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Structure of a Novel Diels–Alder Adduct Derived from a Thebaine Analogue

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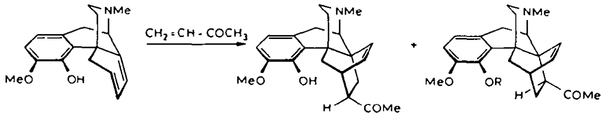
Abstract. (+)-8β-Acetyl-3-methoxy-17-methyl-4-phenoxy-6β,14β-ethenomorphinan, $C_{28}H_{31}NO_3$, $M_r = 429{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}194\,(2)$, $b = 15{\cdot}511\,(3)$, $c = 20{\cdot}543\,(4)$ Å, $V = 2292{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}25$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}87$ cm^{-1}, $F(000) = 920$, $T = 293$ K, $R = 0{\cdot}045$ for 2582 observed $[I > \sigma(I)]$ reflections. The Diels–Alder reaction of (−)-6-demethoxy-β-dihydrothebaine with methyl vinyl ketone gives, besides a recently reported adduct, a second isomer with the acetyl group in the 8β position of the 6β,14β-ethenomorphinan skeleton. This means that both adducts result from addition of the dienophile from the α face of the morphinan-6,8-diene system, with the acetyl substituent directed towards the etheno bridge. There are no unusual bond lengths or angles.

Introduction. Recently, a simple, high-yield synthesis of 6-demethoxy-β-dihydrothebaine (1) was developed (Linders, Adriaansens, Lie & Maat, 1986). This compound undergoes almost quantitatively Diels–Alder reaction with methyl vinyl ketone yielding, besides the earlier reported adduct (2) (~ 60%) (van Koningsveld, Lie & Maat, 1984), a second isomer (3) (~ 35%). In principle, eight isomeric Diels–Alder adducts are possible starting from the morphinan-6,8-diene (1). The fragment peak m/z 57 $[C^+H{=}C(OH)CH_3]$ in the mass spectrum of the second adduct (3) can be explained by a McLafferty rearrangement which is only possible in four isomers, namely the 7α-acetyl- and 8β-acetyl-6β,14β-ethenomorphinan and the 7β-acetyl- and 8α-acetyl-6α,14α-ethenoisomorphinan. The chemical shifts of the vinylic protons of the etheno bridge {δ 6–6·5 [m, 2H, H(18) and H(19)]} rule out the latter two ethenoisomorphinans [similar compounds show δ values lower than 6 for the signals of H(18) and H(19)]. The *endo* rule for Diels–Alder additions predicts the formation of the 8β-acetyl compound. However, unambiguous proof for the structure of (3) could neither be obtained from the mass spectrum nor from the ^{1}H NMR spectrum. Therefore, a single-crystal X-ray analysis was undertaken. A stable, well crystallizing derivative was obtained when the 4-hydroxyl substituent of (3) was converted into the phenyl ether by means of an Ullmann reaction with bromobenzene. The X-ray analysis confirmed the structure of (4) to be 8β-acetyl-3-methoxy-17-methyl-4-phenoxy-6β,14β-ethenomorphinan.



(1)
6-Demethoxy-β-dihydrothebaine

(2)

(3) $R = H$
(4) $R = C_6H_5$

Experimental. Title compound prepared in the Laboratory of Organic Chemistry, Delft, starting from 6-demethoxy-β-dihydrothebaine with methyl vinyl ketone. Crystals grown from diethyl ether, m.p. 403–404 K, $[\alpha]_D^{25{\cdot}0\,°C} = +90°$[chloroform/ethanol 9:1,

