Table 3. *Hydrogen bonding*

D—H···*A*	*D*—H	*D*···*A*	H···*A*	∠*D*—H···*A*
N(1)—H(1)···O(13)	0·96 Å	2·687 Å	1·73 Å	173°
O(13)—H(13*A*)···O(10)^{I}	0·93	2·721	1·80	172
O(13)—H(13*B*)···O(10)^{II}	0·96	2·768	1·82	171
N(2)—H(2)···O(10)^{III}	0·99	2·718	1·73	173

Symmetry code: (I) $x, y, z + 1$; (II) $x + 1, y, z + 1$; (III) $-x, 2 - y, -z$.

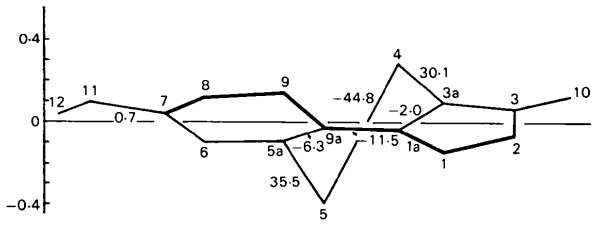

Fig. 4. Conformational angles around the cyclohexadiene ring and the methoxy group. The view is with respect to the least-squares plane through the molecule.

others. O(10) acts as an acceptor for three strong hydrogen bonds. The three H atoms plus atom C(3) form an approximate tetrahedron about the acceptor O(10). The two strongest hydrogen bonds in the structure are those in which atoms N(1) and N(2) are the donors. All of these observations are consistent with the distribution of charge inferred from the derived geometrical parameters. The details of the geometry of the hydrogen bonds are given in Table 3.

The cyclohexadiene ring exists in the half-chair conformation as can be seen from the torsion angles given in Fig. 4. The distances from the best plane through the molecule are also shown in Fig. 4 illustrating the relative flatness of the molecule. The dihedral angle between the planes defined by the atom coordinates of the five-membered and those of the benzene ring is 20°. This molecular flatness and the ability of the system to form strong hydrogen bonds may be responsible for its antineoplastic activity.

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Structure of Diacetylmorphine (Heroin)

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Abstract. $C_{21}H_{23}NO_5$ [7,8-didehydro-4,5α-epoxy-17-methylmorphinan-3,6α-diol diacetate (ester)], orthorhombic, $P2_12_12_1$, $a = 8{\cdot}003$ (5), $b = 14{\cdot}373$ (6), $c = 16{\cdot}392$ (7) Å at 296 K, $D_{calc} = 1{\cdot}32$ Mg m^{-3}, $Z = 4$, $F(000) = 784$, μ(Mo $K\alpha$) = 0·101 mm^{-1}. Direct methods were used to determine the structure from four-circle diffractometer intensity measurements. Least-squares refinement converged with $wR = 0{\cdot}057$. The skeleton of the molecular structure exhibits the T configuration already observed with other morphine derivatives.

Introduction. The present structural analysis of diacetylmorphine (Fig. 1) was carried out in the course of a continuing research project, aimed at identifying

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the products of forensically important crystal tests. [In such tests, the presence of a substance is inferred from the formation of characteristic crystals upon addition of a test reagent (Clarke, 1969).] As part of this work, we have studied the sodium acetate crystal test which is used as a test for the presence of diacetylmorphine (heroin).

Diacetylmorphine hydrochloride in aqueous sodium acetate solution yields well formed, clear hexagonal-shaped crystals of diacetylmorphine free base; these crystals are similar to those described by Sasvári, Simon, Bognár & Makleit (1974) for 6-deoxy-6-azido-dihydroisomorphine. The powder pattern of a crystal prepared in this way taken with a Gandolfi camera compared well with the results of Barnes & Sheppard (1954), with the exception of one extra line at $d = 9{\cdot}25$ Å in Barnes & Sheppard's powder pattern. A complete structure determination was undertaken for the purpose of calculating a powder standard from single-crystal data and to resolve the discrepancy between the 'powder pattern' obtained in this work and the powder pattern reported by Barnes & Sheppard.

