

C(7)	0.7402 (3)	0.3221 (4)	0.3685 (3)	3.0 (1)
C(8)	0.8138 (3)	0.4444 (4)	0.3537 (3)	3.7 (1)
C(9)	0.8542 (3)	0.5340 (4)	0.4522 (3)	3.4 (1)
C(10)	0.8096 (3)	0.5352 (4)	0.5343 (3)	3.1 (1)
C(11)	0.8580 (3)	0.6212 (4)	0.6351 (3)	4.0 (1)
C(12)	0.8957 (3)	0.5241 (5)	0.7344 (3)	4.1 (1)
C(13)	0.8008 (3)	0.4304 (5)	0.7425 (3)	4.1 (1)
C(14)	0.7510 (3)	0.3456 (4)	0.6375 (3)	3.7 (1)
C(15)	0.5619 (3)	0.4679 (5)	0.3541 (3)	3.6 (1)
C(16)	0.5915 (4)	0.6228 (5)	0.3430 (4)	4.9 (2)
C(17)	0.5071 (4)	0.4054 (6)	0.2413 (4)	5.4 (2)
C(18)	0.8047 (4)	-0.0655 (5)	0.4694 (4)	5.2 (2)

Table 2. Geometric parameters (Å, °)

O(1)—C(3)	1.215 (5)	O(2)—C(6)	1.214 (6)
C(1)—C(2)	1.562 (5)	C(1)—C(10)	1.505 (6)
C(1)—C(14)	1.549 (5)	C(2)—C(3)	1.546 (6)
C(2)—C(7)	1.555 (6)	C(2)—C(15)	1.561 (6)
C(3)—C(4)	1.472 (6)	C(4)—C(5)	1.331 (7)
C(5)—C(6)	1.479 (6)	C(5)—C(18)	1.493 (6)
C(6)—C(7)	1.517 (6)	C(7)—C(8)	1.530 (6)
C(8)—C(9)	1.481 (6)	C(9)—C(10)	1.341 (6)
C(10)—C(11)	1.496 (6)	C(11)—C(12)	1.528 (6)
C(12)—C(13)	1.520 (6)	C(13)—C(14)	1.534 (6)
C(15)—C(16)	1.525 (7)	C(15)—C(17)	1.527 (6)
C(2)—C(1)—C(10)	113.7 (3)	O(2)—C(6)—C(7)	122.9 (4)
C(2)—C(1)—C(14)	116.0 (3)	C(5)—C(6)—C(7)	116.6 (3)
C(10)—C(1)—C(14)	108.0 (3)	C(2)—C(7)—C(6)	112.2 (3)
C(1)—C(2)—C(3)	108.0 (3)	C(2)—C(7)—C(8)	112.5 (3)
C(1)—C(2)—C(7)	111.0 (3)	C(6)—C(7)—C(8)	111.3 (3)
C(1)—C(2)—C(15)	109.9 (3)	C(7)—C(8)—C(9)	112.9 (3)
C(3)—C(2)—C(7)	108.9 (3)	C(8)—C(9)—C(10)	124.2 (4)
C(3)—C(2)—C(15)	105.5 (3)	C(1)—C(10)—C(9)	123.5 (4)
C(7)—C(2)—C(15)	113.2 (3)	C(1)—C(10)—C(11)	114.4 (3)
O(1)—C(3)—C(2)	121.6 (4)	C(9)—C(10)—C(11)	122.0 (4)
O(1)—C(3)—C(4)	118.5 (4)	C(10)—C(11)—C(12)	110.2 (4)
C(2)—C(3)—C(4)	119.9 (4)	C(11)—C(12)—C(13)	110.6 (4)
C(3)—C(4)—C(5)	124.0 (4)	C(12)—C(13)—C(14)	111.4 (4)
C(4)—C(5)—C(6)	118.8 (4)	C(1)—C(14)—C(13)	111.6 (3)
C(4)—C(5)—C(18)	123.7 (4)	C(2)—C(15)—C(16)	117.5 (4)
C(6)—C(5)—C(18)	117.5 (4)	C(2)—C(15)—C(17)	112.4 (3)
O(2)—C(6)—C(5)	120.4 (4)	C(16)—C(15)—C(17)	109.5 (4)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods. H atoms were found in difference synthesis and included as fixed contributors with an overall isotropic temperature factor of 0.081 (3) Å². Programs used were: *SHELXS86* (Sheldrick, 1986), *SHELX76* (Sheldrick, 1976) and *ORTEP* (Johnson, 1965). The refinement was by full-matrix least-squares methods. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de São Carlos.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71138 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1046]

