TEXSAN (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1149). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Diacetylmorphine Polymorph

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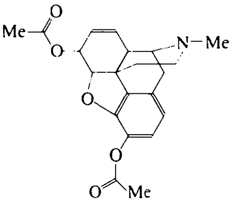
Abstract

The title compound, 7,8-didehydro-4,5-epoxy-17-methylmorphinan-3,6-diyl diacetate, $C_{21}H_{23}NO_5$, was crystallized from a solution of its hydrochloride and sodium acetate. Unlike prior reports in which crystals were hexagonal shaped (orthorhombic) and in space group $P2_12_12_1$, the crystals in the present determination grew as large prisms (monoclinic) and were in space group $P2_1$.

Comment

The addition of sodium acetate to a solution of the hydrochloride of diacetylmorphine induces crystallization of the free base which, along with the morphology of the resulting crystals, has been used as a test to identify diacetylmorphine (Clarke, 1969). This method of crystallization was used by Canfield, Barrick & Giessen (1979) for the first reported crystal structure (orthorhombic, $P2_12_12_1$) of heroin. In this report, we describe a new polymorph of heroin, (I).



(I)

The new heroin polymorph formed as a monoclinic $P2_1$ crystal with two molecules in the asymmetric unit (Fig. 1). These two molecules differ mainly with respect to the conformations of the two acetoxy side chains on atoms C3 and C6, with the largest differences occurring for the C3 side chain. The torsion angle for this functional group (C18—O1—C3—C4) is 86.0 (7)° and the equivalent angle in the second molecule is −94.2 (8)°. The torsion angles of the other acetoxy group (C20—O4—C6—C5) in each of the two molecules agree better, with values of −83.5 (6) and −83.1 (7)°; however, as shown by the superposition of the two molecules in Fig. 2, these acetoxy groups are displaced with respect to each other due to the displacement of atom C6*A* with respect to C6. As expected, the polycyclic ring systems of the two molecules are nearly identical. A comparison of the two ring systems showed a maximum deviation of 0.323 Å at atom C6 and an average r.m.s. deviation of 0.119 Å.

A comparision of the diacetylmorphine structure found in this study with the previously published structure resulted in a 0.114 or 0.054 Å r.m.s. deviation for the polycyclic ring systems (for the two molecules in Fig. 1). The only significant deviation from the previously published structure is in the conformations of the acetoxy side chains at atoms C3 and C6. The conformations are nearly identical to those shown in Fig. 1(*a*), and therefore the differences noted between the two molecules in the new polymorph accurately describe the differences between the molecule shown in Fig. 1(*b*) and the structure reported by Canfield *et al.* (1979).

The unit-cell packing shows similarities to that of the orthorhombic structure (see the supplementary material for a packing diagram), for which interactions between the carbonyl O atoms and the methyl groups of neighboring acetoxy groups were reported, with interatomic

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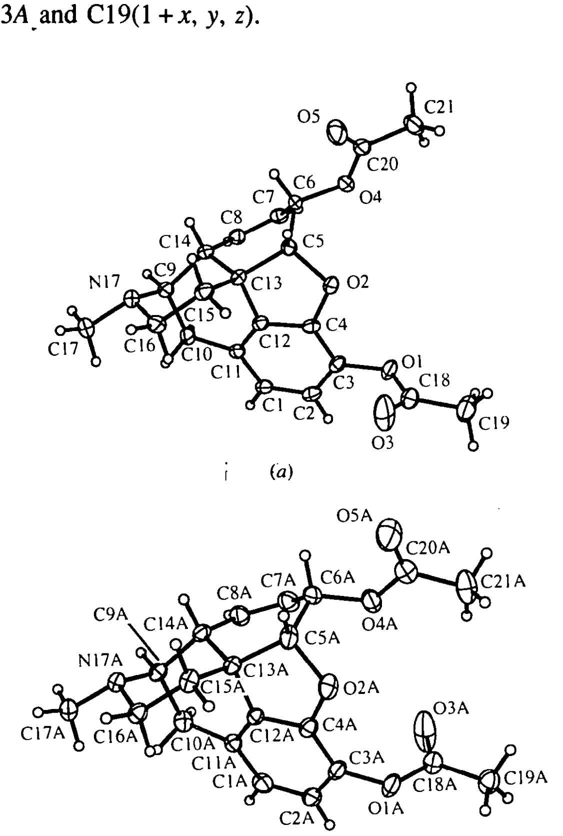
O5···C19 and O3···C21 distances of 3.250 (14) and 3.311 (14) Å, respectively. In the new polymorph, there is a similar close approach of 3.08 Å between atoms O3*A* and C19(1 + *x*, *y*, *z*).



