C(5)—C(9)—O(10)	123.1 (5)	C(1)—C(9)—O(10)	124.1 (5)
C(2)—C(11)—C(12)	118.3 (4)	C(2)—C(11)—C(16)	123.6 (4)
C(13)—C(14)—O(17)	115.8 (4)	C(15)—C(14)—O(17)	124.5 (5)
N(3)—N(27)—O(28)	112.5 (4)	C(22)—O(25)—C(26)	117.6 (4)
C(4)—C(19)—C(20)	123.5 (4)	C(14)—O(17)—C(18)	118.8 (5)

Table 3. *Torsion angles* (°) *for the title compound and ABNOM*

	(II)	ABNOM
Cyclohexane ring		
C(8)—C(1)—C(9)—C(5)	−64.8 (5)	−63.1
C(1)—C(9)—C(5)—C(6)	64.5 (5)	63.5
C(9)—C(5)—C(6)—C(7)	−55.1 (5)	−54.0
C(5)—C(6)—C(7)—C(8)	50.0 (5)	46.0
C(6)—C(7)—C(8)—C(1)	−50.9 (5)	−45.5
C(7)—C(8)—C(1)—C(9)	56.6 (5)	52.7
Piperidine ring		
C(1)—C(2)—N(3)—C(4)	29.1 (6)	58.0
C(2)—N(3)—C(4)—C(5)	−30.5 (6)	−57.5
N(3)—C(4)—C(5)—C(9)	43.8 (5)	57.3
C(4)—C(5)—C(9)—C(1)	−62.6 (5)	−61.8
C(5)—C(9)—C(1)—C(2)	61.9 (5)	61.8
C(9)—C(1)—N(2)—N(3)	−41.7 (5)	−57.7
Torsion angles about the phenyl rings		
C(5)—C(4)—C(19)—C(24)	85.7 (5)	92.2
C(5)—C(4)—C(19)—C(20)	−93.5 (6)	−85.7
N(3)—C(4)—C(19)—C(20)	33.5 (6)	38.1
N(3)—C(4)—C(19)—C(24)	−147.3 (4)	−143.8
C(1)—C(2)—C(11)—C(16)	91.7 (6)	101.6
C(1)—C(2)—C(11)—C(12)	−90.1 (5)	−79.6
N(3)—C(2)—C(11)—C(16)	−35.0 (6)	−22.2
N(3)—C(2)—C(11)—C(12)	43.2 (4)	156.9

H atoms were located by difference Fourier synthesis and allowed to ride on their corresponding non-H atoms (C—H = 1.08 Å). For the methoxy groups, one H atom of each (namely H*A*18 and H*A*26) was located from difference maps while the others were fixed geometrically.

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Structures of Muscarine Picrate and Muscarine Tetraphenylborate

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Abstract

The tetrahydrofuran ring of the muscarine ion [(±)-(2S,4R,5S)-tetrahydro-4-hydroxy-N,N,N,5-tetramethyl-2-furanaminium] of muscarine picrate, as well as that of muscarine tetraphenylborate, is observed in a distorted twist conformation, $^4T_3$. This is different from the conformation observed in the crystal structure of muscarine chloride, but nearly the same as the conformation known from the crystal structure of muscarine iodide. The ring conformations are, however, not exactly identical as can be seen from the different pucker amplitudes. The crystal packing of muscarine tetraphenylborate shows disorder, which is especially dominant for the muscarine ion. The conformation of the tetrahydrofuran ring is undoubtedly an average of different conformations, and therefore the

result of the structure determination illustrates the flexibility of the five-membered ring.

Comment

Muscarine (I) mimics the function of the natural neurotransmitter acetylcholine in the muscarinic part of the cholinergic nervous system. A five-membered ring is found in the molecular skeleton, and this makes muscarine less flexible than acetylcholine, but still only semi-rigid.

