O9A—C7′A—C6′A	114.4 (6)	C8′B—C7′B—C6′B	120.8 (7)
C7′A—C8′A—C8′aA	121.5 (5)	C7′B—C8′B—C8′aB	119.6 (6)
C8′A—C8′aA—C4′aA	119.1 (5)	C8′B—C8′aB—C1′B	122.7 (6)
C8′A—C8′aA—C1′A	122.5 (5)	C8′B—C8′aB—C4′aB	119.4 (6)
C4′aA—C8′aA—C1′A	118.4 (5)	C1′B—C8′aB—C4′aB	117.8 (6)
C7′A—O9A—C10A	116.2 (4)	C7′B—O9B—C10B	118.4 (6)
O5A—C1A—N2A	124.1 (6)	O5B—C1B—N2B	122.4 (6)
O5A—C1A—C6A	121.3 (6)	O5B—C1B—C6B	122.3 (6)
N2A—C1A—C6A	114.5 (5)	N2B—C1B—C6B	115.3 (6)
C1A—N2A—C3A	121.3 (5)	C1B—N2B—C3B	122.1 (5)
N2A—C3A—C4A	113.8 (5)	N2B—C3B—C4B	112.4 (4)
C1′A—C4A—C3A	110.3 (5)	C1′B—C4B—C3B	112.3 (4)
C2′C—C1′C—C8′aC	120.2 (6)	C2′D—C1′D—C8′aD	120.0 (6)
C2′C—C1′C—C4C	120.2 (6)	C2′D—C1′D—C4D	118.4 (6)
C8′aC—C1′C—C4C	119.6 (5)	C8′aD—C1′D—C4D	121.6 (5)
C1′C—C2′C—C3′C	120.2 (7)	C1′D—C2′D—C3′D	120.2 (7)
C4′C—C3′C—C2′C	120.6 (7)	C4′D—C3′D—C2′D	119.9 (7)
C3′C—C4′C—C4′aC	121.8 (7)	C3′D—C4′D—C4′aD	121.9 (7)
C4′C—C4′aC—C5′C	123.8 (7)	C4′D—C4′aD—C5′D	123.1 (6)
C4′C—C4′aC—C8′aC	119.4 (7)	C4′D—C4′aD—C8′aD	119.0 (6)
C5′C—C4′aC—C8′aC	116.8 (7)	C5′D—C4′aD—C8′aD	117.9 (6)
C6′C—C5′C—C4′aC	122.5 (6)	C6′D—C5′D—C4′aD	122.6 (6)
C5′C—C6′C—C7′C	119.8 (7)	C5′D—C6′D—C7′D	120.2 (6)
C8′C—C7′C—O9C	124.6 (6)	C8′D—C7′D—O9D	123.6 (5)
C8′C—C7′C—C6′C	120.9 (7)	C8′D—C7′D—C6′D	120.6 (6)
O9C—C7′C—C6′C	114.5 (7)	O9D—C7′D—C6′D	115.8 (6)
C7′C—C8′C—C8′aC	119.9 (6)	C7′D—C8′D—C8′aD	121.0 (5)
C8′C—C8′aC—C1′C	122.3 (6)	C1′D—C8′aD—C8′D	123.3 (5)
C8′C—C8′aC—C4′aC	120.0 (6)	C1′D—C8′aD—C4′aD	119.0 (6)
C1′C—C8′aC—C4′aC	117.7 (6)	C8′D—C8′aD—C4′aD	117.7 (6)
C7′C—O9C—C10C	116.4 (5)	C7′D—O9D—C10D	117.5 (5)
O5C—C1C—N2C	123.5 (5)	O5D—C1D—N2D	122.7 (5)
O5C—C1C—C6C	122.1 (6)	O5D—C1D—C6D	120.1 (5)
N2C—C1C—C6C	114.3 (6)	N2D—C1D—C6D	117.2 (5)
C1C—N2C—C3C	122.1 (5)	C1D—N2D—C3D	122.3 (5)
N2C—C3C—C4C	110.3 (4)	N2D—C3D—C4D	115.2 (5)
C3C—C4C—C1′C	109.7 (4)	C1′D—C4D—C3D	108.9 (5)

