

Fig. 2. Stereoscopic view of the molecular packing along *a*.

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4,4-Dimethyl-2-oxomorpholinium Bromide. A Novel Six-membered Lactone with a Quaternary Nitrogen

BY GABRIEL GARCIA-GUAJARDO, FRANK R. FRONCZEK AND RICHARD D. GANDOUR*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

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Abstract. $C_6H_{12}NO_2^+Br^-$, $M_r = 210.1$, orthorhombic, $P2_12_12_1$, $a = 11.166(2)$, $b = 11.204(2)$, $c = 6.772(1)$ Å, $V = 847.2(5)$ Å³, $Z = 4$, $D_x = 1.647$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 47.5$ cm⁻¹, $F(000) = 424$, $T = 297$ K, $R = 0.026$ for 1029 observations (of 1258 unique data). The molecule has a flatter ring than found in a 2-morpholone analogue or six-membered lactones. The ring is in the half-chair conformation. The distance between two tetrahedral carbons, C(3) and C(4), is unusually short, 1.475(6) Å.

Introduction. As part of a larger study of structural changes in reactions involving tetrahedral intermediates, we are investigating substituent effects in structures of 2-substituted 2-hydroxy-4,4-dimethyl-

morpholinium salts (Gandour, Stelly, Colucci & Fronczek, 1987). The title compound is the product structure for the reaction under study.

The title compound also has some biological significance. The chloride salt has been used as an algicide and bactericide (Rucka, Oswiecimska, Pawlaczyk-Szpilowa & Witek, 1980) as well as a growth regulator (Borkowski, 1977; Dolnicki, 1980). Because the structure is thought to be a cyclic analogue of acetylcholine, the bromide (Schueler, 1956) and iodide (Nungester & Ames, 1952; Capetola, Gero & Zarro, 1975) salts have been tested for pharmacological activity.

Experimental. The title compound, prepared as described previously (Vielés & Galsomias, 1970) recrystallized from methanol, m.p. 520–521 K decomposition, crystal size 0.16 × 0.36 × 0.48 mm. Space

* To whom correspondence should be addressed.

group from diffraction symmetry *mmm* and systematic absences *h00* with *h* odd, *0k0* with *k* odd, *00l* with *l* odd; cell dimensions from setting angles of 25 reflections having $14 > \theta > 13^\circ$. Data collected on Enraf-Nonius CAD-4 diffractometer, Mo *K* α radiation, graphite monochromator, ω - 2θ scans designed for $I = 50\sigma(I)$, subject to max. scan time = 120 s, scan rates varied 0.45–4.0° min⁻¹. 1258 reflections having $1 \leq \theta \leq 28.5^\circ$, $0 \leq h \leq 15$, $0 \leq k \leq 15$, $0 \leq l \leq 9$ measured and corrected for background, Lorentz, polarization and absorption effects. Absorption corrections by ψ scans, minimum relative transmission coefficient 61.96%. Three standard reflections (200, 040, 004), 3.1% maximum variation. Structure solved by heavy-atom methods, refined by full-matrix least squares based upon *F*, using data for which $I > 3\sigma(I)$, weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using Enraf-Nonius SDP (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974), 229 unobserved data. Non-H atoms refined anisotropically; H atoms located by ΔF and refined isotropically. Final $R = 0.026$ (0.049 for all data), $wR = 0.026$, $S = 1.427$ for 140 variables. Maximum shift 0.30σ in the final cycle, maximum residual density $0.38 \text{ e } \text{Å}^{-3}$, minimum $-0.26 \text{ e } \text{Å}^{-3}$, extinction coefficient $g = 9.6(7) \times 10^{-7} [|F_o| = |F_c|(1 + gI_c)]$. For incorrect enantiomorph, $R = 0.043$ (0.067 all data), $wR = 0.050$, $S = 2.736$.

Discussion. The fractional coordinates of the title compound are given in Table 1.* Fig. 1 is a perspective drawing showing the atom numbering. Selected distances, angles and torsion angles are presented in Table 2, which gives similar values for a 2-morpholone (Sikirica, Vicković, Čaplar, Segar, Lisini, Kajfez & Šunjić, 1979) and mean values for four six-membered lactones† with ring conformations similar to those of the title compound. The range for C–H distances is 0.91 (5)–1.09 (4) Å with an average of 0.98 [6] Å. No unusually short interionic contacts are present.