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Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
C(1)	3044 (6)	−284 (2)	2706 (2)	50 (1)
C(2)	3769 (6)	−178 (2)	3325 (2)	52 (1)
C(3)	3510 (6)	599 (2)	3646 (2)	48 (1)
C(4)	2574 (5)	1267 (2)	3326 (2)	41 (1)
C(5)	1662 (6)	2821 (2)	2479 (2)	47 (1)
C(6)	1949 (6)	3299 (2)	1833 (2)	51 (1)
C(7)	3442 (6)	2810 (2)	1449 (2)	54 (1)
C(8)	2758 (5)	1862 (2)	1338 (2)	41 (1)
C(9)	−91 (5)	874 (2)	1480 (2)	44 (1)
C(10)	1263 (5)	184 (2)	1731 (2)	46 (1)
C(11)	2101 (5)	369 (2)	2388 (2)	42 (1)
C(12)	1920 (5)	1182 (2)	2691 (2)	38 (1)
C(13)	823 (5)	1908 (2)	2364 (2)	39 (1)
C(14)	732 (5)	1769 (2)	1605 (2)	40 (1)
C(15)	−1189 (5)	1855 (2)	2626 (2)	47 (1)
C(16)	−2104 (6)	1000 (2)	2451 (2)	52 (1)
C(17)	203 (6)	3271 (2)	1442 (2)	53 (1)
C(18)	−405 (6)	2482 (2)	1315 (2)	49 (1)
C(19)	2970 (6)	1646 (2)	623 (2)	49 (1)
C(20)	4933 (7)	1476 (4)	401 (2)	73 (2)
C(21)	−2944 (6)	44 (3)	1582 (2)	59 (1)
C(22)	5132 (9)	123 (3)	4586 (3)	85 (2)
C(23)	3444 (6)	2505 (2)	3964 (2)	46 (1)
C(24)	5215 (7)	2549 (3)	3724 (2)	58 (1)
C(25)	6474 (7)	3108 (3)	4016 (2)	72 (2)
C(26)	5979 (9)	3603 (3)	4529 (3)	76 (2)
C(27)	4193 (10)	3549 (3)	4769 (2)	79 (2)
C(28)	2887 (7)	3002 (3)	4483 (2)	59 (1)
N	−1988 (4)	837 (2)	1750 (2)	48 (1)
O(1)	4065 (5)	757 (2)	4268 (1)	64 (1)
O(2)	2073 (4)	1989 (2)	3686 (1)	47 (1)
O(3)	1689 (5)	1623 (2)	245 (1)	67 (1)

1·0 g dm^{-3}]. D_m not measured. Irregular-shaped crystal (maximum dimensions $\sim 0·3 \times 0·3 \times 0·4$ mm) cut from larger plate. Diffraction data collected in $\omega/2\theta$ mode to $\theta_{max} = 30°$ on a Nonius CAD-4 diffractometer using monochromatized Mo $K\alpha$ radiation. Range of indices: h 0→10, k 0→21, l 0→28. Max. recording time 120 s; $\sigma_{count}(I)/I < 0·02$ requested in a scan. 3762 independent reflections collected; no corrections for absorption or extinction. Lattice parameters based on 25 centered reflections with $15 < \theta < 18°$. 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 from a difference map but included in idealized positions [sp^2, d(C—H) = 0·95 Å; sp^3, d(C—H) = 1·00 Å] with isotropic thermal parameters [U(H) = 1·1 U_{eq}(C)] and allowed to ride on parent C atoms. Absolute configuration not determined but chosen to be consistent with the configuration of the morphinan skeleton in previous analysis (van Koningsveld, Jansen, Lie & Maat, 1986). Refinement converged at $R = 0·045$, $wR = 0·042$, $w = 1$, $S = 0·70$ for 290 variables and 3407 observations [2582 with $I > \sigma(I)$ plus those for which $F_c > F_o$]; $(\Delta/\sigma)_{max} = 0·030$. Final ΔF synthesis has $|\rho| < 0·22$ e Å^{-3}. Calculations performed on the 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 were those incorporated in *XRAY72*.

Table 2. *Bond lengths* (Å) *and angles* (°)