O5A—C1A—N2A—C3A	2.2 (10)
C1A—N2A—C3A—C4A	−101.1 (7)
C2′A—C1′A—C4A—C3A	95.4 (6)
N2A—C3A—C4A—C1′A	176.3 (5)
O5B—C1B—N2B—C3B	0.2 (8)
C1B—N2B—C3B—C4B	86.8 (6)
C2′B—C1′B—C4B—C3B	−100.4 (6)
N2B—C3B—C4B—C1′B	176.2 (5)
O5C—C1C—N2C—C3C	−1.5 (9)
C1C—N2C—C3C—C4C	91.3 (6)
N2C—C3C—C4C—C1′C	−175.2 (5)
C2′C—C1′C—C4C—C3C	−101.5 (6)
O5D—C1D—N2D—C3D	4.3 (9)
C1D—N2D—C3D—C4D	−103.0 (7)
C2′D—C1′D—C4D—C3D	95.7 (7)
N2D—C3D—C4D—C1′D	175.2 (5)

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

	N···O	H···O	N—H···O
N2A—H···O5B	2.896 (8)	2.02 (5)	176 (1)
N2B—H···O5A^{i}	2.891 (7)	2.05 (5)	164 (1)
N2C—H···O5D	2.852 (8)	1.82 (5)	166 (1)
N2D—H···O5C^{i}	2.927 (8)	2.03 (5)	162 (1)

Symmetry code: (i) $x, y-1, z$.

Data collection, cell refinement and data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71834 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1082]

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2-Methyl-4-(4-pyridyl)-3-butyn-2-ol: a Two-Dimensional Hydrogen-Bond Network

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Abstract

The asymmetric unit of $C_{10}H_{11}NO$ consists of two chemically similar but crystallographically distinct molecules of 2-methyl-4-(4-pyridyl)-3-butyn-2-ol which are linked *via* a head-to-tail hydrogen bond

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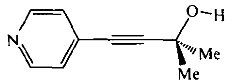
between the pyridine N atom of one molecule and the hydroxyl H atom of another, forming a zigzag chain in the *ac* plane in the direction of the *c* axis.

Comment

A crucial design prerequisite of new solid-state materials capable of exhibiting bulk second-order optical nonlinearities is that these materials form non-centrosymmetric crystal structures (Prasad & Williams, 1991). Intermolecular hydrogen bonding has been shown to be an effective way of creating non-centrosymmetric molecular networks that serve as the basis for non-centrosymmetric materials; examples include nitroanilines (Etter, Huang, Frankenbach & Adsmond, 1991) and hydrogen L-tartrate salts (Aakeröy, Hitchcock & Seddon, 1992). In this context, the structure determination of 2-methyl-4-(4-pyridyl)-3-butyn-2-ol (I) was undertaken in order to determine whether or not this compound was capable of forming such a non-centrosymmetric network and non-centrosymmetric bulk material.



(I)

The molecular structure of the asymmetric unit (with the atomic numbering scheme) is shown in Fig. 1 and a packing diagram, as viewed along the *b* axis, is shown in Fig. 2.

