

conformation of the pendant  $\text{NEt}_3$  function in the  $[\text{NMe}_4]^+$  salt, defined by the three  $\text{B}(1)-\text{N}(2)-\text{C}(i1)-\text{C}(i2)$  torsion angles,  $73.4$  (9),  $176.2$  (9) and  $81.9$  (10) $^\circ$  ( $i = 1-3$ ), closely corresponds to one of the two distinct conformations observed in the  $\text{K}^+$  salt.

There is, however, slight indication that the icosahedral  $\text{B}_{12}$  framework of the  $[\text{NMe}_4]^+$  salt is somewhat less distorted. Thus, the range of B-B connectivity lengths determined herein is  $1.738$  (14)– $1.796$  (14) Å, *c.f.*  $1.74$ – $1.83$  Å for the  $\text{K}^+$  salt. This may be a consequence of the weaker polarizing power of the quaternary ammonium cation *versus* the group  $\text{I}^+$  cation, and is consistent with less observed distortion in  $[\text{HNEt}_3]_2[\text{B}_{12}\text{H}_{12}]$  (Shoham, Schomburg & Lipscomb, 1980) than in  $\text{Ca}[\text{B}_{12}\text{H}_{12}]$  (Solntsev, Kuznetsov & Ponomarev, 1976).

The  $[\text{NMe}_4]^+$  cation has effective  $T_d$  point symmetry, and the conformation about each N-C bond is close to staggered. There are no serious contacts within or between ions, and a crystal packing diagram, as seen along the  $a$  axis, has been deposited.

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## Structure of (+)-5,6,7,8-Tetrahydro-3-methoxy-17-methylmorphinan-4-ol Hemihydrate, a Potential Morphinadien for Diels–Alder Reactions

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**Abstract.**  $\text{C}_{18}\text{H}_{21}\text{NO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,  $M_r = 292.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.480$  (4),  $b = 14.336$  (3),  $c = 21.274$  (3) Å,  $V = 3196.2$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.22$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}) = 0.71069$  Å,  $\mu = 0.087$  mm<sup>-1</sup>,  $F(000) = 1256$ ,  $T = 293$  K,  $R = 0.057$  for 3827 reflections. The H atom at C(14) is in the  $\beta$  position, which means that the B/C ring moiety of the title compound is *cis* fused and contains two double bonds in conjugation. The two independent molecules are linked together by one water molecule *via* hydrogen bonds of  $2.769$  (8) |N(1)⋯O(W)| and  $2.651$  (9) Å |O(2)⋯O(W)|.

**Introduction.** The Diels–Alder reaction of opium alkaloid (–)-thebaine has been investigated with many dienophiles (Bentley, 1971). Several reaction products

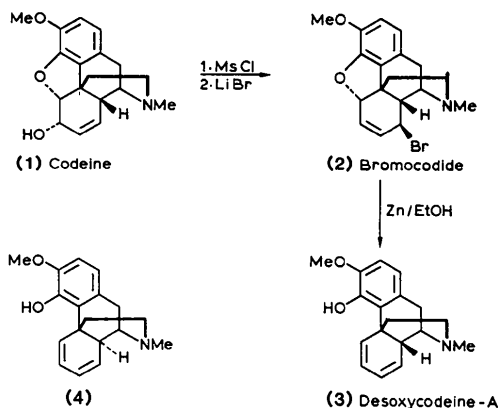
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possess, after further modification, enhanced analgesic activity. Practically all these compounds have the  $6\alpha,14\alpha$ -ethenoisomorphinan skeleton with the lipophilic substituent at position  $7\alpha$ . Only recently did it become clear that isomeric ethenomorphinans are accessible starting from modified thebaine compounds (Crabben-dam, Lie, Linders & Maat, 1984; van Koningsveld, Lie & Maat, 1984*b*). These findings raised our interest in other conjugated morphinans. Codeine (1) is first mesylated with mesyl chloride (methanesulfonyl chloride) and then converted into bromocodide (2) upon treatment with lithium bromide.

When bromocodide (2) is treated with zinc in ethanol, it loses the bromine atom and the  $4,5\alpha$ -epoxy bridge is opened affording the 5,7-morphinadien (3),

trivially named desoxycodine-A (Small & Cohen, 1931). The structure of (3), for which we improved the synthesis (Linders, Adriaansens, Lie & Maat, 1985), has never been fully elucidated. The mass spectrum of (3) shows a peak at  $m/z$  59 with very low abundance. This is typical for morphinans with a *trans*-fused *B/C* ring moiety (4) (Mandelbaum & Ginsburg, 1965), which would have meant a rearrangement of the configuration at position 14 during the treatment with zinc in ethanol. The structure of (3), especially regarding the configuration at position 14, could not be determined unambiguously either from further MS studies or from  $^1\text{H}$  NMR data. Therefore, a single-crystal X-ray analysis was performed, which confirmed structure (3) as a *B/C-cis*-fused 5,7-morphinadien.