(*a*)

(*b*)

Fig. 1. A view of diacetylmorphine showing the two independent molecules in the asymmetric unit and the labeling of the non-H atoms. The two molecules are oriented to improve clarity and are not presented as they relate to each other in the asymmetric unit. Displacement ellipsoids are shown at the 20% probability level and H atoms are drawn as small circles of arbitrary radii.

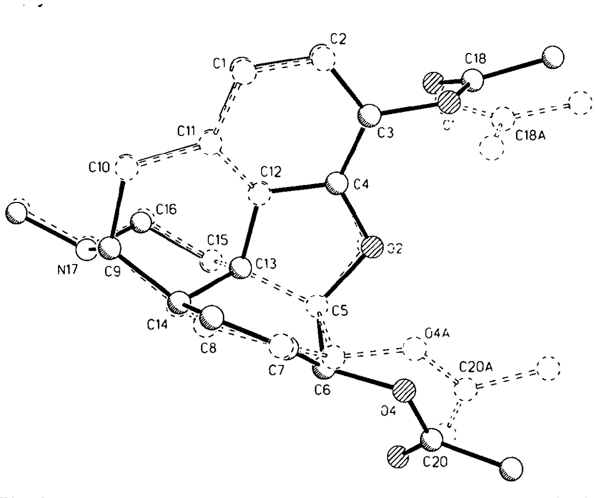


Fig. 2. A comparison of the conformations of the two molecules in the asymmetric unit. The atoms used for the fit and the atoms which define the torsion angles of the acetoxy groups are labeled.

Experimental

Enantiomerically pure heroin was obtained from the National Institutes of Health, Bethesda, MD, USA. Crystals were prepared by microvapor diffusion in a hanging drop composed of 2 µl of an aqueous stock solution containing 49 mg ml^{-1} of diacetylmorphine hydrochloride and 2 µl of 1.0 *M* sodium acetate. The drop was equilibrated against 1 ml of 1.0 *M* sodium acetate and large prisms formed in 48–72 h.

Crystal data

$C_{21}H_{23}NO_5$
$M_r = 369.40$
Monoclinic
$P2_1$
$a = 7.381\,(1)$ Å
$b = 32.096\,(2)$ Å
$c = 7.884\,(1)$ Å
$\beta = 94.94\,(11)°$
$V = 1860.79\,(12)$ Å^3
$Z = 4$
$D_x = 1.319$ Mg m^{-3}
D_m not measured

Cu *Kα* radiation
$\lambda = 1.54178$ Å
Cell parameters from 28 reflections
$\theta = 8.91–26.58°$
$\mu = 0.773$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.30 × 0.20 × 0.18 mm
Colorless

Data collection

Siemens *R*3*m*/*V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2852 measured reflections
2560 independent reflections
2187 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0162$
$\theta_{\rm max} = 56.95°$
$h = -8 \rightarrow 7$
$k = 0 \rightarrow 34$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 97 reflections
random variation of 2%

Refinement

Refinement on F^2
$R(F) = 0.0481$
$wR(F^2) = 0.1384$
$S = 1.006$
2560 reflections
488 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0882P)^2 + 0.4078P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.040$

$\Delta\rho_{\rm max} = 0.352$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.211$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick & Schneider, 1995)
Extinction coefficient: 0.0042 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	−0.0290 (6)	0.21828 (14)	0.9851 (6)	0.0606 (12)
C1	0.2093 (8)	0.2234 (2)	1.4139 (8)	0.0476 (14)
O2	0.2078 (5)	0.29327 (12)	0.9770 (5)	0.0480 (10)
C2	0.1027 (9)	0.2100 (2)	1.2730 (8)	0.051 (2)
C3	0.0979 (8)	0.2308 (2)	1.1182 (8)	0.0475 (15)
O3	0.1890 (10)	0.1871 (3)	0.8574 (8)	0.132 (3)
O4	0.0586 (5)	0.37410 (12)	0.9479 (5)	0.0519 (11)
C4	0.2083 (8)	0.2649 (2)	1.1090 (7)	0.0426 (13)
C5	0.3209 (8)	0.3286 (2)	1.0387 (7)	0.0413 (13)
O5	0.2497 (8)	0.4046 (2)	0.7818 (6)	0.082 (2)