The bond lengths within the pyridine rings (average C—C = 1.38, average N—C = 1.33 Å) do not differ significantly from those of pyridine determined by electron diffraction [C—C = 1.39, N—C = 1.37 Å (Schomaker & Pauling, 1939)] or of 1,4-bis(4-pyridyl)butadiyne [average C—C = 1.38, average N—C = 1.34 Å (Allan, Barrow, Beaumont, Macindoe, Milburn & Werninck, 1988)]. The $C\equiv C$ bond lengths [1.191 (9), 1.190 (8) Å] are similar to the distance of 1.201 (6) Å in the above diyne or the distance of 1.197 Å found from the single-crystal X-ray diffraction study of 2-methyl-4-phenyl-3-butyn-2-ol (Singelenberg & van Eijck, 1987) (where 1.197 Å is the average $C\equiv C$ distance for the three independent molecules of the asymmetric unit). The O$\cdots$N distances [2.851 (9), 2.817 (9) Å] are shorter than the sum of van der Waals radii for N, H and O indicating that the N and H atoms are hydrogen bonded. These distances fit within a range of values, *i.e.* 2.62–2.93 Å, exhibited by other O—H$\cdots$N type hydrogen-bonded solids (Pimentel & McClellan, 1960). The hydrogen bonds cause alignment of the molecules in a head-to-tail fashion, forming zigzag chains in the solid state, as opposed to the tail-to-tail-to-tail hydrogen-bonded trimeric structure which results from hydrogen bonding between hydroxyl groups of three molecules of the above phenyl-alkynol. Regarding the potential of this compound as a nonlinear optical material, it is noteworthy that the crystal structure is non-centrosymmetric. Unfortunately, the chains are arranged in an anti-parallel fashion; thus the efficiency of second-harmonic generation is not expected to be very high.

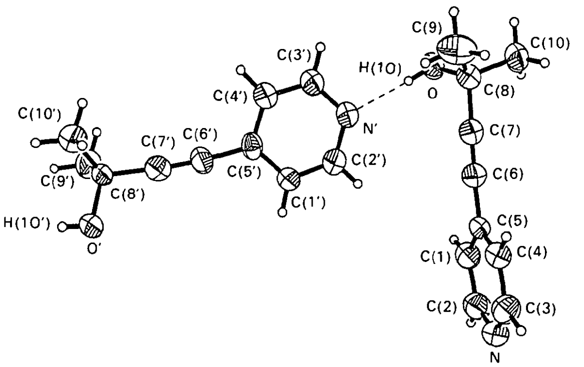


Fig. 1. Displacement ellipsoid drawing of the asymmetric unit of 2-methyl-4-(4-pyridyl)-3-butyn-2-ol showing the atomic numbering scheme and 50% probability displacement ellipsoids.

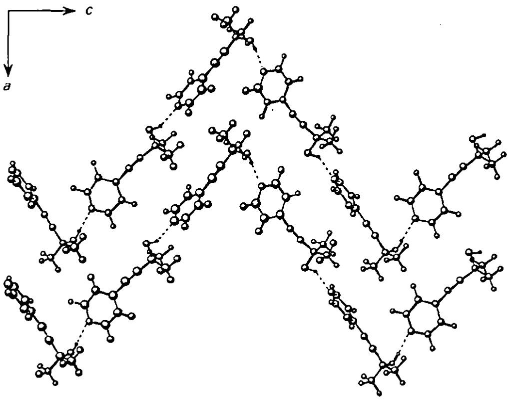


Fig. 2. Packing diagram viewed along the *b* axis showing the zigzag chains in the *ac* plane.

Experimental

2-Methyl-4-(4-pyridyl)-3-butyn-2-ol was prepared according to the standard method (Ciana & Haim, 1984). Crystals were obtained by evaporating a diethyl ether solution of the compound in a crystallizing dish. ^{1}H NMR ($CDCl_3$; coupling constants in Hz): δ 8.54 [*d*, 2, $^3J_{HH}$ = 5.88, H(2) and H(6)], 7.26 [*d*, 2, $^3J_{HH}$ = 5.88, H(3) and H(5)], 2.77 (*s*, 1, OH), 1.62(*s*, 6, CH_3). HRMS calculated (found): 161.0841 (161.0820).