The structure of the title compound has a few notable differences from the 2-morpholone and the six-membered lactones. The C(3)–C(4) distance is quite short for a bond between two tetrahedral C atoms. The N–C distances are longer in the title compound than in the 2-morpholone. The carbonyl C(2) atom is almost

exactly trigonal with all three bond angles close to 120° . The ring is in the half-chair conformation, but is flatter than the six-membered lactones and the 2-morpholone. The torsion angles C(3)–O(1)–C(2)–O(2) and N–C(1)–C(2)–O(2) are closer to 180° , whereas C(1)–C(2)–O(1)–C(3) and N–C(1)–C(2)–O(1) are closer to 0° than in either the lactones or the morpholone.

The results indicate that this structure is not a precise locked-conformational analogue of acetylcholine. Although O(1)–C(3)–C(4)–N is *gauche*, the value is $-54.5(5)^\circ$, while the comparable angle in acetylcholine

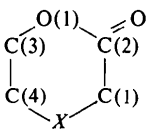
Table 1. Fractional coordinates and equivalent isotropic thermal parameters

E.s.d.'s in the least-significant digits are shown in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}^* (Å ²)
Br	0.01287 (3)	0.01383 (3)	0.40306 (5)	3.321 (6)
O(1)	0.2257 (3)	0.7880 (2)	0.0849 (4)	4.12 (6)
O(2)	0.3336 (2)	0.6277 (2)	0.1261 (4)	4.45 (6)
N	0.1797 (2)	0.7246 (2)	-0.3179 (4)	2.34 (5)
C(1)	0.2365 (3)	0.6378 (3)	-0.1799 (5)	2.59 (6)
C(2)	0.2702 (3)	0.6850 (3)	0.0194 (5)	3.18 (7)
C(3)	0.1543 (4)	0.8645 (4)	-0.0423 (6)	4.35 (9)
C(4)	0.0925 (3)	0.7976 (3)	-0.2000 (6)	3.29 (7)
C(5)	0.2741 (3)	0.8006 (3)	-0.4144 (5)	3.48 (7)
C(6)	0.1123 (3)	0.6576 (4)	-0.4746 (6)	3.99 (8)

$$* B_{\text{eq}} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

Table 2. Comparable distances (Å), angles (°) and torsion angles (°) of six-membered lactones



	<i>X</i> = C	NH	N ⁺ (CH ₃) ₂
O(1)–C(3)	1.457 [9]*	1.444 (4)	1.453 (5)
O(1)–C(2)	1.33 [3]	1.337 (4)	1.333 (4)
C(3)–C(4)	1.511 [9]	1.518 (4)	1.475 (6)
<i>X</i> –C(4)	1.509 [7]	1.443 (4)	1.502 (4)
<i>X</i> –C(1)	1.513 [4]	1.463 (4)	1.491 (4)
C(1)–C(2)	1.51 [1]	1.505 (4)	1.498 (5)
O(2)–C(2)	1.20 [2]	1.200 (4)	1.198 (4)
C(2)–O(1)–C(3)	123.8 [5]	122.0 (2)	121.2 (3)
O(1)–C(3)–C(4)	112 [1]	113.7 (2)	112.8 (3)
<i>X</i> –C(4)–C(3)	111 [1]	105.8 (2)	111.0 (3)
C(1)– <i>X</i> –C(4)	108 [1]	110.5 (2)	107.4 (3)
<i>X</i> –C(1)–C(2)	114 [1]	111.1 (2)	116.2 (3)
O(1)–C(2)–C(1)	120 [1]	119.1 (3)	120.8 (4)
O(2)–C(2)–C(1)	122 [1]	123.9 (3)	120.2 (4)
O(1)–C(2)–O(2)	118 [1]	116.9 (3)	118.9 (4)
C(2)–O(1)–C(3)–C(4)	126 [1] [2]	-23.9	26.5 (5)
C(1)–C(2)–O(1)–C(3)	113 [3]	11.0	-7.1 (5)
C(3)–O(1)–C(2)–O(2)	1170 [3]	-171.8	176.2 (4)
O(1)–C(3)–C(4)– <i>X</i>	150 [2]	50.6	-54.5 (5)
C(3)–C(4)– <i>X</i> –C(1)	161.1 [9]	-67.8	61.3 (6)
C(4)– <i>X</i> –C(1)–C(2)	148 [2]	55.9	-41.6 (5)
<i>X</i> –C(1)–C(2)–O(1)	124 [3]	-25.8	15.9 (4)
<i>X</i> –C(1)–C(2)–O(2)	1159 [3]	157.3	-167.5 (5)

* Standard deviation of mean.

