)	1·230 (5)
N*X*6—O*X*61		1·218 (5)	1·220 (5)
N*X*6—O*X*62		1·238 (5)	1·232 (5)
		C1—O12	C01—O012
C1—C2—C3	113·3 (3)	112·8 (4)	114·0 (4)
C1—C2—O11	110·5 (3)	110·0 (4)	110·8 (4)
C3—C2—O11	104·0 (2)	104·3 (3)	105·2 (3)
C2—C3—C4	108·6 (2)	107·2 (4)	105·9 (4)
C2—C3—O12	125·0 (3)	125·1 (4)	126·0 (4)
C4—C3—O12	126·4 (2)	127·9 (4)	128·1 (4)
C3—C4—C5	101·8 (2)	103·1 (3)	103·5 (3)
C2—O11—C5	108·4 (2)	108·9 (3)	107·6 (3)
C4—C5—C6	114·4 (2)	112·8 (3)	114·7 (4)
C4—C5—O11	104·5 (2)	104·9 (3)	103·7 (3)
C6—C5—O11	103·0 (2)	110·1 (3)	111·1 (3)
C5—C6—N7	113·4 (2)	116·4 (3)	116·7 (3)
C6—N7—C8	122·3 (2)	111·3 (3)	110·6 (3)
C6—N7—C9	111·4 (2)	112·0 (3)	112·1 (3)
C6—N7—C10	95·3 (2)*	106·9 (3)	108·1 (3)
C8—N7—C9	109·0 (1)	109·0 (3)	108·5 (3)
C8—N7—C10	108·6 (2)*	109·1 (3)	108·8 (3)
C9—N7—C10	109·1 (1)*	108·7 (3)	108·6 (3)
		X = 2	*X* = 3
C*X*1—C*X*2—C*X*3		125·5 (4)	124·9 (4)
C*X*2—C*X*3—C*X*4		119·0 (4)	119·4 (4)
C*X*3—C*X*4—C*X*5		120·6 (4)	120·7 (3)
C*X*4—C*X*5—C*X*6		120·0 (4)	119·5 (4)
C*X*5—C*X*6—C*X*1		124·5 (4)	124·5 (4)
C*X*6—C*X*1—C*X*2		110·4 (3)	110·9 (3)
C*X*6—C*X*1—O*X*1		125·1 (4)	124·3 (4)
C*X*2—C*X*1—O*X*1		124·5 (4)	124·8 (4)
C*X*1—C*X*2—N*X*2		119·2 (3)	119·0 (3)
C*X*3—C*X*2—N*X*2		115·3 (4)	116·0 (4)
C*X*3—C*X*4—N*X*4		119·4 (4)	119·3 (4)
C*X*5—C*X*4—N*X*4		120·0 (3)	119·9 (3)
C*X*5—C*X*6—N*X*6		115·9 (4)	116·6 (4)
C*X*1—C*X*6—N*X*6		119·6 (3)	118·8 (3)
C*X*2—N*X*2—O*X*21		120·2 (4)	119·0 (4)
C*X*2—N*X*2—O*X*22		117·6 (3)	117·7 (3)
O*X*21—N*X*2—O*X*22		122·2 (3)	123·4 (4)
C*X*4—N*X*4—O*X*41		118·1 (3)	117·7 (3)
C*X*4—N*X*4—O*X*42		119·1 (3)	119·0 (3)
O*X*41—N*X*4—O*X*42		122·9 (3)	123·3 (3)
C*X*6—N*X*6—O*X*61		119·3 (3)	119·7 (4)
C*X*6—N*X*6—O*X*62		117·9 (3)	118·0 (4)
O*X*61—N*X*6—O*X*62		122·8 (4)	122·4 (4)

	Iodide	Picrate C1—O12	Picrate C01—O012	Iodide (1972)†
θ_0 C2—C3—C4—C5	9·3 (2)	13·9 (5)	16·0 (5)	6
θ_1 C3—C4—C5—O11	−27·4 (2)	−29·7 (4)	−32·9 (4)	−36
θ_2 C4—C5—O11—C2	37·7 (3)	36·0 (4)	39·0 94)	56

105 K. Only bond lengths and some torsion angles were published. A value of 56° was given for one torsion angle in the five-membered ring, probably due to problems caused by the choice of space group.