(I)

The structure determinations of the two muscarine salts, muscarine picrate (MUSPIC) and muscarine tetraphenylborate (MUSTPB), were performed in order to observe the conformation of the muscarine ion with different surroundings. Until now only two salts have been studied crystallographically, muscarine iodide (MUSCAI), by Jellinek (1957), and muscarine chloride (MUSCHL), by Frydenvang & Jensen (1990), and these structure determinations show two different ring conformations. The flexibility of the muscarine ion has been examined by force-field calculations (Frydenvang, 1989), and these calculations indicate that the muscarine ion is very flexible. This is in agreement with results (Lagersted, Frydenvang & Jensen, unpublished results) of an analysis of the tetrahydrofuran ring in the Cambridge Structural Database (CSD, Version 4.3, July 1990 release; Allen et al., 1979).

Final atomic coordinates and displacement parameters are given in Table 1. Bond lengths, bond angles, selected torsion angles, hydrogen-bond dimensions and pseudorotational parameters are given in Table 2. The ions with atomic labelling are shown in Fig.1.

MUSPIC: The muscarine ion and the picrate ion are observed with bond lengths and bond angles within the expected ranges (Table 2). Angles between planes (Fig. 1b) reveal that two nitro groups of the picrate ion are approximately coplanar with the benzene ring, while the angle between the nitro group bonded to C22 and the benzene ring is −56.26 (4)°, in accordance with the results of a search of the CSD. The picrate ions are stacked along the a axis, but not exactly on top of each other, and strain is thereby relieved. The nitro group bonded to C22 is on the unhindered outside of the stack. The aromatic rings are parallel and the distance between the planes is on average 3.3 Å, which is approximately the van der Waals distance. The muscarine ions are situated in

Fig. 1. Views of (a) the muscarine ion and (b) the picrate ion of MUSPIC, and views of (c) the muscarine ion and (d) the tetraphenylborate ion of MUSTPB. Atoms are represented by displacement ellipsoids drawn at the 50% probability level (ORTEPII; Johnson, 1976). For the picrate ion (b), distances from the best plane through the benzene ring and angles between planes of the nitro groups and the benzene ring are shown.

pairs between the stacks of picrate ions. The shortest contact between the muscarine ions is $C4\cdots O12(1-x, 1-y, 3-z)$ 3.341 (2) Å. Crystal packing is governed by the hydrogen bond $O12—H\cdots O21$, van der Waals interactions and electrostatic contacts from the quaternary ammonium group to the O atoms of the picrate ions.

MUSTPB: The muscarine ion is disordered. Fig. 1(c) shows the large displacement parameters. Observed bond lengths and bond angles are different from those in MUSPIC (Table 2), as a result of the disorder. The large displacement parameters give some unrealistic bond lengths [*e.g.* C2—C3 1.31 (2) and C5—C6 1.62 (2) Å]. In an attempt to improve the refinement, some of the atoms in the five-membered ring were split into two different parts, but without success. Only C1 has been kept in two different positions, C11 and C12, with a population factor 0.5. The muscarine ion is therefore undoubtedly present in different conformations in the crystal. The disorder illustrates the flexibility of the muscarine ion. The crystal packing is controlled by the tetraphenylborate ions (TPB). Contacts between these ions are weak van der Waals interactions, and the closest contact observed is $C35\cdots C44(x+1, y, z)$ 3.66 Å. The muscarine ions are situated between the TPB ions. The closest contact observed between the muscarine ions [$O11\cdots C12(x, \frac{1}{2}-y, \frac{1}{2}+z)$ 3.13 (4) Å] arises from the disorder and is not a special favourable interaction. There are no short contacts between the muscarine and the TPB ions. The charges are delocalized and only weak electrostatic contacts are present. A preferred contact between a quaternary ammonium group and a benzene ring as described by Dhanens, Lacombe, Lehn & Vigneron (1984) was not observed here. Furthermore, there is no hydrogen bond involving the hydroxy group in muscarine and therefore this ion can adopt many different conformations.