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1,5-Dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-8-methyl-3H-[1,3]dioxepino[5,6-c]-pyridinium-9-ol Maleate †

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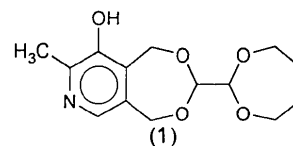
(Received 4 January 1993; accepted 5 March 1993)

Abstract

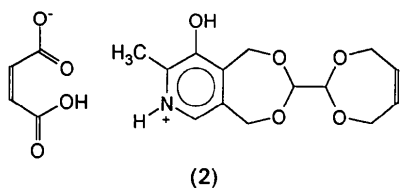
Both dioxepine rings of the title compound, 1,5-dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-9-hydroxy-8-methyl-3H-[1,3]dioxepino[5,6-c]pyridinium maleate, adopt a twist-boat conformation. In the crystal structure the maleate anions are stacked exactly between the pyridine rings of the cations at an average distance of 3.5 Å.

Comment

As a part of our research on the chemistry of vitamin B₆ (Dumić, Glunčić, Kovačević & Kujundžić, 1989), 1,5-dihydro-3-(4,7-dihydro-1,3-dioxepin-2-yl)-8-methyl-3H-[1,3]dioxepino[5,6-c]pyridin-9-ol (1) was prepared as the precursor for pyridoxine (vitamin B₆) (Dumić & Butula, 1989, 1990). In order to establish the structure of the bis-1,3-dioxepin fragment of (1) the crystal structure analysis of its maleic acid salt (2) was undertaken. Details of the synthetic work will be published elsewhere (Dumić, Vinković, Butula & Jadrijević-Mladar, 1993).



† Chemistry of 1,3-dioxepins. Part 7. Part 6: Dumić, Filić, Vinković, Jamnický & Kamenar (1993).



The structure of (2) is built up from the dioxepinopyridinium cations and maleate anions (Fig. 1). The maleate anions and pyridine rings of the dioxepinopyridinium cations are parallel to each other, thus forming plane-to-plane stacks in the crystal structure (Fig. 2). A difference Fourier map showed that the H atom bonded to O8 at a distance of 1.08 (8) Å is involved in forming a short intramolecular hydrogen bond O6...O8 of 2.410 (7) Å (Table 3). Both dioxepine rings of the cation adopt a twist-boat conformation giving the impression of being centrosymmetrically related to each other. The H atom bonded to the pyridinium N atom was clearly located in the difference Fourier map and its position re-

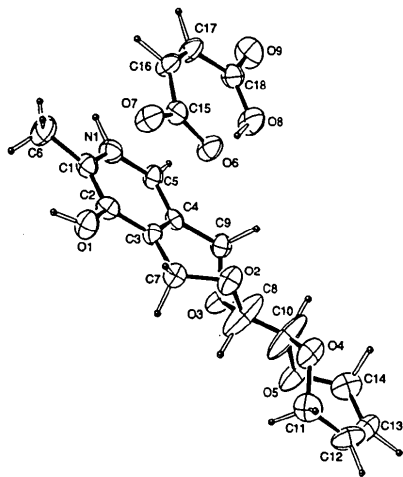


Fig. 1. ORTEP drawing of $C_{18}H_{21}NO_9$, showing the labelling scheme of non-H atoms.

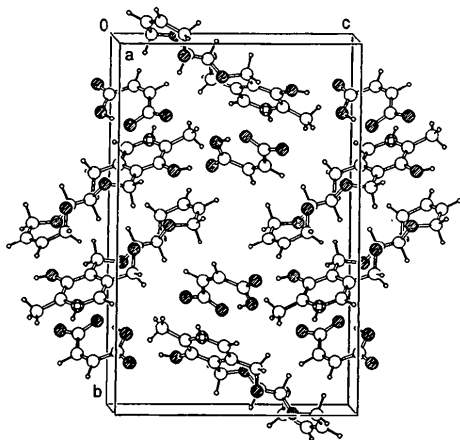


Fig. 2. PLUTON drawing of the unit cell of $C_{18}H_{21}NO_9$.

fined so that the N1—H distance amounts to 1.07 (7) Å. The cations and anions are held together alternately by hydrogen bonds O1(H)...O9 and N1(H)...O7 of 2.675 (8) and 2.714 (7) Å, respectively (Table 3).

