

1-Acetyl-3-[1-(4-methoxyphenyl)-2-oxopropylidene]-1*H*-indol-2(3*H*)-one: a twinned crystal

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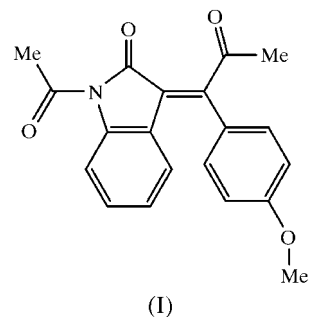
The crystal of the title compound, C₂₀H₁₇NO₄, which was used for collecting intensity data was twinned. Each of the two crystallographically independent molecules in the asymmetric unit has a planar indole moiety perpendicular to a planar oxopropyl moiety. The distribution of the bonds at the central C atom joining the oxopropyl, phenyl and indole substituents is also planar. The packing is stabilized by intermolecular C—H···O interactions, as well as by dipole–dipole and van der Waals interactions.

Comment

The compound 1-acetylisatin is of interest owing to its biological activity (Bieck *et al.*, 1993) and use as a synthetic precursor (Popp, 1975), as well as its photoinduced cycloaddition reactions with a wide range of alkenes. These photoinduced reactions of 1-acetylisatin with alkenes have become one of the synthetic routes to the corresponding spiroxetane derivatives (Xue *et al.*, 2000, 2001; Zhang *et al.*, 2002), in which the asymmetric alkenes give syn- and anti-clinal spiroxetanes as a mixture separable by column chromatography. As an extension of our systematic research into these photoinduced reactions, we have carried out the photoinduced reactions of 1-acetylisatin with alkynes. These reactions produce α - and β -unsaturated carbonyl compounds (Xue *et al.*, 2000). The title compound, (I), was obtained from such a photoreaction between 1-acetylisatin and 1-(*p*-methoxyphenyl)-1-propyne. An X-ray crystal structure analysis was undertaken to elucidate its steric configuration and the results are presented here.

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There are two crystallographically independent molecules, *A* and *B*, in the asymmetric unit of (I). The bond lengths and angles of molecules *A* and *B* agree with each other (Table 1), and are within normal ranges (Allen *et al.*, 1987). It is interesting to note that the torsion angles of the two independent molecules show a tendency to be equal but with opposite signs. This is indicative of pseudo-mirror symmetry between the two isolated molecules, but no pseudosymmetries are observed in the crystal.



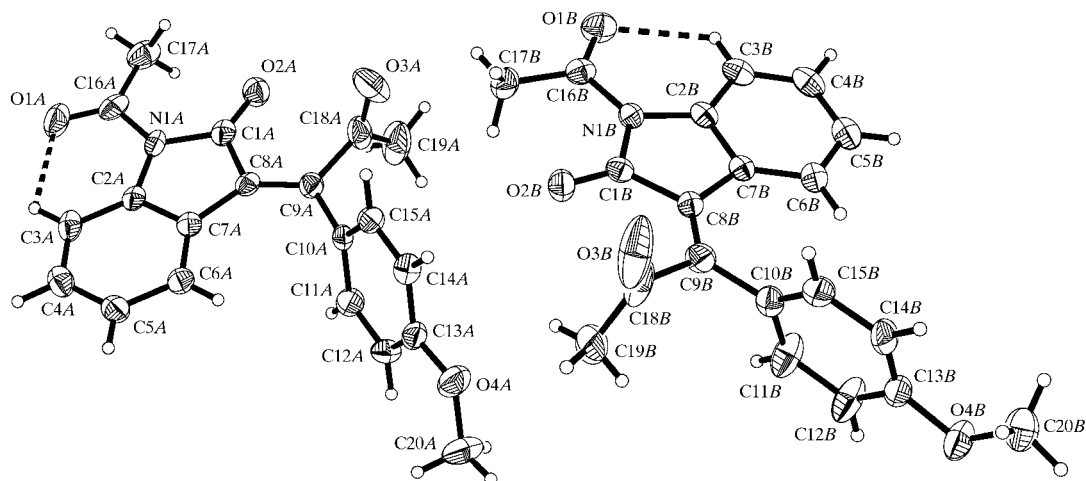
(I)