Both muscarine ions are observed in distorted twist conformations, $^4T_3$, with the pseudorotational parameters as shown in Table 2. Four different structure determinations of the muscarine ion are now available and in three of these the five-membered ring has approximately the
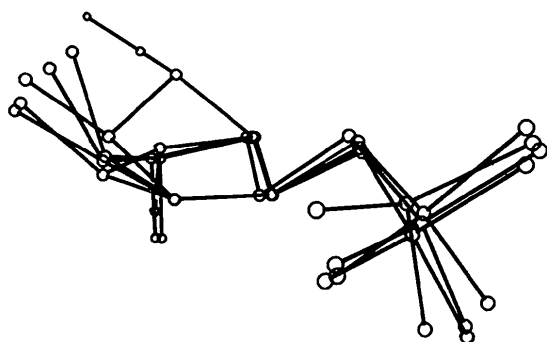
same overall conformation. Only MUSCHL is different. Fig. 2 shows the four muscarine ions superimposed. Differences in the puckering amplitudes have a great influence on the spatial arrangement of the substituents in relation to the five-membered ring. The puckering amplitude for MUSCAI is small, but this result is hardly significant because of the lack of accuracy. The quaternary ammonium group is observed with the torsion angle O—C—C—N in a *gauche* orientation in all four crystal structures. This is the most favourable conformation, but it does not indicate that it is the 'biologically active' conformation of the muscarine ion. The orientation of the quaternary ammonium group is very flexible and can easily change to the extended orientation ($\Delta E < 13$ kJ mol^{-1}) (Frydenvang, 1989).
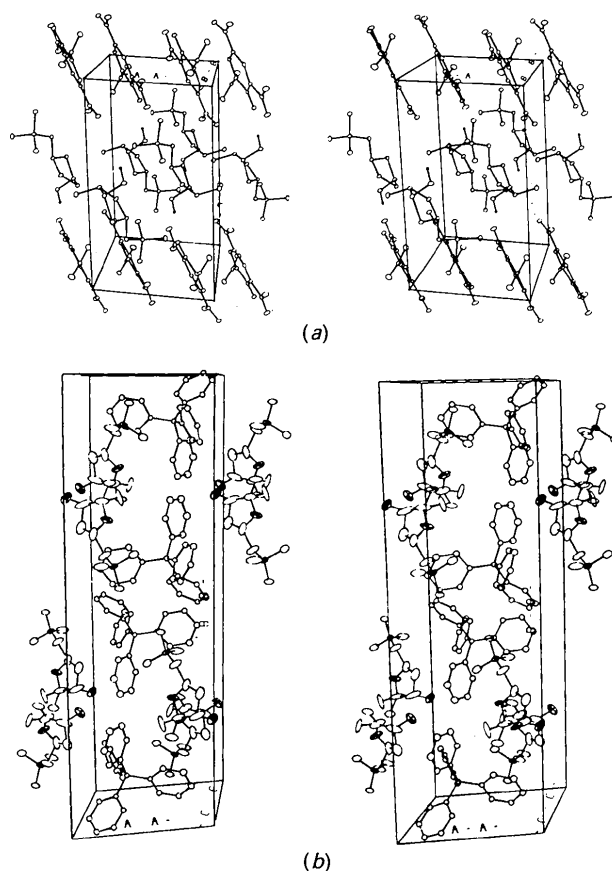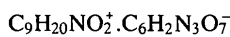

(a)

(b)

Fig. 3. Stereo diagrams of the crystal packing of (a) MUSPIC (x horizontal, z vertical and y in the depth) and (b) MUSTPB (x horizontal, y vertical and z in the depth).

Fig. 2. The four muscarine ions superimposed. MUSCHL is shown with the hydroxy H atom. The O11 atoms are exactly superimposed. The bonds O11—C5 are oriented in the same direction and the atoms C4 are in the same plane.

Experimental

MUSPIC

Crystal data

$C_9H_{20}NO_2^+.C_6H_2N_3O_7^-$
$M_r = 402.36$
Triclinic

$D_x(105$ K$) = 1.501$ Mg m^{-3}
$D_m(293$ K, flotation$) =$
  1.441 Mg m^{-3}

$P\bar{1}$
$a = 7.742\ (2)$ Å
$b = 8.886\ (2)$ Å
$c = 13.101\ (3)$ Å
$\alpha = 97.39\ (2)°$
$\beta = 94.35\ (2)°$
$\gamma = 91.42\ (2)°$
$V = 890.7\ (7)$ Å^3
$Z = 2$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 18.71–23.74°$
$\mu = 0.117$ mm^{-1}
$T = 105$ K
Needles
$0.35 \times 0.35 \times 0.35$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
5549 measured reflections
5191 independent reflections
3707 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.012$
$\theta_{max} = 30.0°$

