

around the exocyclic methylene are 1.507 (5) Å in (4). The methylene bridge bonds around the unsubstituted methylene in (3) are 1.519 (4) Å. The bonds joining the two norbornane moieties average 1.532 (2) and 1.532 (5) Å in (3) and (4), respectively. In general, for molecular mechanics programs such as *MM2* the ethane bond lengths are significantly underestimated (Doms, Van Hemelrijk, Van de Mieroop, Lenstra & Geise, 1985; Doms, Van den Enden, Geise & Van Alsenoy, 1985) although comparative energy calculations remain valid; however, *PCMODEL* (1989) calculations for (3) and (4) using program-generated parameters show better bond-length agreement than in norbornane itself. In norbornane the addition of a torsion-stretch interaction has led to excellent agreement between observed and calculated distances and angles (Allinger, Geise, Pyckhout, Paquette & Gallucci, 1989). Molecular mechanics calculations give strain energies of 227.6 and 245.5 kJ mol⁻¹ for (3) and (4), respectively, with the main difference due to angle strain associated with the exocyclic methylene moiety, *i.e.* C(8)—C(9)—C(8A) = 98.0 (4) at the C(sp²) center. The structures of the parent hydrocarbon, (6) (Chow, Liu & Chao, 1985) and a di-*tert*-butoxy derivative, (7) (Neely, van der Helm, Marchand & Hayes, 1976) have been reported and average values for the chemically equivalent bonds are statistically equivalent to those reported here.

We thank The Welch Foundation (Grant P-074 to WHW, B-963 to APM), the Air Force Office of Scientific Research (Grant AFOSR-88-0132 to APM) and the Texas Christian University and University of North Texas Faculty Research Committees for financial support of this study.

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Acta Cryst. (1990). **C46**, 1279–1282

Structure of Muscarine Chloride

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(Received 7 July 1989; accepted 29 September 1989)

Abstract. Trimethyl(tetrahydro-4-hydroxy-5-methyl-2-furyl)methylammonium chloride, C₉H₂₀NO₂⁺.Cl⁻, *M_r* = 209.7, orthorhombic, *P*2₁2₁2, at *T* = 105 K: *a* = 9.731 (3), *b* = 9.801 (1), *c* = 11.478 (3) Å, *V* = 1094.7 (4) Å³, *Z* = 4, *D_x*(105 K) = 1.272 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.319 mm⁻¹, *F*(000) = 456, m.p. (hot-stage microscope) = 446–449 K (corrected), *R* = 0.033 for 3013 observed [*I* ≥ 3.0σ(*I*)] reflections. Crystals were grown from a solution of (±)-muscarine chloride, but the single crystal is chiral. The tetrahydrofuran ring conformation is intermediate between envelope ³*E* and twist ³*T*₄ and is different from the one known from the

crystal structure of muscarine iodide. For muscarine chloride τ(C—O—C—C) is 112.9 (1)° and τ(O—C—C—N) is 76.8 (2)°. The crystal packing is stabilized by hydrogen bonds O—H⋯Cl⁻ and by weaker electrostatic and van der Waals contacts.

Introduction. Muscarine mimics the function of the neurotransmitter acetylcholine in the muscarinic part of the cholinergic nervous system. Muscarine contains a five-membered ring, which makes it less flexible than acetylcholine, but muscarine is still only semirigid. The crystal structure of (+)-muscarine iodide (MUSCAI) has been known since 1957

(Jellinek, 1957) and it has until now been the only salt of muscarine studied crystallographically. The conformation of the muscarine ion as found for MUSCAI has been used as the only one possible for the muscarine ion in order to establish the 'active conformation' of acetylcholine (Pauling & Petcher, 1971). The present structure determination was carried out in order to obtain accurate bonding parameters for the muscarine ion, and to examine whether the conformation was different from that found earlier (Jellinek, 1957).