C6	0.2062 (8)	0.3668 (2)	1.0776 (7)	0.0409 (13)
C7	0.1308 (8)	0.3646 (2)	1.2453 (8)	0.0459 (14)
C8	0.2395 (8)	0.3544 (2)	1.3815 (8)	0.0465 (14)
C9	0.5286 (8)	0.3187 (2)	1.5108 (8)	0.0482 (15)
C10	0.4283 (9)	0.2784 (2)	1.5518 (8)	0.056 (2)
C11	0.3260 (8)	0.2572 (2)	1.4016 (7)	0.0432 (14)
C12	0.3293 (7)	0.2754 (2)	1.2439 (7)	0.0395 (13)
C13	0.4336 (7)	0.3139 (2)	1.2037 (7)	0.0400 (13)
C14	0.4325 (8)	0.3423 (2)	1.3582 (7)	0.0430 (13)
C15	0.6345 (8)	0.3044 (2)	1.1707 (8)	0.051 (2)
C16	0.7406 (9)	0.2874 (2)	1.3296 (9)	0.061 (2)
N17	0.7217 (7)	0.3132 (2)	1.4757 (7)	0.0571 (14)
C17	0.8356 (11)	0.2977 (3)	1.6263 (11)	0.080 (2)
C18	0.0323 (11)	0.1934 (2)	0.8645 (8)	0.064 (2)
C19	−0.1182 (13)	0.1772 (3)	0.7433 (10)	0.091 (3)
C20	0.0987 (10)	0.3953 (2)	0.8098 (8)	0.053 (2)
C21	−0.0673 (11)	0.4060 (2)	0.6958 (9)	0.072 (2)
O1*A*	0.4553 (6)	0.12531 (14)	0.3081 (6)	0.0705 (14)
C1*A*	0.4015 (9)	0.0917 (2)	0.7494 (10)	0.063 (2)
O2*A*	0.6238 (7)	0.04226 (14)	0.3357 (5)	0.0609 (12)
C2*A*	0.3962 (10)	0.1155 (2)	0.6042 (11)	0.066 (2)
C3*A*	0.4626 (9)	0.1011 (2)	0.4572 (9)	0.056 (2)
O3*A*	0.7157 (11)	0.1536 (3)	0.3845 (9)	0.152 (4)
O4*A*	0.9753 (7)	0.0568 (2)	0.3785 (7)	0.079 (2)
C4*A*	0.5313 (8)	0.0614 (2)	0.4585 (8)	0.0483 (15)
C5*A*	0.7266 (10)	0.0078 (2)	0.4197 (8)	0.060 (2)
O5*A*	1.0664 (12)	0.0147 (2)	0.1841 (8)	0.120 (3)
C6*A*	0.9246 (9)	0.0221 (2)	0.4799 (11)	0.066 (2)
C7*A*	0.9569 (9)	0.0325 (3)	0.6602 (10)	0.069 (2)
C8*A*	0.8745 (9)	0.0140 (2)	0.7789 (10)	0.064 (2)
C9*A*	0.5878 (8)	−0.0191 (2)	0.8755 (7)	0.0465 (14)
C10*A*	0.4995 (10)	0.0238 (2)	0.9062 (8)	0.057 (2)
C11*A*	0.4682 (8)	0.0511 (2)	0.7516 (7)	0.0442 (13)
C12*A*	0.5261 (7)	0.0367 (2)	0.6004 (7)	0.0381 (13)
C13*A*	0.6145 (8)	−0.0045 (2)	0.5714 (7)	0.0409 (13)
C14*A*	0.7261 (8)	−0.0165 (2)	0.7379 (7)	0.0468 (14)
C15*A*	0.4745 (9)	−0.0383 (2)	0.5241 (8)	0.0503 (15)
C16*A*	0.3548 (8)	−0.0467 (2)	0.6681 (8)	0.0509 (15)
N17*A*	0.4639 (7)	−0.05363 (14)	0.8276 (6)	0.0464 (12)
C17*A*	0.3504 (10)	−0.0640 (2)	0.9653 (9)	0.063 (2)
C18*A*	0.5904 (9)	0.1510 (2)	0.2855 (9)	0.058 (2)
C19*A*	0.5651 (10)	0.1735 (2)	0.1226 (9)	0.071 (2)
C20*A*	1.0375 (10)	0.0493 (3)	0.2297 (9)	0.065 (2)
C21*A*	1.0651 (13)	0.0878 (3)	0.1328 (11)	0.094 (3)