C(1)—C(2)	1·384 (6)	C(12)—C(13)	1·532 (5)
C(1)—C(11)	1·383 (5)	C(13)—C(14)	1·574 (5)
C(2)—C(3)	1·385 (5)	C(13)—C(15)	1·547 (5)
C(3)—C(4)	1·400 (5)	C(14)—C(18)	1·500 (5)
C(3)—O(1)	1·362 (5)	C(15)—C(16)	1·524 (5)
C(4)—C(12)	1·392 (5)	C(16)—N	1·464 (5)
C(4)—O(2)	1·390 (4)	C(17)—C(18)	1·325 (5)
C(5)—C(6)	1·534 (5)	C(19)—C(20)	1·508 (7)
C(5)—C(13)	1·557 (5)	C(19)—O(3)	1·206 (5)
C(6)—C(7)	1·533 (6)	C(21)—N	1·452 (5)
C(6)—C(17)	1·491 (6)	C(22)—O(1)	1·409 (7)
C(7)—C(8)	1·568 (5)	C(23)—O(2)	1·393 (5)
C(8)—C(14)	1·564 (5)	C(23)—C(24)	1·369 (6)
C(8)—C(19)	1·513 (5)	C(23)—C(28)	1·374 (6)
C(9)—C(10)	1·536 (5)	C(24)—C(25)	1·390 (7)
C(9)—C(14)	1·532 (5)	C(25)—C(26)	1·352 (7)
C(9)—N	1·475 (5)	C(26)—C(27)	1·379 (9)
C(10)—C(11)	1·506 (5)	C(27)—C(28)	1·396 (8)
C(11)—C(12)	1·412 (5)		

C(2)—C(1)—C(11)	122·1 (3)	C(12)—C(13)—C(14)	110·8 (3)
C(1)—C(2)—C(3)	119·4 (3)	C(12)—C(13)—C(15)	106·8 (3)
C(2)—C(3)—C(4)	119·0 (3)	C(14)—C(13)—C(15)	107·4 (3)
C(2)—C(3)—O(1)	124·4 (3)	C(8)—C(14)—C(9)	112·6 (3)
C(4)—C(3)—O(1)	116·6 (3)	C(8)—C(14)—C(13)	107·3 (3)
C(3)—C(4)—C(12)	122·2 (3)	C(8)—C(14)—C(18)	107·5 (3)
C(3)—C(4)—O(2)	118·2 (3)	C(9)—C(14)—C(13)	107·9 (3)
C(12)—C(4)—O(2)	119·1 (3)	C(9)—C(14)—C(18)	113·0 (3)
C(6)—C(5)—C(13)	111·1 (3)	C(13)—C(14)—C(18)	108·4 (3)
C(5)—C(6)—C(7)	107·5 (3)	C(13)—C(15)—C(16)	111·6 (3)
C(5)—C(6)—C(17)	109·8 (3)	C(15)—C(16)—N	111·0 (3)
C(7)—C(6)—C(17)	107·4 (3)	C(6)—C(17)—C(18)	114·3 (3)
C(6)—C(7)—C(8)	108·6 (3)	C(14)—C(18)—C(17)	115·0 (4)
C(7)—C(8)—C(14)	109·1 (3)	C(8)—C(19)—C(20)	115·2 (3)
C(7)—C(8)—C(19)	108·5 (3)	C(8)—C(19)—O(3)	123·7 (4)
C(14)—C(8)—C(19)	114·5 (3)	C(20)—C(19)—O(3)	121·0 (4)
C(10)—C(9)—N	115·7 (3)	O(2)—C(23)—C(24)	122·7 (3)
C(14)—C(9)—N	109·2 (3)	O(2)—C(23)—C(28)	115·8 (4)
C(10)—C(9)—C(14)	109·2 (3)	C(24)—C(23)—C(28)	121·5 (4)
C(9)—C(10)—C(11)	115·0 (3)	C(23)—C(24)—C(25)	118·8 (4)
C(1)—C(11)—C(10)	118·6 (3)	C(24)—C(25)—C(26)	121·3 (5)
C(1)—C(11)—C(12)	119·4 (3)	C(25)—C(26)—C(27)	119·3 (5)
C(10)—C(11)—C(12)	121·9 (3)	C(26)—C(27)—C(28)	120·9 (5)
C(4)—C(12)—C(11)	117·8 (3)	C(27)—C(28)—C(23)	118·1 (5)
C(4)—C(12)—C(13)	121·1 (3)	C(3)—O(1)—C(22)	118·0 (3)
C(11)—C(12)—C(13)	120·7 (3)	C(4)—O(2)—C(23)	119·9 (3)
C(5)—C(13)—C(12)	113·7 (3)	C(9)—N—C(16)	114·6 (3)
C(5)—C(13)—C(14)	107·0 (3)	C(9)—N—C(21)	112·4 (3)
C(5)—C(13)—C(15)	111·1 (3)	C(16)—N—C(21)	110·6 (3)