$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections
  monitored every 300 reflections
  frequency: 166 min
  intensity variation: 0.4%

Refinement

Refinement on F
Final $R = 0.033$
$wR = 0.042$
$S = 1.484$
3707 reflections
319 parameters
Only coordinates of H atoms refined
Calculated weights $w = 1/[\sigma^2(F)+(0.04F)^2/4]$

$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.376$ e Å^{-3}
$\Delta\rho_{min} = -0.207$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

MUSTPB

Crystal data

$C_9H_{20}NO_2^+.C_{24}H_{20}B^-$
$M_r = 493.50$
Monoclinic
$P2_1/c$
$a = 9.936\ (2)$ Å
$b = 30.210\ (5)$ Å
$c = 9.771\ (1)$ Å
$\beta = 111.34\ (1)°$
$V = 2732\ (2)$ Å^3
$Z = 4$

$D_x\ (105\ K) = 1.20$ Mg m^{-3}
$D_m\ (293\ K,$ flotation$) = 1.16$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 15.62–18.76°$
$\mu = 0.068$ mm^{-1}
$T = 105$ K
Needles
$0.40 \times 0.30 \times 0.25$ mm
Colourless

Data collection

CAD-4 Enraf–Nonius diffractometer
Profile data from ω scans
6848 measured reflections
5957 independent reflections
3375 observed reflections
  $[I > 3\sigma(I)]$
$R_{int} = 0.013$
$\theta_{max} = 27.00°$

$h = 0 \rightarrow 12$
$k = -21 \rightarrow 38$
$l = -12 \rightarrow 11$
3 standard reflections
  monitored every 300 reflections
  frequency: 166 min
  intensity variation: -1.0%

Refinement

Refinement on F
Final $R = 0.130$
$wR = 0.127$
$S = 2.885$
3375 reflections
218 parameters
H-atom parameters not refined
Calculated weights $w = 1$

$(\Delta/\sigma)_{max} = 0.61$
$\Delta\rho_{max} = 0.929$ e Å^{-3}
$\Delta\rho_{min} = -0.725$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and displacement parameters for non-*H *atoms* (Å^2)

$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j;\ B_{iso}$ for the TPB ion.