Experimental. Crystals of (\pm)-muscarine chloride (MUSCHL) (SIGMA Chemical Company) are very hygroscopic and therefore D_m was not measured. The compound was suspended in *N,N*-dimethylformamide and dissolved by adding a few drops of water. Single crystals were obtained by removing water, using P_2O_5 . Crystal size $0.20 \times 0.25 \times 0.25$ mm. Intensity data were sampled with Enraf-Nonius CAD-4 diffractometer and low-temperature device, graphite-monochromated $Mo K\alpha$ radiation. The temperature (105 K) was recorded with a thermocouple, variation within 1 K. Cell parameters and orientation matrix were determined from 18 reflections ($16.65 \leq \theta \leq 21.22^\circ$). No corrections for absorption were made. Three intensity control reflections were measured every 10^4 s, no systematic variation seen. ω scan. $\theta_{max} = 40^\circ$, range of hkl : $0 \leq h \leq 17$, $-9 \leq k \leq 17$, $0 \leq l \leq 26$. 4191 unique reflections, 1178 unobserved. $R_{int} = 0.031$ (on F_{obs}). Friedel pairs were not averaged because the space group is chiral.

Chloride ions were localized by the heavy-atom method. Other non-H atoms were localized by direct methods, using *DIRDIF*. Structure refinement (positional parameters for all atoms and anisotropic thermal parameters for non-H atoms) made by least-squares minimization of $\sum w(|F_o| - k|F_c|)^2$, $1/w = \frac{1}{4}(\sigma^2(I) + (0.04I)^2)/I$. Final $R = 0.033$, $wR = 0.037$, $S = 1.22$. Max. $(\Delta/\sigma) = 0.03$. Residual electron density within 0.5 and $-0.4 e \text{ \AA}^{-3}$. All H atoms were present in $\Delta\rho$ map and thermal parameters for H atoms were fixed at an arbitrary value, $B_{iso} = 1.0 \text{ \AA}^2$. Atomic scattering factors for uncharged atoms, except for Cl^- , are used as implemented in the *SDP Structure Determination Package* (B.A. Frenz & Associates, Inc., 1982), used for all calculations.

The space group $P2_12_12$ is chiral. Hamilton's *R*-value test performed as described by Rogers (1981) suggests that the (2*S*,3*R*,5*S*)-enantiomer is present in this single crystal [significance level $\alpha < 10^{-10}$, $R(+)=0.033$, $wR(+)=0.037$, $R(-)=0.034$, $wR(-)=0.039$].

Discussion. The final coordinates and thermal parameters (B_{eq}) of muscarine chloride are given in

Table 1. Fractional atomic coordinates and B_{eq} values (\AA^2)

$$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Cl(1)	1.000	1.000	1.02669 (4)	1.116 (6)
Cl(2)	1.000	0.500	0.64546 (4)	1.237 (6)
C(1)	0.7706 (2)	0.7389 (2)	0.7965 (1)	1.48 (2)
C(2)	0.6834 (1)	0.7726 (1)	0.6917 (1)	1.05 (2)
C(3)	0.6338 (1)	0.6508 (1)	0.6205 (1)	0.92 (2)
C(4)	0.5047 (2)	0.7076 (1)	0.5634 (1)	1.04 (2)
C(5)	0.4439 (1)	0.7961 (1)	0.6607 (1)	0.89 (2)
C(6)	0.3436 (1)	0.7112 (1)	0.7326 (1)	0.86 (2)
N(7)	0.2518 (1)	0.7894 (1)	0.81518 (9)	0.80 (2)
C(8)	0.3326 (2)	0.8821 (2)	0.8934 (1)	1.15 (2)
C(9)	0.1475 (2)	0.8712 (2)	0.7492 (1)	1.29 (2)
C(10)	0.1764 (2)	0.6874 (2)	0.8894 (1)	1.25 (2)
O(11)	0.5592 (1)	0.8383 (1)	0.73132 (9)	1.04 (2)
O(12)	0.7276 (1)	0.6050 (1)	0.53497 (9)	1.46 (2)

Table 2. Bond lengths (\AA), angles ($^\circ$), selected torsion angles ($^\circ$), dimensions of hydrogen bonds and selected distances between substituents (\AA)