Crystal data

$C_{10}H_{11}NO$
M_r = 161.21

Cu *Kα* radiation
λ = 1.54178 Å

Orthorhombic
$P2_12_12_1$
$a = 8.238$ (2) Å
$b = 8.968$ (2) Å
$c = 25.165$ (5) Å
$V = 1859.2$ (7) $Å^3$
$Z = 8$
$D_x = 1.15$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 25–40°$
$\mu = 0.605$ mm^{-1}
$T = 296$ K
Rectangular block
0.38 × 0.24 × 0.24 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: empirical
$T_{min} = 0.94$, $T_{max} = 1.00$
3250 measured reflections
3222 independent reflections
1855 observed reflections
$[F_o > 6\sigma(F_o)]$

$R_{int} = 0.0496$
$\theta_{max} = 62.5°$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 28$
3 standard reflections monitored every 150 reflections
intensity variation: ≤1%

Refinement

Refinement on *F*
$R = 0.0664$
$wR = 0.0971$
$S = 1.11$
1855 reflections
223 parameters
$w = 1/[\sigma^2(F_o) + 0.005F_o^2]$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.33$ e $Å^{-3}$
$\Delta\rho_{min} = -0.25$ e $Å^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* ($Å^2$)

U_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for C, N and O.

	x	*y*	*z*	U_{iso}/U_{eq}
O	0.2692 (6)	0.4152 (6)	0.0214 (2)	0.061 (2)
H(1O)	0.3550 (74)	0.4080 (61)	0.0353 (22)	0.042 (18)
N	0.9142 (6)	0.4598 (7)	−0.1887 (2)	0.060 (2)
C(1)	0.7367 (8)	0.3529 (7)	−0.1243 (2)	0.055 (2)
C(2)	0.8594 (8)	0.3432 (8)	−0.1621 (3)	0.061 (2)
C(3)	0.8473 (8)	0.5911 (8)	−0.1787 (2)	0.061 (2)
C(4)	0.7237 (7)	0.6127 (8)	−0.1426 (2)	0.053 (2)
C(5)	0.6628 (7)	0.4888 (7)	−0.1156 (2)	0.048 (2)
C(6)	0.5267 (8)	0.5037 (8)	−0.0803 (2)	0.059 (2)
C(7)	0.4097 (8)	0.5126 (7)	−0.0527 (2)	0.055 (2)
C(8)	0.2642 (7)	0.5272 (7)	−0.0187 (2)	0.054 (2)
C(9)	0.2584 (10)	0.6802 (7)	0.0065 (3)	0.085 (3)
C(10)	0.1117 (8)	0.4950 (10)	−0.0511 (3)	0.075 (3)
O′	1.3574 (5)	0.5457 (6)	0.2280 (2)	0.054 (1)
H(1O′)	1.4108 (80)	0.5477 (77)	0.2528 (26)	0.067 (23)
N′	0.5776 (6)	0.4536 (6)	0.0709 (2)	0.054 (2)
C(1′)	0.8649 (7)	0.4375 (8)	0.0858 (2)	0.056 (2)
C(2′)	0.7284 (8)	0.4185 (7)	0.0555 (2)	0.060 (2)
C(3′)	0.5641 (7)	0.5087 (7)	0.1198 (2)	0.054 (2)
C(4′)	0.6909 (7)	0.5314 (7)	0.1534 (2)	0.054 (2)
C(5′)	0.8473 (7)	0.4944 (6)	0.1371 (2)	0.044 (2)
C(6′)	0.9812 (7)	0.5102 (7)	0.1728 (2)	0.052 (2)
C(7′)	1.0831 (8)	0.5189 (6)	0.2062 (2)	0.049 (2)
C(8′)	1.2012 (6)	0.5251 (6)	0.2508 (2)	0.043 (2)
C(9′)	1.1935 (8)	0.3799 (6)	0.2819 (2)	0.060 (2)
C(10′)	1.1601 (9)	0.6561 (7)	0.2869 (3)	0.063 (2)

Table 2. *Selected geometric parameters* (Å, °)

