Acta Crystallographica Section C
**Crystal Structure Communications**
ISSN 0108-2701

# Syn- and anticlinal isomers of 2a′-acetoxy-1,7′-diacetyl-7′,7a′-dihydro-2-oxospiro[1*H*-indole-3(2*H*),2′(2a′*H*)-oxeto[3,2-*b*]indole]

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Received 21 November 2001
Accepted 4 December 2001
Online 16 January 2002

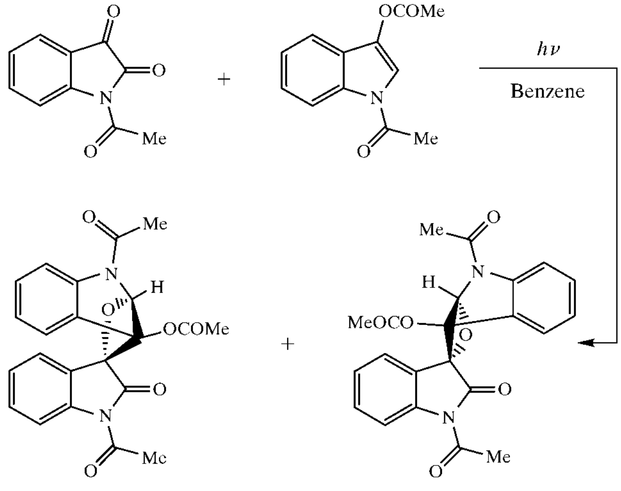
In the syn- and anticlinal isomers of the title compound, $C_{22}H_{18}N_2O_6$, the indole moiety is not completely planar, with the pyrrolidine ring being distorted very slightly towards a conformation intermediate between half-chair and envelope. The molecular and packing structures in the crystals of these isomers are stabilized by C—H···O interactions.

## Comment

1*H*-Indole-2,3-dione (isatin) derivatives having an acetyl substituent are of interest due to their biological activities (Bieck *et al.*, 1993) and their use as synthetic precursors (Popp, 1975). The photoreactions of 1-acetylisatin with alkenes are one of the synthetic routes to spiroxetane derivatives (Xue *et al.*, 2000, 2001), in which asymmetric alkenes give *syn*- and *anti*-spiroxetane isomers as a mixture separable by column chromatography and fractional crystallization. As part of our ongoing research on the regioselectivity of the photoreactions of 1-acetylisatin and the stereochemical properties of the products, we have isolated the title compounds, (I) and (II), which were obtained from the irradiation of 1-acetylisatin with 3-acetoxy-1-acetylindole in benzene solution. The crystal structure determinations of (I) and (II) (Figs. 1 and 2) were undertaken in order to elucidate their conformation and to determine their steric configurations.

The crystal structure analyses of the title compounds show (I) to be the synclinal and (II) to be the anticlinal isomer. These isomers refer to the relative configuration between the isatin (C1–C8/N2) and indole (C9–C16/N1) moieties.

The bond lengths and angles in (I) and (II) are within normal ranges (Allen *et al.*, 1987). In compound (I), the bond lengths and angles in the isatin and indole moieties are comparable. The oxetane ring (O6/C7/C16/C9) is not planar, with a dihedral angle of 166.6 (3)° between the O6/C7/C9 and C7/C16/C9 planes. Atoms C7, C9 and C16 are the chiral centers. However, since compounds (I) and (II) do not crystallize in a chiral space group, each structure contains molecules having opposite chirality.



(I)

(II)

Though the isatin moiety is almost planar due to the conjugation of the N—C and C=O bonds, the indole moiety is not completely coplanar with the pyrrolidine ring (N1/C9/C16/C15/C10) of the indole moiety, showing a slight puckering towards a conformation intermediate between half-chair and envelope (Duax *et al.*, 1976). The puckering amplitude $Q_2$ is 0.075 (3) Å and the local pseudo-twofold axis and pseudo-mirror contains atoms C15 and C9, respectively. The dihedral

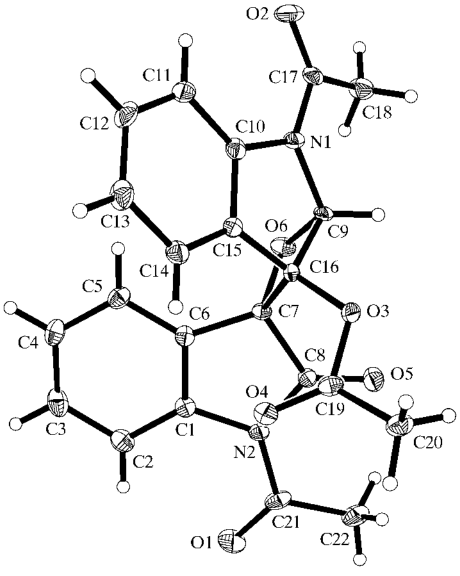


**Figure 1**
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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DOI: 10.1107/S0108270101020820

angle between the pyrrolidine and benzene rings in the indole system is 3.3 (2)°.