Table 2 (*cont.*)

	Iodide	Picrate C1—O12	Picrate C01—O012	Iodide (1972)†
θ_3 C5—O11—C2—C3	−30·9 (3)	−26·3 (4)	−28·4 (4)	−39
θ_4 O11—C2—C3—C4	12·2 (3)	6·5 (5)	6·6 (5)	25
O11—C5—C6—N7	±157·5 (2)	±68·9 (5)	±58·7 (5)	±162
C2—O11—C5—C6	±157·5 (2)	±157·7 (3)	±162·7 (4)	±168
Pseudorotational parameters				
P (phase) (°)	75·0	66·1	65·1	80·9
θ_m (amplitude) (°)	36·6	35·2	38·5	50·9
	$^1T_5$	E_5-$^1T_5$	E_5-$^1T_5$	$^1T_5$-^1E

* C10 in the iodide compound is C8 after the symmetry operation x, y, $0·5 - z$.

† Pauling & Petcher (1972).

The overall conformation of the muscarone ion was, however, correct. The ring conformation is a distorted twist, $^1T_5$ (Table 2), and the fragment (O—C—C—N) is *trans*.

(±)-*Muscarone picrate*. The crystals of muscarone picrate changed on cooling to 105 K from the room-temperature monoclinic space group, $P2_1/n$ ($\beta \simeq 105°$), to the triclinic space group, $P\bar{1}$. Comparison of the dimensions of the two pairs of ions in the asymmetric unit is given in Table 2. Bond lengths vary by less than 0·019 Å and bond angles by less than 1·9°, *i.e.* hardly significantly. Torsion angles within the ring of muscarone differ by up to 3·2°, and for the O—C—C—N fragment the difference in torsion angle is 10·2°. The overall conformation of the five-membered ring is the same, but the puckering amplitudes differ by 3·3°.

The dimensions of the two picrate ions in the asymmetric unit are not identical. The numbers in Figs. 1(*e*) and 1(*f*) refer to the displacements of the atoms from the best plane through the benzene ring. The two picrate ions are not exactly related by the symmetry operation $(0·5 + x, 0·5 - y, 0·5 + z)$, as they would be in $P2_1/n$. Deviations from the pseudo-symmetry are greatest for the nitro groups N26 and N36. They are rotated in the same direction relative to their respective benzene rings and not in opposite directions as expected from the fact that the two independent picrate ions are pseudo-mirror image forms. This gives rise to different contacts from the two independent picrate ions to other ions in the unit cell (*cf. Crystal packing*). Picrate ions with conformations similar to both of those present in this salt were found in the Cambridge Structural Database, CSD (version 4.3, July 1990 release; Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979).

Crystal packing

Stereoviews of the crystal packings are shown in Fig. 2. The positive charge of the quaternary ammonium group is delocalized and the packing is governed by charge–charge and van der Waals interactions. Details of the geometry of the closest contacts in both structures are deposited.