O—C(8)	1.424 (8)	O′—C(8′)	1.421 (6)
O—H(1O)	0.792 (59)	O′—H(1O′)	0.763 (63)
N—C(2)	1.321 (9)	N′—C(2′)	1.340 (8)
N—C(3)	1.324 (9)	N′—C(3′)	1.330 (7)
C(1)—C(2)	1.392 (9)	C(1′)—C(2′)	1.370 (8)
C(1)—C(5)	1.380 (9)	C(1′)—C(5′)	1.396 (8)
C(3)—C(4)	1.378 (9)	C(3′)—C(4′)	1.360 (8)
C(4)—C(5)	1.396 (9)	C(4′)—C(5′)	1.392 (8)
C(5)—C(6)	1.436 (8)	C(5′)—C(6′)	1.430 (8)
C(6)—C(7)	1.191 (9)	C(6′)—C(7′)	1.190 (8)
C(7)—C(8)	1.479 (8)	C(7′)—C(8′)	1.486 (8)
C(8)—C(9)	1.511 (9)	C(8′)—C(9′)	1.521 (8)
C(8)—C(10)	1.526 (9)	C(8′)—C(10′)	1.525 (8)
N^i···O′	2.817 (9)	N′···O	2.851 (9)
N^i···H(1O′)	2.062 (60)	N′···H(1O)	2.081 (61)
C(8)—O—H(1O)	113.3 (41)	C(8′)—O—H(1O′)	101.3 (52)
C(2)—N—C(3)	117.7 (5)	C(2′)—N′—C(3′)	115.7 (5)
C(2)—C(1)—C(5)	119.0 (6)	C(2′)—C(1′)—C(5′)	118.4 (5)
N—C(2)—C(1)	123.0 (6)	N′—C(2′)—C(1′)	124.8 (5)
N—C(3)—C(4)	123.9 (6)	N′—C(3′)—C(4′)	124.5 (6)
C(3)—C(4)—C(5)	118.4 (6)	C(3′)—C(4′)—C(5′)	119.5 (5)
C(1)—C(5)—C(4)	117.8 (5)	C(1′)—C(5′)—C(4′)	117.1 (5)
C(1)—C(5)—C(6)	121.6 (6)	C(1′)—C(5′)—C(6′)	122.5 (5)
C(4)—C(5)—C(6)	120.5 (6)	C(4′)—C(5′)—C(6′)	120.3 (5)
C(5)—C(6)—C(7)	177.1 (6)	C(5′)—C(6′)—C(7′)	173.9 (6)
C(6)—C(7)—C(8)	178.7 (7)	C(6′)—C(7′)—C(8′)	175.6 (6)
O—C(8)—C(7)	108.9 (5)	O′—C(8′)—C(7′)	107.0 (4)
O—C(8)—C(9)	110.2 (5)	O′—C(8′)—C(9′)	110.9 (5)
C(7)—C(8)—C(9)	110.4 (6)	C(7′)—C(8′)—C(9′)	109.3 (5)
O—C(8)—C(10)	105.6 (5)	O′—C(8′)—C(10′)	110.0 (5)
C(7)—C(8)—C(10)	109.9 (5)	C(7′)—C(8′)—C(10′)	109.5 (5)
C(9)—C(8)—C(10)	111.7 (6)	C(9′)—C(8′)—C(10′)	110.1 (4)
N′···H(1O)—O	164.0 (40)	N^i···H(1O′)—O	170.3 (40)

Symmetry code: (i) $\frac{5}{2} - x, 1 - y, \frac{1}{2} + z$.

All non-H atoms were located by direct methods and refined anisotropically. Hydroxyl H atoms were located and refined isotropically; remaining H atoms were calculated and fixed in idealized positions (C—H = 0.96 Å, $U = 0.08$ $Å^2$) Computer program used: *SHELXTL* (Sheldrick, 1985).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71684 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1055]

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Structure of a Diels–Alder Adduct at a 5,7-Disubstituted Thebaine Derivative

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Abstract

The structure of (+)-ethyl 3,18-dimethoxy-5β,17-dimethyl-4,5α-epoxy-6β,14β-ethenomorphinan-8β-carboxylate (3), $C_{25}H_{31}NO_5$, is described. Diels–Alder reaction of the thebaine analogoue (−)-5β-methyl-7-methoxy-6-demethoxythebaine (2), with ethyl propenoate gives rise to anomalous α-face approach of the dienophile, yielding the title compound (3), in which the etheno bridge is at the 6β,14β position and the ethoxycarbonyl substituent is at the 8β position.