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

O1—C18	1.349 (8)	O1*A*—C18*A*	1.319 (8)
O1—C3	1.403 (7)	O1*A*—C3*A*	1.406 (8)
C2—C3	1.389 (9)	C2*A*—C3*A*	1.376 (10)
C3—C4	1.371 (8)	C3*A*—C4*A*	1.372 (9)
O3—C18	1.180 (9)	O3*A*—C18*A*	1.161 (8)
O4—C20	1.338 (8)	O4*A*—C20*A*	1.319 (9)
O4—C6	1.447 (6)	O4*A*—C6*A*	1.440 (8)
C5—C6	1.536 (8)	C5*A*—C6*A*	1.566 (10)
O5—C20	1.192 (8)	O5*A*—C20*A*	1.191 (10)
C6—C7	1.480 (8)	C6*A*—C7*A*	1.460 (11)
C18—C19	1.496 (11)	C18*A*—C19*A*	1.471 (9)
C20—C21	1.496 (10)	C20*A*—C21*A*	1.478 (11)
C18—O1—C3	117.0 (5)	C18*A*—O1*A*—C3*A*	118.9 (5)
C4—C3—C2	117.4 (6)	C4*A*—C3*A*—C2*A*	117.6 (6)
C4—C3—O1	123.4 (6)	C4*A*—C3*A*—O1*A*	120.4 (6)
C2—C3—O1	119.0 (5)	C2*A*—C3*A*—O1*A*	121.9 (6)
C20—O4—C6	116.8 (5)	C20*A*—O4*A*—C6*A*	118.6 (6)
O4—C6—C7	108.7 (5)	O4*A*—C6*A*—C7*A*	109.5 (6)
O4—C6—C5	112.5 (4)	O4*A*—C6*A*—C5*A*	109.8 (6)
C7—C6—C5	113.3 (4)	C7*A*—C6*A*—C5*A*	115.6 (5)
O3—C18—O1	121.6 (6)	O3*A*—C18*A*—O1*A*	121.5 (7)
O3—C18—C19	125.9 (7)	O3*A*—C18*A*—C19*A*	125.9 (7)
O1—C18—C19	112.4 (7)	O1*A*—C18*A*—C19*A*	112.6 (6)
O5—C20—O4	123.6 (6)	O5*A*—C20*A*—O4*A*	121.6 (7)
O5—C20—C21	124.1 (6)	O5*A*—C20*A*—C21*A*	126.0 (8)
O4—C20—C21	112.2 (6)	O4*A*—C20*A*—C21*A*	112.4 (8)

SHELXL (Sheldrick & Schneider, 1995) was used for the structure refinement and *SHELXTL-Plus* (Sheldrick, 1991) was used for data collection, cell refinement, data reduction, structure solution, molecular graphics and the preparation of material for publication.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a packing diagram, have been deposited with the IUCr (Reference: AB1311). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6′-Diethylamino-2′-methylaminospiro-[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one

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Abstract

The title compound, $C_{25}H_{24}N_2O_3$, is one of the fluoran derivatives. The molecule has a Y-style structure which is composed of a half-chair xanthene moiety and an almost planar isobenzofuran fragment. The C—O single-bond distance of 1.528 (6) Å in the lactone ring is longer than those normally found in both lactone and 2′-nitrofluoran.

Comment

During the study of 6′-diethylamino-2′-substituted fluoran derivatives (Liu, Wang, Liu & Miao, 1995), we obtained the title compound, (I) (where R_1 = Et_2N, R_2 = $NHCH_3$, R_3 = H), and determined its crystal structure. The structure analysis shows that the molecule has a Y-like shape, with the isobenzofuran moiety, which