C(1)—C(2)	1.509 (2)	C(5)—C(6)	1.525 (2)
C(2)—C(3)	1.526 (2)	C(5)—O(11)	1.444 (2)
C(2)—O(11)	1.442 (2)	C(6)—N(7)	1.512 (2)
C(3)—C(4)	1.523 (2)	N(7)—C(8)	1.499 (2)
C(3)—O(12)	1.414 (2)	N(7)—C(9)	1.498 (2)
C(4)—C(5)	1.533 (2)	N(7)—C(10)	1.505 (2)
C(1)—C(2)—C(3)	115.7 (1)	C(6)—C(5)—O(11)	110.5 (1)
C(1)—C(2)—O(11)	108.5 (1)	C(2)—O(11)—C(5)	110.2 (1)
C(3)—C(2)—O(11)	104.7 (1)	C(5)—C(6)—N(7)	116.2 (1)
C(2)—C(3)—C(4)	101.8 (1)	C(6)—N(7)—C(8)	111.9 (1)
C(2)—C(3)—O(12)	114.6 (1)	C(6)—N(7)—C(9)	110.8 (1)
C(4)—C(3)—O(12)	110.5 (1)	C(6)—N(7)—C(10)	107.8 (1)
C(3)—C(4)—C(5)	102.2 (1)	C(8)—N(7)—C(9)	109.5 (1)
C(4)—C(5)—C(6)	109.4 (1)	C(8)—N(7)—C(10)	108.6 (1)
C(4)—C(5)—O(11)	105.7 (1)	C(9)—N(7)—C(10)	108.1 (1)
O(11)—C(2)—C(3)—C(4)		MUSCHL	MUSCAI
C(2)—C(3)—C(4)—C(5)		35.5 (1)	-10.6
C(3)—C(4)—C(5)—O(11)		-37.9 (1)	22.3
C(4)—C(5)—O(11)—C(2)		27.4 (1)	-26.4
C(5)—O(11)—C(2)—C(3)		-5.4 (1)	20.5
C(2)—O(11)—C(5)—C(6)		-19.0 (1)	-6.4
O(11)—C(5)—C(6)—N(7)		112.9 (1)	143.7
		76.8 (1)	73.1
Hydrogen bonds			
O(12)...Cl(2)		3.113 (1) \text{\AA}	O(12)...I 3.57 \text{\AA}
O(12)—H...Cl(2)		177 (2)^\circ	
Distances between substituents (\text{\AA})			
	MUSCHL		MUSCAI
C(1)...C(6)	4.228 (2)		4.56
C(1)...O(12)	3.303 (2)		3.60
C(6)...O(12)	4.494 (2)		4.66

Table 1.* Bond lengths, bond angles and selected torsion angles are given in Table 2. The muscarine ion with atomic numbering is shown in Fig. 1. Detailed comparison of bond lengths and angles in

* Lists of structure factors, anisotropic thermal parameters, H atom positions and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52695 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the present structure with those in the crystal structure of MUSCAI is excluded due to the lack of accuracy of the previous structure determination. The overall conformations of the muscarine ions in the two crystals are, however, clearly different. This can be seen from the torsion angles (*cf.* Table 2) which show that the five-membered ring has a conformation intermediate between envelope 3E and twist 3T_4 in MUSCHL, while it adopts a distorted twist 4T_5 conformation in MUSCAI. Rao, Westhof & Sundaralingam (1981) have used a different numbering of the tetrahydrofuran ring (Fig. 2*a*), compared to the numbering used in this work (Fig. 2*b*). The pseudorotation parameters (Rao, Westhof & Sundaralingam, 1981) for MUSCHL are $P = 169.9^\circ$ and $\theta_m = 39.2^\circ$ and for MUSCAI $P = 31.6^\circ$ and $\theta_m = 26.6^\circ$. A puckering amplitude of 39.2° compares reasonably well with theoretical calculations (Cremer & Pople, 1975), while the amplitude for MUSCAI is much smaller than expected. A perspective drawing (Fig. 3) of the two muscarine ions shows that the

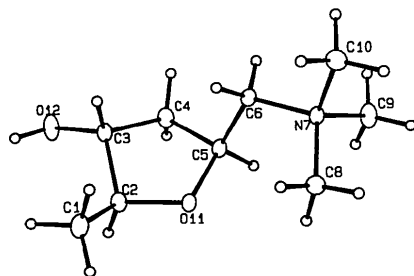


Fig. 1. The muscarine ion in muscarine chloride. Non-H atoms are represented by thermal ellipsoids at the 50% probability level.