The mean planes through the isatin and indole moieties make dihedral angles of 89.1 (1) and 65.4 (1)°, respectively, with the oxetane ring; the two moieties make a dihedral angle of 53.3 (1)° with one another. The acetyl groups attached at atoms N1 and N2 make angles of 4.1 (2) and 7.5 (2) Å, respectively, with the isatin and indole moiety. The acetyloxy substituent forms a plane and makes an angle of 67.8 (1)° with the indole moiety.

In compound (II), there are two crystallographically independent molecules in the asymmetric unit. The bond lengths, angles and chirality of molecules *A* and *B* agree with one another. The bond lengths and angles within the two molecules are comparable with those of (I), albeit with a different configuration.

In molecules *A* and *B*, the oxetane ring is not planar, with a dihedral angle between the O6/C7/C9 and C7/C16/C9 planes of 166.0 (4)° in molecule *A* and 166.6 (4)° in molecule *B*. In Fig. 2, atom C7 is the *R* chiral center and atoms C9 and C16 are the *S* chiral centers. The isatin moiety is planar in both molecules *A* and *B*, whereas the indole moiety is not planar. The pyrrolidine ring of the indole moiety is in a conformation intermediate between half-chair and envelope, with the puckering amplitude $Q_2$ = 0.080 (4) Å and the local pseudo-