	x	y	z	B_{eq}/B_{iso}
MUSPIC				
C1	1.0400 (2)	0.7802 (1)	1.4886 (1)	1.40 (2)
C2	0.8518 (2)	0.7622 (1)	1.44510 (8)	1.05 (2)
C3	0.7762 (2)	0.6016 (1)	1.44138 (9)	1.12 (2)
C4	0.7229 (2)	0.6030 (1)	1.55099 (9)	1.08 (2)
C5	0.6479 (2)	0.7609 (1)	1.57054 (8)	0.99 (2)
C6	0.6660 (2)	0.8210 (1)	1.68474 (9)	1.06 (2)
N7	0.5648 (1)	0.9611 (1)	1.71790 (7)	1.00 (2)
C8	0.3741 (2)	0.9302 (2)	1.6938 (1)	1.58 (2)
C9	0.5989 (2)	1.0005 (1)	1.83271 (9)	1.39 (2)
C10	0.6204 (2)	1.0944 (1)	1.66728 (9)	1.46 (2)
O11	0.7436 (1)	0.85626 (9)	1.51193 (6)	1.22 (1)
O12	0.6219 (1)	0.5754 (1)	1.37456 (6)	1.59 (2)
C21	0.7369 (1)	0.6467 (1)	1.10337 (8)	0.97 (2)
C22	0.8381 (2)	0.7461 (1)	1.04873 (9)	1.03 (2)
C23	0.8936 (2)	0.7111 (1)	0.95243 (9)	1.07 (2)
C24	0.8568 (2)	0.5645 (1)	0.90163 (8)	1.07 (2)
C25	0.7659 (2)	0.4586 (1)	0.94670 (9)	1.07 (2)
C26	0.7098 (2)	0.4966 (1)	1.04429 (9)	1.01 (2)
O21	0.6802 (1)	0.6930 (1)	1.18770 (6)	1.33 (1)
N22	0.8798 (1)	0.8994 (1)	1.10091 (8)	1.23 (2)
O221	0.9596 (1)	0.9140 (1)	1.18625 (7)	1.92 (2)
O222	0.8339 (2)	1.0065 (1)	1.05613 (8)	2.28 (2)
N24	0.9198 (1)	0.5226 (1)	0.80101 (7)	1.31 (2)
O241	0.8787 (1)	0.3967 (1)	0.75417 (7)	2.04 (2)
O242	1.0134 (1)	0.6163 (1)	0.76698 (7)	1.73 (2)
N26	0.6177 (1)	0.3770 (1)	1.08590 (8)	1.14 (2)
O261	0.5711 (1)	0.4008 (1)	1.17365 (7)	2.10 (2)
O262	0.5873 (1)	0.2547 (1)	1.03069 (7)	2.05 (2)
MUSTPB				
C6	0.271 (1)	0.1248 (3)	0.549 (1)	7.4 (3)
N7	0.3513 (6)	0.1076 (2)	0.6952 (6)	3.1 (1)
C8	0.492 (1)	0.1335 (3)	0.757 (1)	6.0 (3)
C9	0.3871 (8)	0.0603 (2)	0.6846 (8)	4.0 (2)
C10	0.290 (1)	0.1134 (3)	0.809 (1)	9.3 (3)
C11	0.350 (2)	0.2430 (9)	0.397 (2)	8.7 (6)
C2	0.246 (2)	0.2384 (4)	0.474 (2)	13.6 (4)
C3	0.109 (2)	0.2310 (4)	0.395 (2)	12.2 (5)
O11	0.2932 (8)	0.2022 (2)	0.5850 (8)	7.8 (2)
O12	0.0083 (8)	0.2469 (3)	0.4639 (9)	8.5 (2)
C4	0.089 (1)	0.1809 (5)	0.392 (1)	8.6 (4)
C5	0.198 (1)	0.1724 (4)	0.552 (1)	7.6 (3)
C12	0.283 (3)	0.2740 (7)	0.393 (4)	12.0 (9)
B	0.6584 (7)	0.1038 (2)	0.3248 (7)	1.7 (1)
C21	0.7346 (6)	0.1073 (2)	0.5073 (6)	1.58 (9)
C22	0.7306 (7)	0.0716 (2)	0.5996 (7)	2.5 (1)
C23	0.7955 (7)	0.0730 (2)	0.7516 (7)	2.4 (1)
C24	0.8686 (6)	0.1104 (2)	0.8210 (6)	2.3 (1)
C25	0.8799 (7)	0.1455 (2)	0.7359 (7)	2.7 (1)
C26	0.8135 (7)	0.1434 (2)	0.5827 (7)	2.4 (1)
C31	0.7288 (6)	0.0615 (2)	0.2677 (6)	1.61 (9)
C32	0.6568 (6)	0.0425 (2)	0.1285 (6)	1.9 (1)
C33	0.7184 (6)	0.0104 (2)	0.0688 (6)	2.2 (1)
C34	0.8560 (6)	-0.0056 (2)	0.1476 (6)	2.2 (1)
C35	0.9287 (7)	0.0113 (2)	0.2883 (6)	2.3 (1)
C36	0.8661 (6)	0.0442 (2)	0.3446 (6)	2.1 (1)

C41	0.4831 (6)	0.0960 (2)	0.2752 (6)	1.9 (1)
C42	0.4240 (6)	0.0569 (2)	0.3084 (6)	2.1 (1)
C43	0.2772 (7)	0.0495 (2)	0.2663 (7)	2.3 (1)
C44	0.1791 (7)	0.0802 (2)	0.1849 (7)	3.0 (1)
C45	0.2304 (8)	0.1184 (3)	0.1449 (8)	3.4 (1)
C46	0.3792 (7)	0.1264 (2)	0.1896 (7)	2.8 (1)
C51	0.6894 (6)	0.1492 (2)	0.2491 (6)	2.0 (1)
C52	0.7525 (7)	0.1495 (2)	0.1430 (7)	3.0 (1)
C53	0.7756 (8)	0.1887 (3)	0.0781 (8)	4.0 (2)
C54	0.7386 (8)	0.2286 (3)	0.1197 (8)	3.8 (2)
C55	0.6737 (8)	0.2299 (3)	0.2225 (8)	3.3 (1)
C56	0.6480 (7)	0.1911 (2)	0.2844 (7)	2.6 (1)