Comment

Diels–Alder reaction of the opium alkaloid (−)-thebaine (Bentley, 1971) with several dienophiles yields exclusively 7-substituted 6α,14α-ethenoisomorphinans, although this reaction of (−)-morphinan-6,8-dienes may yield, in principle, eight isomers. Two stereoisomeric structures, namely the 6β,14β-ethenomorphinan or 6α,14α-ethenoisomorphinan structure, are formed by α-face or β-face approach, respectively, from the diene system by the dienophile. The position of the new substituent (*R*) determines four regioisomers for each stereoisomer (Fig. 1).

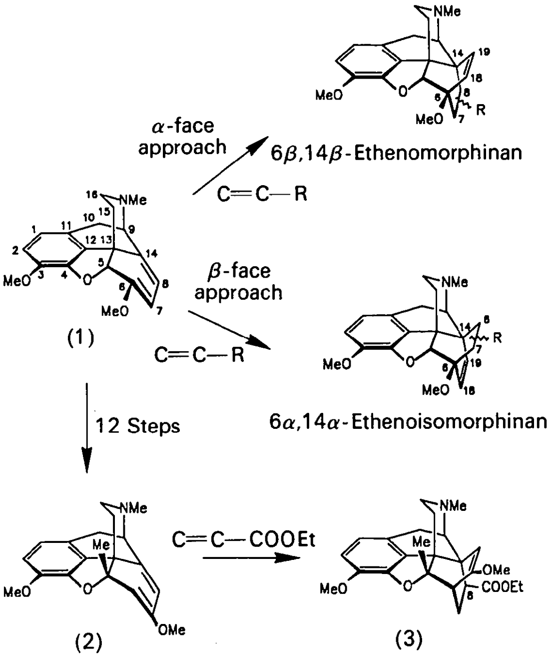

Fig. 1. Diels–Alder reactions forming 6α,14α-ethenoisomorphinans and 6β,14β-ethenomorphinans.

In our search for novel Diels–Alder adducts, in which the substituent is present at the 8 position, we (Meuzelaar, Woudenberg, Sinnema & Maat, 1993; Woudenberg, Meuzelaar & Maat, 1993) developed a route for the synthesis of 7-methoxy-5β-methyl-6-demethoxythebaine (2). Diels–Alder reaction of (2) with ethyl propenoate yielded one cycloadduct. In the ^{1}H NMR spectrum the signal of the vinyl proton H(19) was present at δ 5.09. This indicates a 6α,14α-ethenoisomorphinan structure, because in a series of 21 6α,14α-ethenoisomorphinans derived from thebaine, Fulmor *et al.* (1967) found H(18) at δ 5.91 ± 0.08 and H(19) at δ 5.48 ± 0.06, whereas Linders, Prazeres, Lie & Maat (1989) demonstrated downfield shifts for H(18) and H(19) from δ 6.0 and higher in a series of 6β,14β-ethenomorphinans. However, the presence of the methoxy group at the 18 position with its shielding effect makes the assignment of the 6α,14α-ethenoisomorphinan structure ambiguous. Neither the mass spectrum nor the ^{1}H and ^{13}C NMR spectra could give definitive proof of the structure. Therefore, we performed a single-crystal X-ray analysis of adduct (3), which gave the final proof for the 6β,14β-ethenomorphinan structure with the ethoxycarbonyl group at the 8β position. To our knowledge, this is the first reported single-crystal X-ray study of a 4,5α-epoxy-6β,14β-ethenomorphinan obtained by Diels–Alder reaction, in which the dienophile approached the diene system from the α face. This is in contrast to the case of thebaine (1) itself, where the Diels–Alder reaction takes place exclusively from the β face. The results can be explained by the electronic effect of the methoxy group combined with the steric hindrance of the

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