Recent discoveries of opiate-related peptide compounds in the mammalian brain (enkephalins) (Hughes, Smith, Kosterlitz, Fothergill, Morgan & Morris, 1975) have generated further interest in analgesics, as these enkephalins have been shown to interact with opiate receptors in the brain (Chang & Fong, 1976; Simantov & Snyder, 1976). Therefore, structural information on other morphine-related compounds, such as heroin, may prove significant in understanding the mechanism of enkephalin activity in mammalian brain.

Precession photographs were used to determine approximate cell dimensions; they also showed the systematic absences for the orthorhombic space group $P2_12_12_1$. Cell dimensions were refined by least-squares methods using the positions of 15 reflections carefully determined on the same diffractometer used for the subsequent intensity measurements.

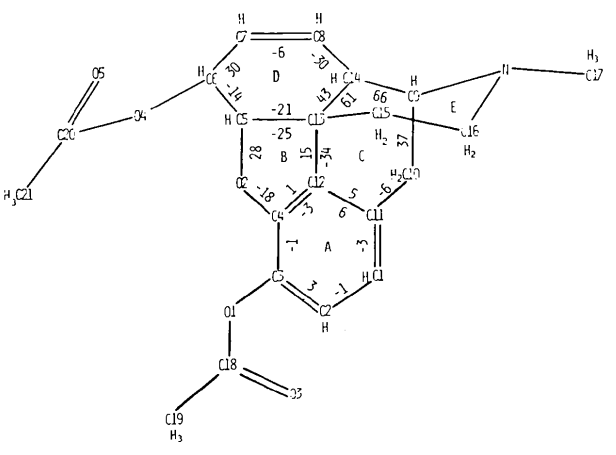

Fig. 1. Configuration drawing of diacetylmorphine with endocyclic torsion angles for rings *A*, *B*, *C* and *D*.

1422 independent reflections (maximum $\sin\theta/\lambda = 0{\cdot}539$ Å^{-1}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) were measured with a Syntex $P2_1$ diffractometer with the θ–2θ technique on a crystal $0{\cdot}7 \times 0{\cdot}2 \times 0{\cdot}2$ mm; of these, 964 had $F^2 > 2\sigma(F_o^2)$ and were regarded as observed. Two empirical checks were made to test for the necessity for absorption corrections. The first was a fast scan of 500 low-angle reflections in all four quadrants; the second was a measurement of the intensities of each of five reflections as the crystal was systematically rotated around the diffraction vector (Ψ scans). Both tests indicated that intensity varied with path length through the crystal by an average of <2% and a maximum of 5%; therefore, no absorption corrections were made. After Lorentz and polarization corrections, the absolute scale and approximate temperature factor were determined by a Wilson plot. Data reduction, structure factor calculations, least-squares refinements, and Fourier syntheses were carried out using routines in the XRAY system (1976) of crystallographic programs. Figures were drawn with the program *ORTEP* (Johnson, 1965). For direct phasing methods, the program *MULTAN* (Germain, Main & Woolfson, 1971) was used. For C, N, and O the scattering factors of Cromer & Mann (1968) were used and for H those of Stewart, Davidson & Simpson (1965).

An E map computed from 151 normalized structure factors phased by *MULTAN* and weighted according to *MULTAN*'s estimate of the probability of the correctness of the phase ($E \geq 1{\cdot}35$) showed the positions of 18 of the 27 non-hydrogen atoms. A difference synthesis revealed the remaining non-hydrogen atoms except those of one of the acetyl groups, which were located after a least-squares refinement cycle and a further difference synthesis.

The positional and isotropic thermal parameters were refined by full-matrix least squares to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0{\cdot}098$. A difference synthesis taken at this point showed the approximate positions of many of the H atoms; this information was used to find the positions of one of the H atoms in each of the three terminal methyl groups. Otherwise, however, H atoms were included at their idealized positions (C—H = 1·0 Å).