Table 2. Bond lengths (Å), bond angles (°), selected torsion angles (°), hydrogen-bond dimensions (Å, °) and pseudorotational parameters (°) (Rao, Westhof & Sundaralingam, 1981).

The muscarine ion

	MUSPIC	MUSTPB	MUSCHL	MUSCAI*
Bond lengths				
C1—C2	1.521 (2)	1.49 (3)/1.47 (3)	1.509 (2)	
C2—C3	1.522 (2)	1.31 (2)	1.526 (2)	
C2—O11	1.458 (1)	1.49 (1)	1.442 (2)	
C3—C4	1.522 (2)	1.53 (2)	1.523 (2)	
C3—O12	1.423 (1)	1.48 (2)	1.414 (2)	
C4—C5	1.531 (2)	1.56 (1)	1.533 (2)	
C5—C6	1.517 (2)	1.62 (2)	1.525 (2)	
C5—O11	1.441 (1)	1.27 (1)	1.444 (2)	
C6—N7	1.521 (2)	1.46 (1)	1.512 (2)	
C7—C8	1.497 (2)	1.53 (1)	1.499 (2)	
N7—C9	1.502 (1)	1.486 (9)	1.498 (2)	
N7—C10	1.499 (2)	1.46 (1)	1.505 (2)	
O12—H121	0.85 (2)			
Bond angles				
C1—C2—C3	113.3 (1)	119 (1)/103 (1)	115.7 (1)	
C1—C2—O11	109.90 (8)	110 (1)/150 (2)	108.5 (1)	
C3—C2—O11	104.66 (1)	107 (1)	104.7 (1)	
C2—C3—C4	101.57 (9)	106 (1)	101.8 (1)	
C2—C3—O12	112.3 (1)	114 (1)	114.6 (1)	
C4—C3—O12	106.71 (9)	103 (1)	110.5 (1)	
C3—C4—C5	101.14 (9)	97 (1)	102.2 (1)	
C4—C5—C6	110.91 (9)	106.0 (9)	109.4 (1)	
C4—C5—O11	106.09 (9)	109 (1)	105.7 (1)	
C6—C5—O11	111.21 (9)	109.8 (9)	110.5 (1)	
C2—O11—C5	109.25 (8)	109.3 (8)	110.2 (1)	
C5—C6—N7	116.38 (9)	112.8 (8)	116.2 (1)	
C6—N7—C8	110.93 (9)	107.8 (7)	111.9 (1)	
C6—N7—C9	107.92 (9)	109.6 (6)	110.8 (1)	
C6—N7—C10	111.80 (9)	118.2 (8)	107.8 (1)	
C8—N7—C9	108.28 (9)	108.2 (6)	109.5 (1)	
C8—N7—C10	109.3 (1)	102.4 (7)	108.6 (1)	
C9—N7—C10	108.52 (9)	110.2 (7)	108.1 (1)	

Selected torsion angles

	MUSPIC	MUSTPB	MUSCHL	MUSCAI*
O11—C2—C3—C4	-36.2 (1)	-30 (1)	35.5 (1)	-10.6
C2—C3—C4—C5	40.6 (1)	35 (1)	-37.9	22.3
C3—C4—C5—O11	-31.4 (1)	-29 (1)	27.4 (1)	-26.4
C4—C5—O11—C2	9.2 (1)	13 (1)	-5.4 (1)	20.5
C5—O11—C2—C3	17.1 (1)	11 (1)	-19 (1)	-6.4
O11—C5—C6—N7	74.4 (1)	75 (1)	76.8 (1)	73.1
C2—O11—C5—C6	129.85 (9)	128.5 (9)	112.9 (1)	143.7