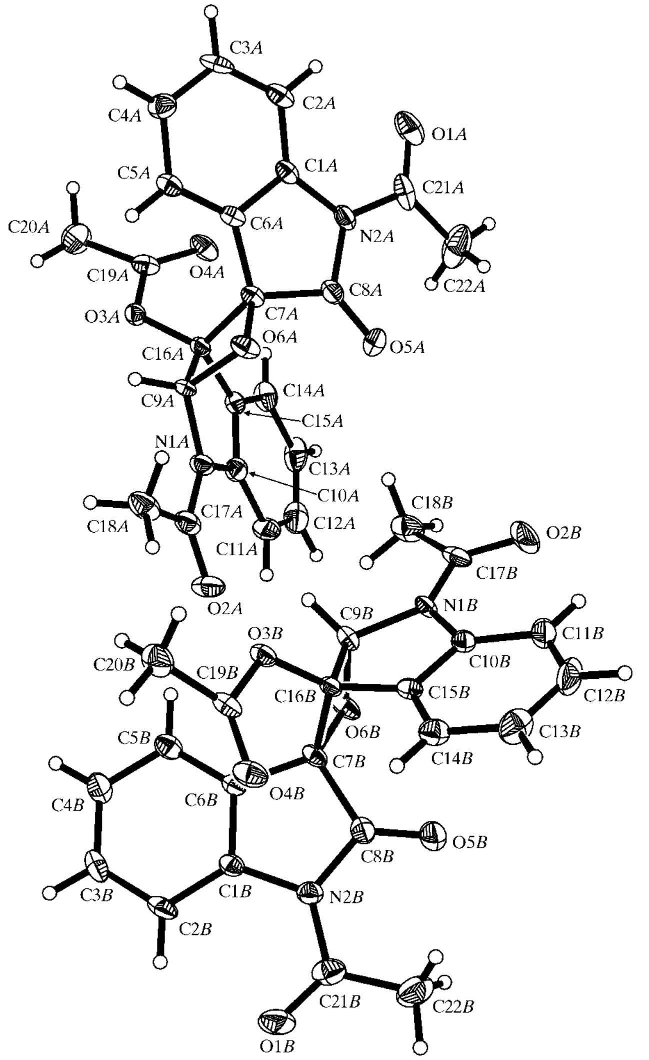

**Figure 2**
The structure of (II) showing 40% probability displacement ellipsoids and the atom-numbering scheme.

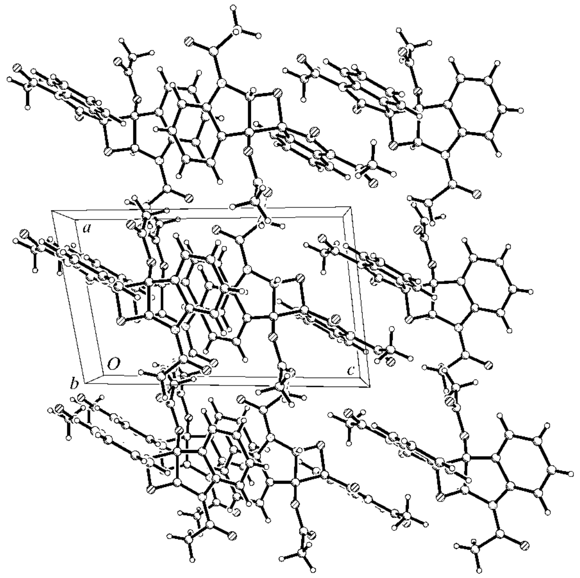

**Figure 3**
Packing diagram of (I) viewed down the *b* axis.

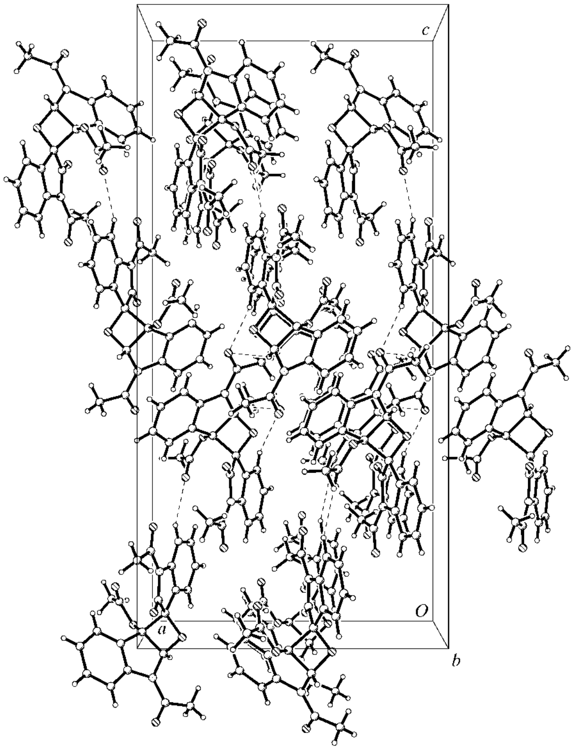

**Figure 4**
Packing diagram of (II) viewed down the *b* axis.

twofold axis and pseudo-mirror containing atoms C15 and C9, respectively, in both molecules. The dihedral angles between the pyrrolidine and benzene rings in the indole moiety are 4.1 (2) and 3.9 (2)° in molecules *A* and *B*, respectively.

In molecules *A* and *B*, the mean planes through the isatin and indole moieties make average dihedral angles of 89.6 (4) and 65.7 (3)°, respectively, with the oxetane ring. The average dihedral angle between the isatin and indole moieties is 43.4 (4)°.

The acetyl group attached at atom N2 makes an angle of 6.3 (4)°, on average, with the isatin moiety for both molecules, while that attached at atom N1 is twisted at an angle of 5.5 (4)° in molecule *A* and 4.3 (3)° in molecule *B* with respect to the indole plane. The plane passing through the acetoxy group attached at atom C16 makes an average dihedral angle of 64.9 (4)° with the indole plane.

The relative conformation about the bond joining the isatin and indole moieties of isomers (I) and (II) is defined by the C6—C7—C16—C15 torsion angle of −27.4 (4)° in (I), and 145.0 (4)° in molecules *A* and *B* of (II). These indicate that (I) is (−)synclinal, and that molecules *A* and *B* of (II) are (−)anticlinal.

In the structure of (I), there is one intramolecular interaction (C14—H14···O4) and two weak intermolecular interactions (C18—H18*B*···O4 and C20—H20*B*···O1; Table 2 and Fig. 3) interconnecting molecular columns stacked along the *b* axis into a three-dimensional network. In the structure of (II), there is also a weak intramolecular interaction (C14—H14···O4) in molecules *A* and *B*. Molecules *A* and *B* are interconnected by intermolecular C—H···O interactions (Table 4 and Fig. 4) into a three-dimensional molecular arrangement. These weak C—H···O interactions, together with van der Waals and dipole–dipole interactions, stabilize the molecular and packing structure in the two crystals.

## Experimental

A solution of 1-acetylisatin (0.05 *M*) in the presence of an excess of 3-acetoxy-1-acetylindole in benzene was irradiated with light having $\lambda \geq 400$ nm. Upon completion of the reaction, the solvent was removed *in vacuo* and the residue was separated by flash chromatography, on a silica-gel column using petroleum ether–ethyl acetate as eluent, and fractional crystallization to afford compounds (I) and (II). Single crystals suitable for X-ray diffraction were obtained by recrystallization from an acetone–petroleum ether mixture.