Refinement of positional and isotropic thermal parameters for all non-hydrogen atoms converged (maximum shift = $0{\cdot}060\sigma$, average shift = $0{\cdot}008\sigma$) with $wR = \sum W(|F_o| - |F_c|)^2/\sum W|F_o|^2 = 0{\cdot}073$. Weighting of reflections for least-squares refinement was based on estimated standard deviations from counting statistics.

Refinement continued for positional and anisotropic temperature factors for all non-hydrogen atoms, and positional parameters only for H atoms; after each four cycles the temperature factor for each H atom was set equal to that of the C atom to which it was attached. The parameters were divided into four blocks for refine-

ment at this stage, to produce the largest matrices that would fit into the available core. The final $wR = 0.057$, maximum shift = 0.168σ, average shift = 0.039σ. A final difference synthesis with all data showed no peaks greater than 0·46 e Å^{-3}.*

Final positional parameters are given in Table 1; the labeling used is that of Fig. 1. Fig. 2 shows the packing of the molecules in the unit cell. Bond distances are given in Fig. 3; the average standard deviation for non-hydrogen atoms is 0·014 Å, with a maximum standard deviation of 0·018 Å. Calculated torsion angles for endocyclic rings *A*, *B*, *C* and *D* are shown in Fig. 1; the average standard deviation is 1·5°, with a maximum standard deviation of 2·6°.

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34646 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

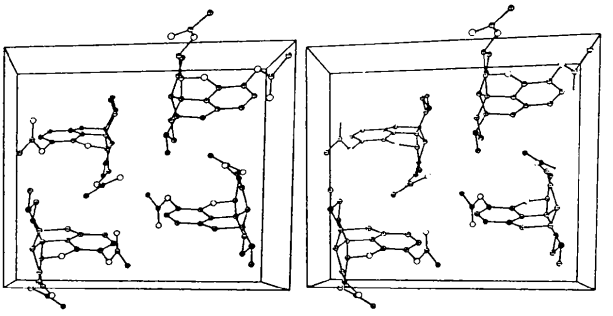

Fig. 2. Arrangement of the molecules in the unit cell (O oxygen). From an origin in the lower left front corner, **c** is to the right, **b** is vertical and **a** is into the page.

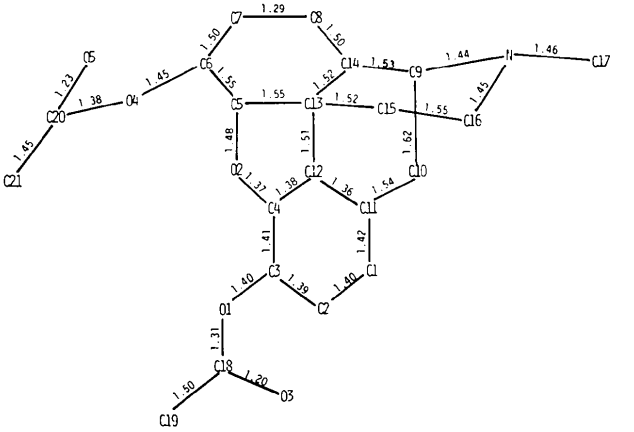

Fig. 3. Bond distances (Å). The estimated average standard deviation in bond length is 0·014 Å in diacetylmorphine.