Experimental

Crystal data

$C_{14}H_{18}NO_5 \cdot C_4H_3O_4^-$

$M_r = 394.36$

Monoclinic

$P2_1/n$

$a = 6.465 (3) \text{ \AA}$

$b = 20.720 (7) \text{ \AA}$

$c = 13.717 (4) \text{ \AA}$

$\beta = 95.61 (2)^\circ$

$V = 1829 (1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.43 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 18 reflections

$\theta = 6-10^\circ$

$\mu = 0.109 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.46 \times 0.29 \times 0.12 \text{ mm}$

Colourless

Crystal source: chemical synthesis

Data collection

Philips PW1100 diffractometer

$\theta-2\theta$ scans

Absorption correction:

none

5666 measured reflections

1198 independent reflections

1152 observed reflections

$[F > 2.0\sigma(F)]$

$R_{int} = 0.0259$

$\theta_{max} = 30^\circ$

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 23$

$l = 0 \rightarrow 17$

3 standard reflections

frequency: 120 min

intensity variation: 6.6%

Refinement

Refinement on F

Final $R = 0.057$

$wR = 0.061$

$S = 2.139$

1152 reflections

290 parameters

Coordinates only of H1C6,

H2C6 and H3C6 refined;

all parameters refined for

H1M, H1O1 and H1N;

only U refined for all

other H atoms

Calculated weights

$w = 1.977/[\sigma^2(F)]$

$(\Delta/\sigma)_{max} = -0.005$

$\Delta\rho_{max} = 0.362 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.305 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Data collection: Philips PW 1100/10 software 1974. Cell refinement: Philips PW 1100/10 software 1974. Data reduction: STRUFA (ZOK7; Vicković, 1975). Program(s) used to solve structure: MULTAN80 (Main *et al.*, 1980). Program(s) used to refine structure: SHELX76 (Sheldrick, 1976). Molecular graphics: PLUTON (Spek, 1982); ORTEPII (Johnson, 1976).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
O1	0.1923 (7)	0.1484 (3)	0.7428 (4)	0.067 (2)
O2	0.2035 (6)	0.1123 (2)	0.4556 (3)	0.064 (2)
O3	-0.1260 (6)	0.0673 (2)	0.4179 (3)	0.066 (2)

O4	0.3374 (6)	0.0512 (3)	0.2918 (3)	0.070 (2)
O5	0.0079 (7)	0.0046 (3)	0.2663 (4)	0.094 (3)
O6	0.2643 (7)	0.2723 (2)	0.5531 (4)	0.066 (2)
O7	0.4048 (6)	0.3020 (2)	0.6986 (3)	0.073 (2)
O8	-0.0378 (8)	0.2979 (3)	0.4428 (3)	0.074 (2)
O9	-0.2950 (7)	0.3666 (3)	0.4370 (4)	0.084 (2)
N1	-0.3029 (8)	0.2154 (3)	0.6552 (4)	0.053 (2)
C1	-0.133 (1)	0.2028 (3)	0.7180 (5)	0.050 (2)
C2	0.0191 (9)	0.1639 (3)	0.6861 (5)	0.047 (3)
C3	0.0022 (8)	0.1413 (3)	0.5902 (4)	0.042 (3)
C4	-0.1787 (9)	0.1550 (3)	0.5284 (4)	0.039 (2)
C5	-0.3289 (9)	0.1929 (3)	0.5639 (5)	0.048 (3)
C6	-0.123 (1)	0.2348 (4)	0.8157 (6)	0.078 (4)
C7	0.1854 (9)	0.1050 (3)	0.5572 (5)	0.054 (3)
C8	0.085 (1)	0.0667 (6)	0.3999 (7)	0.126 (5)
C9	-0.2115 (9)	0.1305 (4)	0.4256 (5)	0.052 (3)
C10	0.130 (1)	0.0540 (7)	0.3136 (8)	0.144 (6)
C11	0.431 (1)	-0.0103 (5)	0.2883 (7)	0.077 (4)
C12	0.3729 (1)	-0.0424 (4)	0.1932 (7)	0.083 (4)
C13	0.194 (1)	-0.0353 (4)	0.1373 (6)	0.078 (4)
C14	0.018 (1)	0.0019 (4)	0.1659 (7)	0.076 (4)
C15	0.2673 (9)	0.3069 (3)	0.6289 (5)	0.051 (3)
C16	0.099 (1)	0.3543 (4)	0.6394 (5)	0.063 (3)
C17	-0.068 (1)	0.3688 (4)	0.5793 (5)	0.064 (3)
C18	-0.138 (1)	0.3432 (4)	0.4811 (5)	0.055 (3)