Pseudorotation parameters

$E - T$	$^4T_3$	$^4T_3$	^3E	$^4T_5$
Phase, P	-5.7 (1)	0 (2)	169.6 (1)	31.6
Amplitude, θ_m	41.5 (1)	36.3 (9)	39.2 (1)	26.6

Muscarin picrate

Bond lengths		Bond angles	
C21—C22	1.455 (2)	C22—C21—C26	110.9 (1)
C21—C26	1.456 (1)	C22—C21—O21	121.5 (1)
C21—O21	1.244 (1)	C26—C21—O21	127.5 (1)
C22—C23	1.364 (2)	C21—C22—C23	126.3 (1)
C22—N22	1.461 (1)	C21—C22—N22	116.8 (1)
C23—C24	1.397 (2)	C23—C22—N22	117.0 (1)
C24—C25	1.378 (2)	C22—C23—C24	117.9 (1)
C24—N24	1.447 (1)	C23—C24—C25	121.2 (1)
C25—C26	1.384 (2)	C23—C24—N24	119.1 (1)
C26—N26	1.451 (2)	C25—C24—N24	119.7 (1)
N22—O221	1.226 (1)	C24—C25—C26	120.0 (1)

N22—O222	1.228 (1)	C21—C26—C25	123.6 (1)
N24—O241	1.227 (1)	C21—C26—N26	120.5 (1)
N24—O242	1.238 (1)	C25—C26—N26	115.96 (9)
N26—O261	1.225 (1)	C22—N22—O221	118.4 (1)
N26—O262	1.232 (1)	C22—N22—O222	117.84 (9)
		O221—N22—O222	123.7 (1)
		C24—N24—O241	118.7 (1)
		C24—N24—O242	117.82 (9)
		O241—N24—O242	123.5 (1)
		C26—N26—O261	119.35 (9)
		C26—N26—O262	118.5 (1)
		O261—N26—O262	122.2 (1)

Hydrogen-bond dimensions

D—H···A	D···A	H···A	D—H···A
O12—H121···O21	2.843 (1)	2.03 (2)	157.6 (5)

Muscarine Tetraphenylborate

Bond lengths		Bond angles	
B—C21	1.667 (8)	C21—B—C31	109.1 (4)
B—C31	1.650 (9)	C21—B—C41	110.1 (5)
B—C41	1.646 (9)	C21—B—C51	110.2 (4)
B—C51	1.639 (9)	C31—B—C41	108.8 (4)
C21—C22	1.415 (9)	C31—B—C51	108.8 (5)
C21—C26	1.388 (8)	C41—B—C51	109.8 (4)
C22—C23	1.389 (8)	B—C21—C22	121.8 (5)
C23—C24	1.380 (8)	B—C21—C26	124.5 (5)
C24—C25	1.38 (1)	C22—C21—C26	113.6 (5)
C25—C26	1.400 (8)	C21—C22—C23	123.3 (6)
C31—C32	1.409 (7)	C22—C23—C24	120.5 (6)
C31—C36	1.398 (7)	C23—C24—C25	118.5 (5)
C32—C33	1.384 (9)	C24—C25—C26	119.9 (6)
C33—C34	1.389 (8)	C25—C26—C21	124.1 (6)
C34—C35	1.396 (8)	B—C31—C32	121.0 (5)
C35—C36	1.39 (1)	B—C31—C36	124.1 (5)
C41—C42	1.409 (9)	C32—C31—C36	114.9 (5)
C41—C46	1.406 (8)	C31—C32—C33	123.1 (5)
C42—C43	1.382 (9)	C32—C33—C34	120.5 (5)
C43—C44	1.370 (9)	C33—C34—C35	118.1 (6)
C44—C45	1.37 (1)	C34—C35—C36	120.4 (5)
C45—C46	1.40 (1)	C35—C36—C31	123.1 (5)
C51—C52	1.39 (1)	B—C41—C42	122.5 (5)
C51—C56	1.414 (9)	B—C41—C46	123.5 (6)
C52—C53	1.40 (1)	C42—C41—C46	114.0 (5)
C53—C54	1.37 (1)	C41—C42—C43	123.4 (5)
C54—C55	1.38 (1)	C42—C43—C44	120.9 (6)
C55—C56	1.38 (1)	C43—C44—C45	118.3 (6)
		C44—C45—C46	120.9 (6)
		C45—C46—C41	122.4 (7)
		B—C51—C52	123.6 (6)
		B—C51—C56	121.3 (6)
		C52—C51—C56	115.1 (6)
		C51—C52—C53	122.3 (7)
		C52—C53—C54	120.4 (8)
		C53—C54—C55	119.4 (8)
		C54—C55—C56	120.2 (7)
		C55—C56—C51	122.4 (7)

* Jellinek (1957).