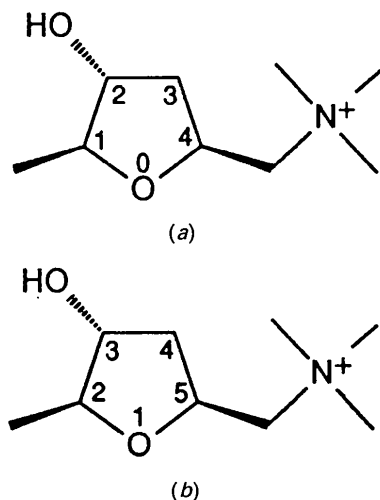


Fig. 2. (a) The numbering used for the tetrahydrofuran ring by Rao, Westhof & Sundaralingam (1981). (b) The numbering used in this work.

change in ring conformation is accompanied by a substantial change in the mutual arrangement of the substituents. The distances between substituents are all longer in MUSCAI than in MUSCHL (*cf.* Table 2). The difference in the $C(1)\cdots C(6)$ distance is 0.33 \AA , nearly the same as for $C(1)\cdots O(12)$ (0.30 \AA). The difference for $C(6)\cdots O(12)$ is 0.17 \AA .

The chloride ions in the crystals of MUSCHL are situated on two special positions, and the surroundings of the chloride ions are therefore not identical (Fig. 4). Cl(1) (0.00, 0.00, 0.027) has contacts to four quaternary ammonium groups. Cl(2) (0.00, 0.50, 0.645) has contacts to only two quaternary ammonium groups, but accepts strong hydrogen bonds from two hydroxy groups (*cf.* Table 2). Short contacts between muscarine ions exist between $C(5)\cdots O(12)$ [$3.228(2) \text{ \AA}$]. C(5) has a partial positive charge (Gasteiger & Marsili, 1980), and the contact may be a weak hydrogen bond ($C-H\cdots O$) (Taylor & Kennard, 1982) [$C(5)-H\cdots O$ 128.2°].

Molecular-mechanics (Burkert & Allinger, 1982) calculations performed on the muscarine ion show great flexibility (Frydenvang, 1989). It can be concluded that the muscarine ion is very flexible and that packing forces can induce several ring conformations.

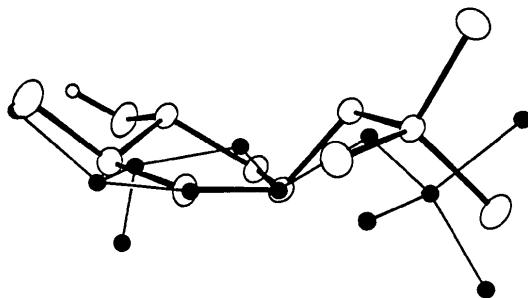


Fig. 3. A perspective drawing of MUSCHL and MUSCAI (Jellinek, 1957), illustrating the differences in arrangement of substituents (MUSCAI represented as filled circles). H(121) is given for MUSCHL in order to identify O(12).

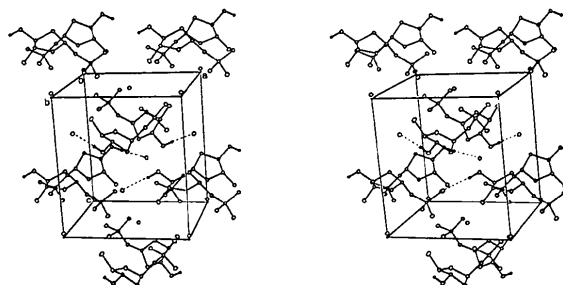


Fig. 4. Stereoview of the packing of MUSCHL. **a** horizontal, **c** vertical and **b** out of the plane of the paper.