Table 2. Geometric parameters (Å, °)

O1—C2	1.339 (8)	C1—C2	1.374 (9)
O2—C7	1.418 (8)	C1—C6	1.491 (11)
O2—C8	1.396 (11)	C2—C3	1.391 (9)
O3—C8	1.410 (9)	C3—C4	1.405 (8)
O3—C9	1.429 (9)	C3—C7	1.509 (9)
O4—C10	1.401 (9)	C4—C5	1.375 (9)
O4—C11	1.413 (12)	C4—C9	1.494 (9)
O5—C10	1.413 (13)	C8—C10	1.275 (15)
O5—C14	1.386 (11)	C11—C12	1.481 (13)
O6—C15	1.262 (8)	C12—C13	1.327 (11)
O7—C15	1.244 (7)	C13—C14	1.461 (12)
O8—C18	1.281 (10)	C15—C16	1.483 (10)
O9—C18	1.231 (9)	C16—C17	1.327 (9)
N1—C1	1.355 (8)	C17—C18	1.477 (10)
N1—C5	1.332 (9)		
C7—O2—C8	111.9 (5)	O2—C8—O3	112.8 (8)
C8—O3—C9	114.1 (7)	O3—C8—C10	118.62 (71)
C10—O4—C11	117.7 (8)	O2—C8—C10	118.96 (77)
C10—O5—C14	114.1 (7)	O3—C9—C10	111.2 (6)
C1—N1—C5	123.4 (6)	O5—C10—C8	114.0 (8)
N1—C1—C6	116.5 (6)	O4—C10—C8	121.2 (7)
N1—C1—C2	118.1 (6)	O4—C10—O5	112.1 (6)
C2—C1—C6	125.4 (6)	O4—C11—C12	111.2 (7)
O1—C2—C1	122.6 (6)	C11—C12—C13	126.4 (8)
C1—C2—C3	120.4 (6)	C12—C13—C14	124.0 (8)
O1—C2—C3	116.9 (5)	O5—C14—C13	113.6 (7)
C2—C3—C7	117.4 (5)	O6—C15—O7	122.6 (6)
C2—C3—C4	119.1 (5)	O7—C15—C16	117.1 (6)
C4—C3—C7	123.5 (5)	O6—C15—C16	120.3 (6)
C3—C4—C9	122.3 (5)	C15—C16—C17	130.5 (7)
C3—C4—C5	118.5 (5)	C16—C17—C18	130.0 (7)
C5—C4—C9	119.2 (6)	O9—C18—C17	118.1 (7)
N1—C5—C4	120.3 (6)	O8—C18—C17	121.1 (7)
O2—C7—C3	112.6 (5)	O8—C18—O9	120.8 (7)

Table 3. Hydrogen-bonding geometry (Å, °)

D	H	A	D—H	D...A	D—H...A
O1	H1O1	O9 ⁱ	0.91 (7)	2.675 (8)	153 (6)
N1	H1N	O6 ⁱⁱ	1.07 (7)	2.714 (7)	169 (6)
O8	H1O8	O6	1.08 (8)	2.410 (7)	168 (8)

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

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71176 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1031]

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1-Methanesulfonyl-1a,2,6,6a-tetrahydro-1H,4H-[1,3]dioxepino[5,6-b]azirine †

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Abstract

The dioxepine part of the title heterocycle adopts a chair conformation. The position of O1 opposite to the lone pair at the N atom and the inequality of the bond angles O1—S1—N1 \gg O2—S1—N1 suggest an $n-\sigma^*$ interaction of

† Chemistry of 1,3-dioxepins. Part 8. Part 7: Vinković, Dumić & Kamenar (1993).