**Experimental.** Title compound prepared in Laboratory of Organic Chemistry, Delft. Very poorly scattering crystals grown from ethanol, m.p. 395–396 K,  $[\alpha]_D^{25.0^\circ\text{C}} = 117^\circ$  [ethanol, 1.0 g dm $^{-3}$ ]. Determination carried out with available crystals, though poor quality restricted accuracy.  $D_m$  not measured. Crystal: 0.50 × 0.35 × 0.10 mm. CAD-4 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\omega$  scan (width = 0.95 + 0.35 tan  $\theta$ ) $^\circ$ ,  $\theta_{\text{max}} = 29^\circ$ . Cell parameters from 25 reflections with  $10 < \theta < 16^\circ$ . 4712 reflections ( $h$ : 0→14,  $k$ : 0→19,  $l$ : 0→29) collected and corrected for Lorentz-polarization; no correction for absorption. Max. recording time 120 s,  $\sigma_{\text{count}}(I)/I < 0.02$  requested in a scan. Three reference reflections showed decay of 6%; correction applied. Structure solved by direct methods and refined by (blocked) full-matrix least squares on  $F$ ; all non-H atoms with anisotropic thermal parameters. H atoms located by difference Fourier map but included in idealized positions [ $sp^2$ ,  $d(\text{C}-\text{H}) = 0.95 \text{ \AA}$ ;  $sp^3$ ,  $d(\text{C}-\text{H}) = 1.00 \text{ \AA}$ ] with isotropic thermal parameters set to 1.1 times that of the bonded atom, H parameters not refined. Model converged with 3827 observations [2399 with  $I > 1.0 \sigma(I)$  plus those for which  $F_c > F_o$ ], 389 variables,  $R = 0.057$ ,  $wR = 0.051$ ,  $w = 1$ ,  $S = 0.64$ ;  $\Delta/\sigma < 0.3$ . Final  $\Delta F$  synthesis has  $|\rho| < 0.29 \text{ e \AA}^{-3}$ . Calculations performed

on Delft University Amdahl 470/V7B computer with programs of the *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and *MULTAN* (Germain, Main & Woolfson, 1971) packages. Atomic scattering factors from *XRAY72*.

Table 1. Final coordinates and equivalent isotropic thermal parameters

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Molecule (I)	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
C(1)	0.2968 (6)	0.1645 (5)	0.0459 (3)	0.065
C(2)	0.2097 (6)	0.0973 (4)	0.0630 (3)	0.065
C(3)	0.2290 (5)	0.0466 (4)	0.1170 (3)	0.058
C(4)	0.3374 (5)	0.0639 (4)	0.1541 (2)	0.055
C(5)	0.6036 (6)	0.0629 (5)	0.2060 (3)	0.069
C(6)	0.6859 (7)	0.0115 (5)	0.1749 (4)	0.081
C(7)	0.7255 (7)	0.0391 (5)	0.1129 (3)	0.080
C(8)	0.7092 (6)	0.1268 (5)	0.0936 (3)	0.073
C(9)	0.5995 (6)	0.2836 (4)	0.1066 (2)	0.060
C(10)	0.4975 (6)	0.2562 (4)	0.0591 (3)	0.065
C(11)	0.4061 (5)	0.1809 (4)	0.0805 (2)	0.055
C(12)	0.4279 (5)	0.1295 (4)	0.1354 (2)	0.051
C(13)	0.5443 (5)	0.1502 (4)	0.1770 (2)	0.054
C(14)	0.6499 (5)	0.1961 (4)	0.1379 (2)	0.058
C(15)	0.5033 (6)	0.2195 (5)	0.2278 (2)	0.066
C(16)	0.4615 (6)	0.3115 (5)	0.1984 (3)	0.071
C(17)	0.5215 (8)	0.4396 (4)	0.1306 (3)	0.086
C(18)	0.0564 (7)	-0.0578 (6)	0.1001 (4)	0.112
N(1)	0.5592 (5)	0.3488 (3)	0.1564 (2)	0.063
O(1)	0.1487 (4)	-0.0204 (3)	0.1404 (2)	0.077
O(2)	0.3528 (4)	0.0178 (3)	0.2094 (2)	0.071
Molecule (II)				
C(1)	0.7385 (7)	0.0808 (5)	0.4475 (3)	0.075
C(2)	0.6673 (6)	0.1590 (5)	0.4308 (3)	0.073
C(3)	0.7148 (6)	0.2179 (4)	0.3863 (3)	0.063
C(4)	0.8335 (6)	0.2007 (4)	0.3587 (3)	0.063
C(5)	1.1134 (7)	0.1929 (6)	0.3346 (4)	0.089
C(6)	1.1915 (8)	0.2254 (6)	0.3781 (5)	0.107
C(7)	1.2092 (8)	0.1760 (7)	0.4371 (4)	0.104
C(8)	1.1718 (8)	0.0883 (6)	0.4414 (3)	0.088
C(9)	1.0441 (6)	-0.0473 (5)	0.3993 (3)	0.072
C(10)	0.9301 (7)	-0.0246 (5)	0.4408 (3)	0.083
C(11)	0.8589 (6)	0.0632 (5)	0.4218 (3)	0.067
C(12)	0.9080 (6)	0.1249 (4)	0.3777 (3)	0.064
C(13)	1.0356 (6)	0.1058 (4)	0.3450 (3)	0.064
C(14)	1.1186 (6)	0.0401 (5)	0.3844 (3)	0.066
C(15)	1.0039 (6)	0.0545 (5)	0.2828 (3)	0.076
C(16)	0.9421 (7)	0.0387 (5)	0.2958 (3)	0.081
C(17)	0.9600 (9)	-0.1872 (5)	0.3488 (4)	0.102
C(18)	0.5356 (7)	0.3202 (6)	0.3912 (3)	0.094
N(1)	1.0167 (5)	-0.0954 (4)	0.3394 (2)	0.069
O(1)	0.6554 (4)	0.2971 (3)	0.3650 (2)	0.076
O(2)	0.8747 (4)	0.2567 (3)	0.3110 (2)	0.080
O(11)	0.7656 (4)	0.3796 (3)	0.2349 (2)	0.059