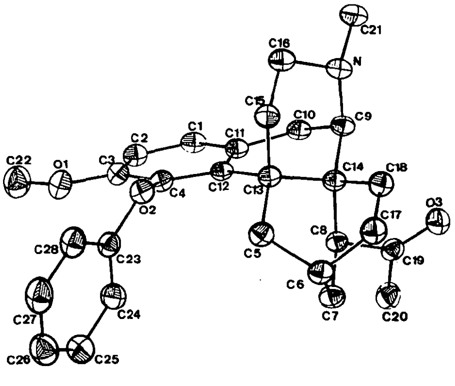

Fig. 1. *ORTEP* plot (Johnson, 1965) of the title compound. Boundary surfaces are drawn to enclose 50% probability.

Discussion. Coordinates and U_{eq} values are listed in Table 1 for the non-H atoms. Bond lengths and angles are shown in Table 2.* The molecular structure is illustrated in Fig. 1, which also shows the atomic-numbering scheme adopted. The etheno bridge is in the 6*β*,14*β* position and the acetyl substituent is in the 8*β* position of the morphinan skeleton, which means that the Diels–Alder reaction of 6-demethoxy-*β*-dihydrothebaine (1) with methyl vinyl ketone occurs from the α face of the diene system as was observed earlier for the 7*β*-substituted adduct (van Koningsveld, Lie & Maat, 1984). This is in contrast to the Diels–Alder reaction of thebaine itself or thebaine analogues with the 4,5α-epoxy ring closed, where the addition takes place from the *β* face (van Koningsveld, Maat & Lie, 1984), which may be explained by release of the strain in the thebaine molecule after opening of the epoxy ring. In the case of 6-methoxymorphinan-6,8-dienes the electronic effect of the 6-methoxy group contributes to the formation of the 7-substituted ethenomorphinans as the major product. Obviously, the absence of the 6-methoxy group allows cycloaddition of methyl vinyl ketone in two ways, yielding a mixture of the 7*β*- and the 8*β*-acetyl substituted isomers. The substituents are in the *β* position, both directed towards the double bond of the etheno bridge, in agreement with the Diels '*endo* rule'. Conversion of these new compounds into etorphine-like derivatives may extend the knowledge of structure–activity relationships of opiates.

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* Lists of structure factors, anisotropic temperature factors of the non-H atoms and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44040 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure and Thermal Motion of Triphenylboroxin

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Abstract. $C_{18}H_{15}B_3O_3$, $M_r = 311{\cdot}7$, monoclinic, $P2_1/c$, $a = 10{\cdot}715\ (2)$, $b = 13{\cdot}652\ (3)$, $c = 11{\cdot}703\ (2)$ Å, $\beta = 100{\cdot}38\ (1)°$, $V = 1683{\cdot}9\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}230$ g cm^{-3}, λ(Mo $K\alpha$) (graphite monochromator) $= 0{\cdot}71073$ Å, $\mu = 0{\cdot}74$ cm^{-1}, $F(000) = 648$, $T = 295\ (1)$ K, $R = 0{\cdot}041$ for 130 variables (group refinement incorporating the **TLS** model for rigid-body motion) and the 758 unique reflections having $I > 3\sigma(I)$. The weighted R factor based on F^2 for all 3851 unique reflections is 0·100. The central B_3O_3 ring is found to be nearly planar, but has a small envelope distortion; one of the B atoms is displaced by 0·119 (7) Å out of the plane of the other five atoms. The average B—O bond length is 1·386 (2) Å. The molecular dimensions determined are similar to those found previously for the related compounds 1,3,5-triphenylbenzene and *sym*-triphenyltriazine, but the conformations of the three molecules differ. The phenyl rings in the hydrocarbon adopt a propeller-like arrangement, while in the boroxin and triazine the phenyl groups are nearly coplanar with the central B_3O_3 or C_3N_3 ring. Possible relationships between thermal-motion descriptions and the intramolecular potential-energy surfaces for these molecules are considered.

Introduction. The structure of triphenylboroxin is of interest because of the possibility that the filled 2*p* orbitals on the O atoms might interact with the empty 2*p* orbitals on the B atoms to produce a conjugated system. A search of the May 1986 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for the B_3O_3 ring fragment revealed only two full determinations (Yalpani & Boese, 1983) of structures other than polyborates. Both of them contain

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