MUSPIC was prepared from DL-muscarine chloride (Sigma Chemical Co.) and picric acid dissolved in hot ethanol; single crystals were obtained from slow cooling of hot ethanol solution. MUSTPB was prepared from DL-muscarine chloride (Sigma Chemical Co.) and sodium tetraphenylborate, as described by Mulzer, Angermann, Münch, Schlichthörl & Hentzschel (1987); single crystals were obtained from slow cooling of hot acetone-water solution. Data reduction: BEGIN, SDP (B. A. Frenz & Associates, Inc., 1982). Program(s) used to solve structure: MULTAN (Main et al., 1980). Program(s) used to refine structure: LSFM, SDP (B. A. Frenz & Associates, Inc., 1982). Molecular graphics: ORTEPII (Johnson, 1976).

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Structure of 4,9-Dibromo-1,6-dioxa-spiro[4.4]nona-3,8-diene-2,7-dione, C₇H₂Br₂O₄

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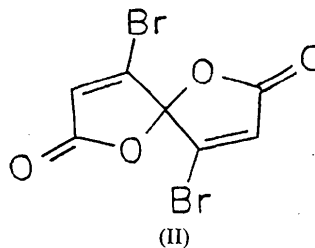Slovak Technical University, CS - 812 37 Bratislava,
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Abstract

The molecule consists of two rings connected through a single C atom. The angle between the least-squares planes defined by the rings is 90.7 (4)°.

The crystal structure consists of isolated 4,9-dibromo-1,6-dioxaspiro[4.4]nona-3,8-diene-2,7-dione molecules. The C—Br distances are 1.855 (10) and 1.837 (10) Å.

Comment

The preparation of 2-furanones has attracted considerable attention because these structures are present in many physiologically active substrates (Pattenden, 1978; Alonso, Orti, Branchadell, Oliva, Ortuno, Bertrán & Font, 1990). The chemistry of 2-furanones has been repeatedly reviewed (Rao, 1964, 1976). As part of a research program relating to the synthesis and structural study of pharmacologically interesting 2-furanone compounds, we have studied the synthesis and synthetic utilization of some derivatives of 1,4-pentadien-3-one-1,5-dicarboxylic acid (I). The bromination product of (I), 4-oxo-2,3,5,6-tetrabromopimelic acid, readily cyclizes upon heating to give the spiro-unsaturated lactone (II) in good yield.

(II)

The unsaturated dibromospirolactone (II) has not been described previously and its structure could not be elucidated solely from spectroscopic data (IR, UV, ¹H and ¹³C NMR). The signals of the olefinic protons (singlet at 6.68 p.p.m.) and of the quaternary C atom (at 109.01 p.p.m. in ¹³C NMR spectra) are both very weak.

The X-ray diffraction study shows that the molecule consists of two spiro-fused unsaturated lactone rings which are planar within experimental error. The Br atoms lie in the spirolactone planes [O(1)—C(5)—C(4)—Br(1) = − 176.3 (6), O(9)—C(5)—C(6)—Br(2) = − 179.3 (7)°]. The double bonds adjacent to single bonds are enlarged and corresponding single bonds shortened (see Table 2). There is conjugation: C(4)=C(3)—C(2)=O(10) and C(6)=C(7)—C(8)=O(11), respectively. The crystal structure is in good agreement with the ¹H and ¹³C NMR spectra which indicate equivalence of corresponding atoms in the two rings.

The interesting structure and synthetic usefulness of (II) has led us to begin a systematic study of this fortuitous finding (Végh, Jakubcová, Kožíšek, Benckova & Dvorský, 1992).

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