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Acta Cryst. (1990). **C46**, 1282–1284

Structure of 3-Dimethylamino-2-(2-formyl-3,4-dihydro-1-naphthyl)-*N,N*-dimethyl-2-propeniminium Chloride Dihydrate: A Vilsmeier Intermediate

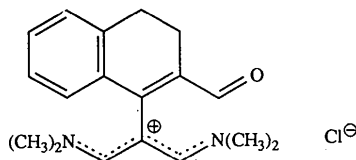
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(Received 9 March 1989; accepted 23 January 1990)

Abstract. $[C_{18}H_{23}N_2O]^+ \cdot Cl^- \cdot 2H_2O$, $M_r = 354.878$, monoclinic, $P2_1$, $a = 9.0806$ (23), $b = 7.5717$ (15), $c = 14.4414$ (51) Å, $\beta = 106.922$ (24)°, $V = 949.94$ (46) Å³, $Z = 2$, $D_x = 1.241$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 19.3$ cm⁻¹, $F(000) = 380$, $T = 300$ K, $R = 0.046$, $wR = 0.045$ for 1261 reflections with $F_o \geq 2\sigma(F_o)$. The unit cell consists of the two cations and two anions linked by hydrogen bonds involving the four water molecules. The remarkable stability of the trisubstituted allyl cation is due to delocalization of the positive charge along the chain.

Introduction. Vilsmeier reagents (Mundy & Ellerd, 1988) are important synthetic tools in organic chemistry. As part of a continuing study of Vilsmeier reagents, the reaction of $POCl_3/(CH_3)_2NCHO$ with 3,4-dihydro-1-methylnaphthalene was reported by Katritzky & Marson (1987). In addition to the final product 1-[2-(*N,N*-dimethylamine)-1-formylvinylene]-3,4-dihydronaphthalene-2-carboxaldehyde (I), another product was obtained on several occasions. This product differed in the melting point but appeared to be very similar to (I). Therefore, an X-ray study was undertaken to determine the nature of this apparent intermediate in the reaction.



Experimental. The title compound forms canary-yellow crystals from ethyl acetate. Upon heating, the crystals appear to lose solvent at about 363 K followed by a color change. At 413 K there still appeared to be unmelted material. In contrast the final product (I) has a melting point 406–407 K.

Intensity data were collected with nickel-filtered $Cu K\alpha$ radiation using a $P\bar{1}$ diffractometer upgraded to a Nicolet *P3*. The crystal had dimensions $0.03 \times 0.17 \times 0.25$ mm and was mounted on a glass fiber. The cell constants and orientation matrix were determined from 24 reflections in the 2θ range 10.0 – 31.5° . The intensity data were measured using a variable speed (1.9 – $29.3^\circ \text{ min}^{-1}$) θ – 2θ scan. The 2θ range was 1.5 – 112.5° ($-9 \leq h \leq 9$, $0 \leq k \leq 8$, $0 \leq l \leq 15$). Two standard reflections were measured after every 98 reflections and showed a slow decrease of about 5% [$6\sigma(I)$] over the time of data collection. The standards were used to derive a correction for the data. A total of 1495 measurements was reduced to 1366 unique reflections. The 1261 reflections with $F_{obs} \geq 2\sigma(F_{obs})$ were used in the analysis.

The structure was solved by direct methods and refined on F by blocked-cascade least-squares methods. The refinement of the chirality parameter, η , defined by Rogers (1981) was used to establish the absolute configuration given in Fig. 1. A difference Fourier synthesis was used to locate the 27 H atoms. The H-atom positions in the four methyl groups were idealized to a tetrahedral arrangement. The other H-atom positions were those found in the difference Fourier synthesis. An isotropic U of 0.05 Å² was used for all the H atoms. The H-atom parameters were not refined. An extinction correc-

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