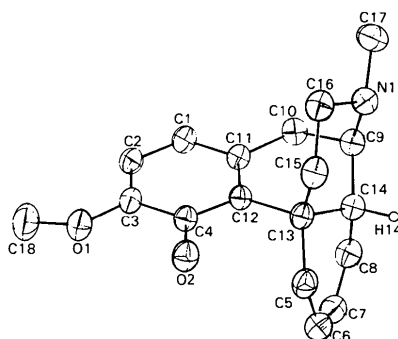


Fig. 1. ORTEP plot (Johnson, 1965) of one of the two independent molecules of the title compound. Boundary surfaces are drawn to enclose 50% probability.

**Discussion.** The final parameters are given in Table 1.\* Bond lengths and bond angles are listed in Table 2. Fig. 1 shows the molecular structure of one molecule along with the adopted numbering scheme. The two independent molecules are linked together by one water molecule *via* hydrogen bonds of 2.769 (8) [N(1)⋯O(W)] and 2.651 (9) Å [O(2)⋯O(W)]. There is no essential difference between the two independent molecules, except for the rotational orientation of the methoxy group. The angle between the C(3)O(1)C(18) plane and the aromatic ring plane is 16.5 (8) and 1.7 (8)° in (I) and (II) respectively. The interaction of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42521 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and bond angles (°) in the independent molecules (I) and (II) and short O(W) contacts