Table 1. *Final positional parameters* (×10⁴) *for diacetylmorphine*

	x	*y*	*z*
C(1)	5202 (14)	2773 (7)	6368 (6)
C(2)	6669 (17)	3144 (7)	6032 (7)
C(3)	7944 (16)	3471 (8)	6529 (9)
C(4)	7799 (16)	3404 (8)	7385 (7)
C(5)	7858 (11)	3793 (6)	8725 (5)
C(6)	7210 (14)	4805 (6)	8789 (6)
C(7)	5405 (14)	4941 (7)	8564 (6)
C(8)	4259 (13)	4319 (7)	8657 (6)
C(9)	3506 (13)	2574 (7)	8633 (6)
C(10)	3406 (14)	2536 (7)	7645 (6)
C(11)	5090 (13)	2747 (6)	7229 (6)
C(12)	6376 (14)	3014 (7)	7719 (6)
C(13)	6435 (13)	3068 (7)	8640 (5)
C(14)	4681 (14)	3350 (6)	8923 (5)
C(15)	6923 (13)	2143 (8)	9026 (6)
C(16)	5574 (15)	1393 (6)	8848 (5)
C(17)	2729 (13)	979 (7)	8938 (7)
C(18)	10567 (15)	3526 (9)	5874 (7)
C(19)	11839 (14)	4175 (8)	5523 (8)
C(20)	9872 (16)	5562 (8)	8554 (7)
C(21)	10765 (13)	6035 (7)	7904 (7)
N	3930 (11)	1730 (6)	9061 (5)
O(1)	9275 (11)	3967 (5)	6180 (5)
O(2)	8882 (8)	3720 (4)	7973 (5)
O(3)	10684 (10)	2693 (5)	5886 (5)
O(4)	8229 (10)	5443 (4)	8316 (4)
O(5)	10348 (9)	5217 (5)	9197 (4)

Discussion. The main structural features of diacetylmorphine (heroin) are very similar to those of morphine (Mackay & Hodgkin, 1955; Gylbert, 1973; Bye, 1976) and codeine (Lindsey & Barnes, 1955; Kartha, Ahmed & Barnes, 1962) and several other morphine derivatives, *e.g.* 6-deoxy-6-azidodihydroisomorphine (Sasvári *et al.*, 1974).

The packing of diacetylmorphine (Fig. 2) appears to show some interaction between a methyl group on one molecule with that of a neighboring carbonyl oxygen group on another molecule. This apparent interaction is supported by the relatively short interatomic distances of O(5)–C(19) = 3·250 (14) and O(3)–C(21) = 3·311 (14) Å.

These distances fall into the range of 3·00 to 3·28 Å listed by Donohue (1968) as 'short C–O distances', and by Hamilton & Ibers (1968) as 'possible hydrogen bonds'; such interactions have also been described as polarization bonds (Dougill & Jeffrey, 1953). Their nature remains unclear (Donohue, 1968).

Finally, we note that the powder pattern calculated from the final structure agrees well with our Gandolfi X-ray pattern and does not show a line with $d = 9.25$ Å as reported by Barnes & Sheppard (1954), which may have been due to an impurity.

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2:1 Adduct of Perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene and Carbon Tetrachloride

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Abstract. $C_{28}Cl_{18}\cdot\frac{1}{2}CCl_4$, $M_r = 1051{\cdot}4$, monoclinic, $C2/c$, $a = 25{\cdot}794$ (14), $b = 8{\cdot}676$ (4), $c = 17{\cdot}258$ (9) Å, $\beta = 94{\cdot}47$ (4)°, $V = 3849$ (3) Å^3, $Z = 4$, λ(Mo $K\alpha$) = 0·71069 Å, $D_c = 1{\cdot}81$ Mg m^{-3}. The structure was solved with *MULTAN* and refined by block-diagonal least-squares methods. The final R value is 0·057 for 1610 observed reflections. The perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene (PDP) and carbon tetrachloride molecules are located at special positions (inversion centres and twofold axes, respectively), with an occupancy factor of 0·5 for the carbon tetrachloride. The PDP molecule is slightly distorted due principally to repulsions between adjacent non-bonded Cl atoms.

Introduction. Ballester and co-workers have studied in detail the thermal reaction of perchlorodiphenylacetylene (Ballester, Castañer & Armet, 1979). Besides the initial compound, the reaction yields three products which are difficult to separate. The crystal structure of one of them, perchloro-1,2,3-triphenylnaphthalene, has

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