The orientation of the oxopropyl group (atoms O3, C9, C18 and C19) is opposite in the two independent molecules, as shown by the following torsion angles: C8—C9—C18—O3 96.8 (4)° for molecule *A* and −91.7 (5)° for molecule *B*, and C8—C9—C18—C19 −90.6 (4)° for molecule *A* and 94.0 (5)° for molecule *B*. The methoxy group (atoms O4 and C20) tends to be coplanar with the attached phenyl ring, as usually observed in the anisoles (Domiano *et al.*, 1979), but the orientation of the methyl group is also opposite, as shown by the C12—C13—O4—C20 and C14—C13—O4—C20 torsion angles of −2.4 (5) and 179.5 (3)°, respectively, in molecule *A*, and 172.0 (3) and −9.4 (5)°, respectively, in molecule *B*.

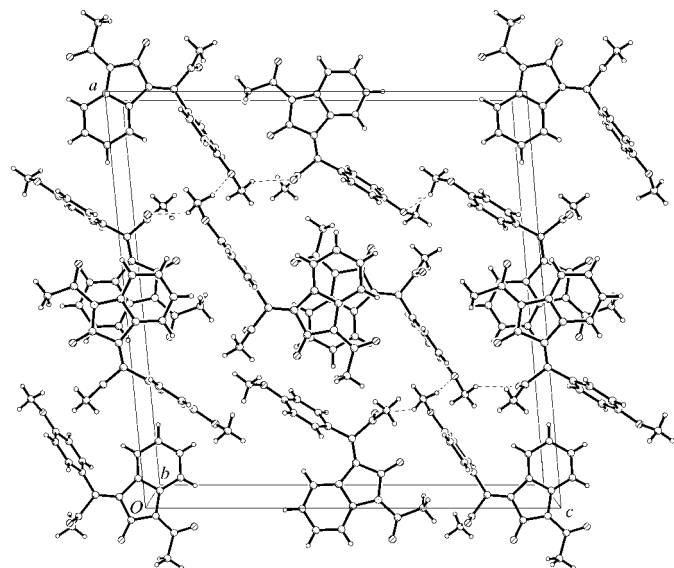
In both molecules, the indole moiety (atoms C1—C8 and N1) is planar, with the dihedral angle between the planes of the heterocyclic and benzene rings being 1.2 (2)° in molecule *A* and 1.6 (2)° in molecule *B*. In addition, the plane of the oxopropyl group is almost perpendicular to that of the indole moiety. The phenyl ring makes dihedral angles of 74.5 (1) and 71.4 (1)° with the planes of the oxopropyl and indole substituents, respectively, in molecule *A*; the corresponding angles are 73.7 (1) and 84.3 (1)° in molecule *B*. The distribution of bonds at the central atom, C9, joining the oxopropyl, phenyl and indole substituents, is planar. Since these three substituents are orthogonal, there is a lack of π -conjugation through the central C9 atom, in spite of its sp^2 bonding state.

There is an intramolecular C3—H3···O1 interaction in both molecules *A* and *B* (Fig. 1), forming a closed six-membered ring. This interaction adds to that of the π -conjugation of the acetyl group, so that this group is coplanar with the indole system.

In the packing of (I), both molecules *A* and *B* are linked by two weak intermolecular hydrogen bonds, C20B—H20E···O3Aⁱ and C20B—H20F···O4Bⁱⁱ (Table 2), into molecular ribbons parallel to the *c* direction (Fig. 2) [symmetry codes: (i) $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$]. The packing is stabilized by these interactions, as well as by dipole–dipole and van der Waals interactions.