### Compound (I)

*Crystal data*

$C_{22}H_{18}N_2O_6$
$M_r = 406.38$
Triclinic, $P\overline{1}$
$a = 8.9350$ (4) Å
$b = 9.1189$ (3) Å
$c = 13.4690$ (6) Å
$\alpha = 75.897$ (1)°
$\beta = 89.831$ (1)°
$\gamma = 62.201$ (1)°
$V = 933.64$ (7) Å$^3$
$Z = 2$
$D_x = 1.446$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 4055 reflections
$\theta = 2.6$–28.3°
$\mu = 0.11$ mm$^{-1}$
$T = 183$ (2) K
Block, colorless
0.38 × 0.32 × 0.20 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.961$, $T_{max} = 0.979$
4475 measured reflections
3160 independent reflections
2252 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 15$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.071$
$wR(F^2) = 0.194$
$S = 0.95$
3160 reflections
275 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å$^{-3}$
$\Delta\rho_{min} = -0.52$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.058 (9)

**Table 1**
Selected interatomic distances (Å) for (I).

| | | | |
|---|---|---|---|
| O6—C9 | 1.454 (3) | C7—C16 | 1.571 (4) |
| O6—C7 | 1.459 (3) | C9—C16 | 1.531 (4) |

**Table 2**
Hydrogen-bonding and short-contact geometry (Å, °) for (I).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C14—H14···O4 | 0.93 | 2.53 | 3.155 (4) | 125 |
| C18—H18*B*···O4$^{i}$ | 0.96 | 2.54 | 3.271 (6) | 133 |
| C20—H20*B*···O1$^{ii}$ | 0.96 | 2.59 | 3.323 (4) | 133 |

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, 2 - y, 2 - z$.

### Compound (II)

*Crystal data*

$C_{22}H_{18}N_2O_6$
$M_r = 406.38$
Orthorhombic, $Pna2_1$
$a = 14.5310$ (2) Å
$b = 8.7676$ (1) Å
$c = 30.0679$ (1) Å
$V = 3830.71$ (7) Å$^3$
$Z = 8$
$D_x = 1.409$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 8192 reflections
$\theta = 2.7$–28.4°
$\mu = 0.10$ mm$^{-1}$
$T = 183$ (2) K
Block, colorless
0.50 × 0.30 × 0.22 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.950$, $T_{max} = 0.978$
17 100 measured reflections
3370 independent reflections
2679 reflections with $I > 2\sigma(I)$
$R_{int} = 0.095$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 17$
$k = -10 \rightarrow 10$
$l = -26 \rightarrow 35$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.115$
$S = 0.99$
3370 reflections
547 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0607P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å$^{-3}$
$\Delta\rho_{min} = -0.36$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0061 (7)

**Table 3**
Selected interatomic distances (Å) for (II).

| | | | |
|---|---|---|---|
| O6*A*—C7*A* | 1.442 (5) | O6*B*—C9*B* | 1.452 (5) |
| O6*A*—C9*A* | 1.453 (5) | O6*B*—C7*B* | 1.455 (5) |
| C7*A*—C16*A* | 1.567 (6) | C7*B*—C16*B* | 1.581 (6) |
| C9*A*—C16*A* | 1.531 (6) | C9*B*—C16*B* | 1.515 (6) |

**Table 4**
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C2*B*—H2*B*···O4*A*$^{i}$ | 0.93 | 2.43 | 3.232 (6) | 144 |
| C5*A*—H5*A*···O2*B*$^{ii}$ | 0.93 | 2.44 | 3.308 (7) | 156 |
| C5*B*—H5*B*···O2*A* | 0.93 | 2.44 | 3.311 (6) | 155 |
| C9*A*—H9*A*···O2*B*$^{ii}$ | 0.98 | 2.50 | 3.287 (6) | 138 |
| C9*B*—H9*B*···O2*A* | 0.98 | 2.52 | 3.296 (5) | 136 |
| C13*A*—H13*A*···O6*A*$^{iii}$ | 0.93 | 2.59 | 3.360 (6) | 141 |
| C14*A*—H14*A*···O4*A* | 0.93 | 2.41 | 3.046 (6) | 125 |
| C14*B*—H14*B*···O4*B* | 0.93 | 2.42 | 3.062 (6) | 126 |

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

H atoms were fixed geometrically and treated as riding on their parent C atoms, with aromatic C—H distances in the range 0.93–0.98 Å. Due to the absence of any significant anomalous scatterers in compound (II), the 3301 Friedel equivalents were merged before the final refinements. The choice of absolute structure was arbitrary.

For both compounds, 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).

The authors would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/PFIZIK/610961. AU thanks Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1545). Services for accessing these data are described at the back of the journal.

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