	(I)	(II)	(I)	(II)
C(1)–C(2)	1.376 (9)	1.393 (10)	C(9)–C(10)	1.522 (8)
C(1)–C(11)	1.383 (8)	1.397 (9)	C(9)–C(14)	1.516 (8)
C(2)–C(3)	1.374 (8)	1.363 (9)	C(9)–N(1)	1.474 (7)
C(3)–C(4)	1.406 (8)	1.397 (8)	C(10)–C(11)	1.513 (8)
C(3)–O(1)	1.371 (7)	1.372 (8)	C(11)–C(12)	1.399 (7)
C(4)–C(12)	1.394 (8)	1.398 (9)	C(12)–C(13)	1.537 (7)
C(4)–O(2)	1.359 (7)	1.365 (8)	C(13)–C(14)	1.533 (8)
C(5)–C(6)	1.314 (10)	1.319 (13)	C(13)–C(15)	1.530 (8)
C(5)–C(13)	1.526 (9)	1.508 (10)	C(15)–C(16)	1.525 (9)
C(6)–C(7)	1.438 (10)	1.453 (14)	C(16)–N(1)	1.460 (8)
C(7)–C(8)	1.333 (11)	1.320 (13)	C(17)–N(1)	1.467 (8)
C(8)–C(14)	1.504 (9)	1.502 (10)	C(18)–O(1)	1.399 (9)
	(I)	(II)		
C(2)–C(1)–C(11)	121.9 (5)	122.0 (6)		
C(1)–C(2)–C(3)	119.6 (5)	118.7 (6)		
C(2)–C(3)–C(4)	119.7 (5)	120.5 (6)		
C(2)–C(3)–O(1)	125.7 (5)	125.2 (6)		
C(4)–C(3)–O(1)	114.6 (5)	114.3 (5)		
C(3)–C(4)–C(12)	120.5 (5)	120.9 (6)		
C(3)–C(4)–O(2)	119.8 (5)	119.4 (5)		
C(12)–C(4)–O(2)	119.7 (5)	119.7 (5)		
C(13)–C(5)–C(6)	121.6 (6)	121.7 (8)		
C(5)–C(6)–C(7)	119.8 (7)	120.8 (8)		
C(6)–C(7)–C(8)	120.3 (7)	119.1 (8)		
C(7)–C(8)–C(14)	118.9 (6)	119.5 (7)		
C(10)–C(9)–C(14)	108.8 (5)	110.5 (5)		
C(10)–C(9)–N(1)	116.1 (5)	116.6 (5)		
C(14)–C(9)–N(1)	108.0 (4)	107.8 (5)		
C(9)–C(10)–C(11)	115.4 (5)	114.2 (5)		
C(1)–C(11)–C(10)	119.1 (5)	119.3 (6)		
C(1)–C(11)–C(12)	119.3 (5)	118.9 (6)		
C(10)–C(11)–C(12)	121.6 (5)	121.7 (6)		
C(4)–C(12)–C(11)	118.9 (5)	118.9 (6)		
C(4)–C(12)–C(13)	120.3 (4)	119.7 (5)		
C(11)–C(12)–C(13)	120.6 (5)	121.1 (5)		
C(5)–C(13)–C(12)	113.4 (5)	113.0 (5)		
C(5)–C(13)–C(14)	106.1 (5)	106.4 (5)		
C(5)–C(13)–C(15)	111.2 (4)	112.6 (5)		
C(12)–C(13)–C(14)	110.0 (4)	111.0 (5)		
C(12)–C(13)–C(15)	108.0 (4)	106.5 (5)		
C(14)–C(13)–C(15)	107.9 (5)	107.3 (5)		
C(8)–C(14)–C(13)	110.8 (5)	111.7 (6)		
C(8)–C(14)–C(9)	114.5 (5)	113.8 (5)		
C(9)–C(14)–C(13)	110.0 (5)	109.4 (5)		
C(13)–C(15)–C(16)	110.6 (4)	110.9 (5)		
C(15)–C(16)–N(1)	111.5 (5)	112.2 (6)		
C(9)–N(1)–C(16)	114.1 (5)	113.1 (5)		
C(9)–N(1)–C(17)	111.7 (5)	112.5 (5)		
C(16)–N(1)–C(17)	111.4 (5)	111.8 (5)		
C(3)–O(1)–C(18)	118.1 (5)	117.8 (5)		

Table 3. Exocyclic angles in some morphinan-like structures illustrating mutual interaction between methyl protons and aromatic ring proton

Reference	C(2)–C(3)–O(1)	C(4)–C(3)–O(1)
(a)	127 (1)°	117 (1)°
(a)	124 (2)	118 (2)
(b)	124 (1)	117 (1)
(c)	126.9 (3)	116.8 (3)
(d)	125.4 (3)	113.8 (3)

References: (a) van Koningsveld & Olieman (1980); (b) van Koningsveld, Lie & Maat (1984a); (c) van Koningsveld, Maat & Lie (1984); (d) van Koningsveld, Lie & Maat (1984b).

the C(18) methyl protons with the C(2) proton is reflected in the values of the exocyclic ring angles: C(2)–C(3)–O(1) is 125.7 (5) and 125.2 (6)° and C(4)–C(3)–O(1) is 114.6 (5) and 114.3 (5)° in (I) and (II) respectively. This effect has been observed in many other –OCH<sub>3</sub> substituted phenyl rings. The relevant data in some morphinan-like structures are summarized in Table 3.

The hydrogen atom at C(14) is in the  $\beta$  position and, consequently, the morphinan skeleton has the *cis*-fused B/C ring moiety. The intensity of the MS peak at the *m/z* 59 caused by fragmentation of the piperidine ring was very low in this particular morphinan, which is in contrast to other morphinans with a *cis*-fused B/C ring moiety. Apparently, fragmentation leading to aromatization is a preferred pathway; this may be concluded from the high peak at *m/z* 146 of the 3,4-dihydro-2-methylisoquinoline fragment. Furthermore, the X-ray analysis shows that (3) possesses a potential diene system for Diels–Alder reactions.

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