Figure 1

A view of the two independent molecules of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.


Figure 2

The packing structure of (I) viewed down the *b* axis, showing the formation of molecular ribbons.

Experimental

Compound (I) was isolated using silica-gel column chromatographic separation of the reaction mixture of 1-acetylatisin with 1-(*p*-methoxyphenyl)-1-propyne. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of an acetone–petroleum ether solution.

Crystal data

$C_{20}H_{17}NO_4$
 $M_r = 335.35$
 Monoclinic, $P2_1/n$
 $a = 22.1109$ (4) Å
 $b = 6.9308$ (1) Å
 $c = 22.1109$ (4) Å
 $\beta = 95.128$ (1)°
 $V = 3374.85$ (10) Å³
 $Z = 8$

$D_x = 1.320$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 7006 reflections
 $\theta = 2.7$ – 28.3°
 $\mu = 0.09$ mm⁻¹
 $T = 213$ (2) K
 Block, yellow
 $0.40 \times 0.32 \times 0.24$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 20 195 measured reflections
 8083 independent reflections
 3756 reflections with $I > 2\sigma(I)$

$R_{int} = 0.091$
 $\theta_{max} = 28.3^\circ$
 $h = -28 \rightarrow 29$
 $k = -7 \rightarrow 9$
 $l = -29 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.145$
 $S = 0.82$
 8083 reflections
 459 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.29$ e Å⁻³
 $\Delta\rho_{min} = -0.25$ e Å⁻³
 Extinction correction: *SHELXTL*
 Extinction coefficient: 0.0094 (6)

Table 1

Selected geometric parameters (Å, °).

N1A–C1A	1.421 (4)	N1B–C1B	1.416 (4)
N1A–C2A	1.432 (4)	N1B–C2B	1.433 (4)
N1A–C16A	1.419 (4)	N1B–C16B	1.410 (4)
C8A–C9A	1.341 (4)	C8B–C9B	1.345 (4)
C9A–C10A	1.487 (4)	C9B–C10B	1.484 (4)
C9A–C18A	1.506 (5)	C9B–C18B	1.510 (5)
C8A–C9A–C10A	125.6 (3)	C8B–C9B–C10B	126.0 (3)
C8A–C9A–C18A	122.1 (3)	C8B–C9B–C18B	122.1 (3)
C10A–C9A–C18A	112.3 (3)	C10B–C9B–C18B	112.0 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C3A–H3A \cdots O1A	0.93	2.29	2.839 (5)	117
C3B–H3B \cdots O1B	0.93	2.29	2.841 (4)	117
C20B–H20E \cdots O3A ⁱ	0.96	2.40	3.209 (5)	141
C20B–H20F \cdots O4B ⁱⁱ	0.96	2.47	3.319 (5)	148

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The crystal used to collect the present data was twinned. There are two orientational domains, with the *a* and *c* lattice parameters interchanged. The origin of the twinning is due to the unit-cell *a* and *c* axes being equal in length within experimental error. When these unit cells are stacked to form the crystal structure, some unit cells are stacked one way and the rest are stacked the other way round, giving rise to this unique type of twinning. If the structure is solved in the standard $P2_1/c$ space group, its twinned crystal structure would not have been so obvious. For this type of twinning, the reflections from both twin components overlap with each other. Without introducing the twin law, refinement converges to $R = 0.16$ and $wR = 0.43$. Introduction of the twin command *TWIN* (001/010/100) in the refinement immediately reduced wR for all reflections and wR for reflections $>$ threshold to 0.145 and 0.122, respectively, and the refinement proceeded satisfactorily, with R converging to 0.057. The scale factor, *BASF*, for the two twin components obtained by least-squares structure refinement was 0.296. The H atoms were fixed geometrically and were treated as riding on the parent C atoms, with C—H distances in the range 0.93–0.96 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1555). Services for accessing these data are described at the back of the journal.

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