† Mean of absolute value.

* Lists of H-atom coordinates, distances and angles involving H atoms, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43039 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† (4*R*,5*S*)-6-(Phenylsulfinyl)dimethylvalonolactone (Feres, Hatton, Jennings, Tyrell & Williams, 1983); compactin (Brown, Smale, King, Hasenkamp & Thompson, 1976); D-glucono-1,5-lactone (Hackert & Jacobson, 1971); dicarbobenzoxy-D-hydroxy-L-lysine lactone (de Kok & Romers, 1981).

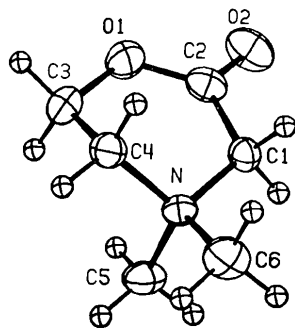


Fig. 1. Perspective drawing of 4,4-dimethyl-2-oxomorpholinium bromide. Distances (Å) and angles ($^{\circ}$) involving methyl groups: N—C(5), 1.504 (4); N—C(6), 1.502 (4); C(1)—N—C(5), 110.1 (3); C(1)—N—C(6), 109.2 (3); C(4)—N—C(5), 112.2 (3); C(4)—N—C(6), 108.9 (3); C(5)—N—C(6), 109.1 (3).

ranges* in absolute value from 64 to 89 $^{\circ}$, with a mean of 77.5 $^{\circ}$. The conformation about the ester moiety is quite different. In the lactone, C(3)—O(1)—C(2)—O(2) is 176.2 (4) $^{\circ}$ whereas the corresponding torsion angle in the acyclic ester ranges from -5.4 to 5.2 $^{\circ}$. The torsion angle C(2)—O(1)—C(3)—C(4) is 26.5 (5) $^{\circ}$ in the title compound, whereas in acetylcholine it has two ranges of absolute values, 78–94 and 154–180 $^{\circ}$, depending on the counterion.

* See Datta, Mondal & Pauling (1980) for a summary of all acetylcholine structures solved through 1980, and Jensen (1982) for the tartrate salts.

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Structure of a Difuran and a Dipyrans

BY MARJORIE M. HARDING, L. H. SUTCLIFFE* AND A. D. WHITEHOUSE

Department of Inorganic, Physical and Industrial Chemistry, Liverpool University, PO Box 147, Liverpool L69 3BX, England

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Abstract. 2,3,6,7-Tetrahydro-2,2,4,6,6,8-hexamethylbenzo[1,2-*b*:4,5-*b'*]difuran (I), C₁₆H₂₂O₂, $M_r = 246.3$, monoclinic, $P2_1/c$, $a = 5.330$ (1), $b = 10.263$ (1), $c = 12.384$ (1) Å, $\beta = 95.74$ (1) $^{\circ}$, $V = 674$ Å³, $Z = 2$, $D_m = 1.21$, $D_x = 1.214$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.43$ cm⁻¹, $F(000) = 268$, $T = 290$ K, final $R = 0.047$ for 1594 observed reflections.

* Present address: Chemistry Department, Royal Holloway and Bedford New College, University of London, Surrey TW20 0EX, England.

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3,4,8,9-Tetrahydro-2,2,5,7,7,10-hexamethylbenzo[1,2-*b*:4,5-*b'*]dipyrans (II), C₁₈H₂₆O₂, $M_r = 274.39$, monoclinic, $P2_1/c$, $a = 8.046$ (2), $b = 9.369$ (3), $c = 10.392$ (2) Å, $\beta = 90.45$ (2) $^{\circ}$, $V = 783.4$ Å³, $Z = 2$, $D_m = 1.10$, $D_x = 1.164$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 5.40$ cm⁻¹, $F(000) = 300$, $T = 290$ K, final $R = 0.063$ for 924 observed reflections. Both molecules have symmetry $\bar{1}$ and bond lengths and angles close to expected values. The geometry around the O atom in (I) is consistent with the observation that this molecule forms free radicals more readily than (II).