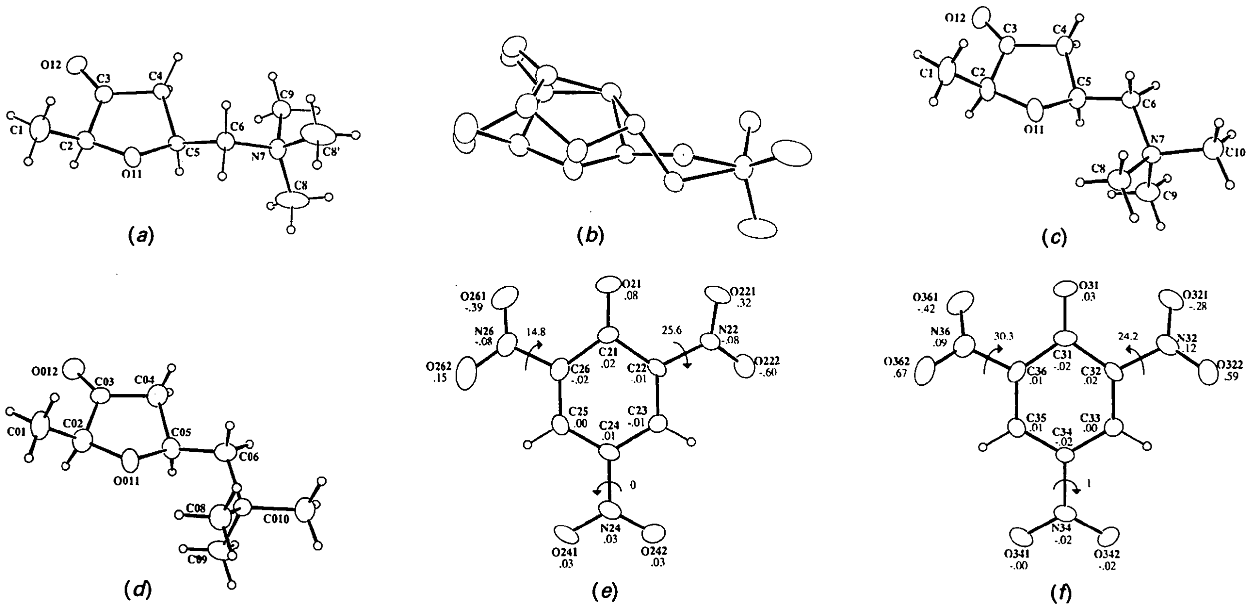

Fig. 1. *ORTEP*II (Johnson, 1976) plots of the ions with numbering scheme. Thermal ellipsoids are at the 50% probability level. (*a*) The muscarone ion from muscarone iodide. (*b*) The two mirror image forms of muscarone share each equivalent position in the crystals of muscarone iodide. (*c*) and (*d*) The two muscarone ions in muscarone picrate. (*e*) and (*f*) The two picrate ions in muscarone picrate. Numbers refer to atom displacements from the best plane through the benzene ring (Å). The rotation of the nitro groups relative to the plane of the benzene ring is indicated.

(±)-*Muscarone iodide* (Fig. 2*a*). The muscarone ion has contacts to four iodide ions. The closest C···I contact, 3·985 (3) Å (I, 0·5 + *x*, 0·5 − *y*, −*z* − 0·5), involves C5, and there are several close contacts from C atoms in the quaternary ammonium group to iodide ions. Calculations performed with *SYBYL* (Version 5.3; Tripos Associates Inc., 1990) using the method described by Gasteiger & Marsili (1980) indicate that C5 as well as C6 and C8–C10 of the quaternary ammonium group have a partial positive charge. The contacts may be weak hydrogen bonds (C—H···I) (Taylor & Kennard, 1982). The angles C—H···I are nearly linear. Two close contacts, C4···I [4·095 (1) Å, I (0·5 + *x*, 0·5 − *y*, −*z* − 0·5) and I (0·5 + *x*, 0·5 − *y*, 0·5 − *z*)] are also observed. The calculated charge on C4 indicates that the atom is practically uncharged. The contact may be the result of other attractive packing forces in the crystal. Contacts between muscarone ions involve the carbonyl group and the quaternary ammonium group. The three methyl groups all have close contacts to different carbonyl O atoms. Contacts with lengths 3·141 (3) and 2·904 (3) Å from C8 to two different O atoms are found, but only one of the O atoms is present in each equivalent position. The contacts may again be weak hydrogen bonds (C—H···O). The N—C···O angles are nearly linear giving close contacts to more than one H atom.

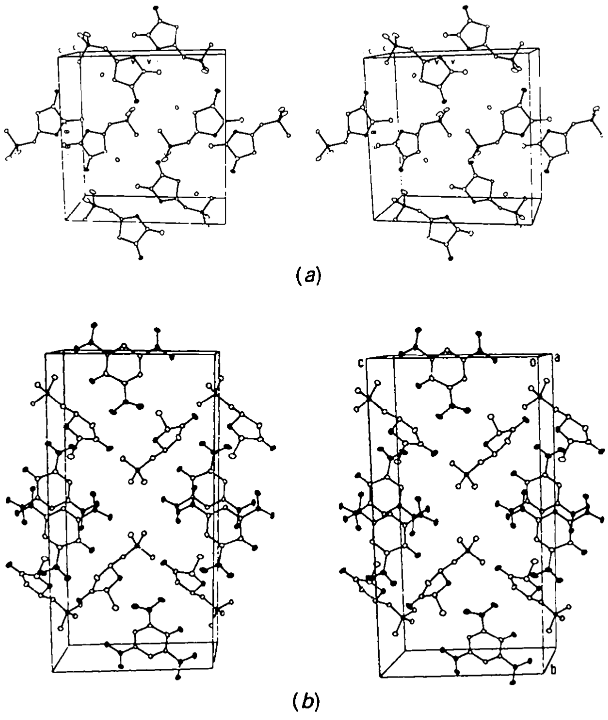

Fig. 2. Stereoviews of the packing diagrams. N and O appear as black circles. (*a*) Muscarone iodide. Only one enantiomer is printed at each equivalent position. *a* horizontal, *b* vertical and *c* out of the plane of the paper. (*b*) Muscarone picrate. *c* horizontal, *b* vertical and *a* out of the plane of the paper.

(±)-*Muscarone picrate* (Fig. 2*b*). The picrate ions are packed in two columns along the *a* axis. The picrate ion (C21...) and the symmetry-related ions are situated in one column and the other picrate ion (C31...) and its symmetry-related ions are in the other column. The benzene rings in a column are parallel and they are stacked nearly but not exactly on top of each other. The angle between the benzene rings and the *yz* plane is approximately −25°, and the stacking is therefore not directly seen in Fig. 2(*b*). The distances between the benzene rings differ slightly in the two columns, 3·22 (1) and 3·23 (1) in the 'C21' column and 3·19 (1) and 3·21 (1) Å in the 'C31' column. The closest contact is C33···C35 (1 − *x*, −*y*, 1 − *z*) 3·186 (6) Å, shorter than the closest van der Waals contact distance between benzene rings. The shift in the stacking of the picrate ions relieves strain and the nitro groups N26 and N36, which are involved in the conformational difference between the picrate ions, are situated on the unhindered outer surface of the picrate columns. Nearly all short contacts are charge–charge interactions from partially charged atoms in the muscarone ions to the O atoms in the nitro groups. The closest contact is C3···O361 (*x* − 1, *y* + 1, *z*) 2·921 (6) Å. A similar close contact is not seen for C03···O261 (1 − *x*, 1 − *y*, 1 − *z*) 3·337 (6) Å, owing to the difference in the conformation of the picrate ions. Contacts between muscarone ions involve the carbonyl oxygen and the quaternary ammonium group. The closest contacts are O12···C010 (−*x*, 1 − *y*, 1 − *z*) 3·292 (6) Å and the corresponding contact O012···C10 (1 − *x*, 1 − *y*, −*z*) 3·309 (6) Å. These contacts are longer than those in the iodide salt due to crystal packing.

The conformation of the muscarone ion

The conformations of the five-membered rings in these compounds are very similar, despite the fact that the conformation of the fragment (O—C—C—N) has changed. In a search of the CSD for the 3-oxotetrahydrofuran ring system only two compounds were found. Structures which contain a cyclopentanone ring system were then extracted and examined as well as the two tetrahydrofuran compounds (Lagersted, Frydenvang & Jensen, 1992). The ring system in all these structures has nearly the same conformation as that observed for the muscarone ion with the carbonyl group in the planar part of the ring. Molecular-mechanics calculations [method described by Burkert & Allinger (1982), included in *MIMIC* (Liljefors & Allinger, 1985; Liljefors, Tai, Li & Allinger, 1987)] have been performed on the muscarone ion (Frydenvang, 1989). The results of these calculations indicate that the ring is rather flexible, but that the global minimum-energy conformation of the five-membered ring is similar to that observed in the crystal structures. The fragment (O—C—C—N) can change orientation without affecting the ring conformation. The region +*gauche* to *trans* is accessible in the (+)-(2*S*,5*S*)-enantiomer of muscarone. Other possible orientations of the (O—C—C—N) fragment cause steric interactions for some ring conformations. Pseudorotational parameters, calculated by the method described by Rao, Westhof & Sundaralingam (1981) are given in Table 2. The magnitude of the amplitudes [except for (±)-muscarone iodide from 1972] and the preferred conformations correspond to results obtained by *ab initio* calculations for cyclopentanone (Cremer & Pople, 1975). The two crystal structure determinations indicate that the five-membered ring of the muscarone ion prefers one minimum-energy conformation with the carbonyl group in the planar part of the ring, while the side chain adopts both the *gauche* and the *trans* orientation.

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Structure of the 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Bis(fluoroacetonitrile) Complex

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Abstract. $C_{12}H_{24}O_6.2C_2H_2FN$, $M_r = 382.416$, monoclinic, $P2_1/n$, $a = 8.3125\,(11)$, $b = 8.3049\,(17)$, $c = 15.2308\,(14)$ Å, $\beta = 100.950\,(9)°$, $V = 1032.3\,(3)$ Å^3, $Z = 2$, $D_x = 1.23$ g cm^{-3}, $\lambda = 0.70930$ Å, $\mu = 0.10$ mm^{-1}, $F(000) = 408$, room temperature, $R_F = 0.065$, $wR = 0.040$ for 1039 reflections. The 18-crown-6 molecule has approximate D_{3d} symmetry. The two fluoroacetonitrile molecules are situated one