

1-Acetyl-2-oxo-4'-methyl-2a'-phenylspiro[3H-indole-3,2'(2a'H,5a'H)-oxeto[3,2-d]oxazole]

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Key indicators

Single-crystal X-ray study

$T = 183\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.073

wR factor = 0.192

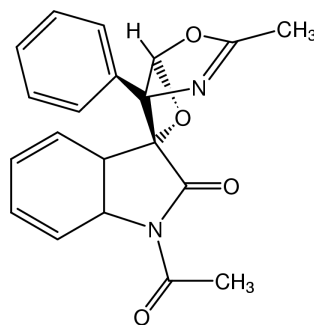
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_4$, the oxetane and oxazoline rings are almost planar, while the heterocyclic ring of the indole moiety is distorted from planarity towards an envelope conformation. The phenyl ring is in a $+sp$ conformation with respect to the indole moiety. The packing is stabilized by intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi$ interactions, as well as dipole-dipole and van der Waals interactions.

Comment

The photoinduced cycloaddition reactions of 1-acetylisatin with alkenes have been intensively investigated and have become one of the synthetic routes to obtain spiroxetane derivatives (Xue *et al.*, 2000, 2001). The reactions cover a wide range of electron-rich alkenes, in which an asymmetric alkene gives *syn*- and *anti*-spiroxetane isomers as a mixture separable by column chromatography and fractional crystallization. In continuing our systematic research on this area, we have prepared the title compound, (I), which was obtained from such a photoreaction of 1-acetylisatin with 2-methyl-4-phenyloxazole. As a part of this study, we have undertaken an X-ray crystal structure analysis of (I) to elucidate its steric conformation and the relative configuration of the rings.



(I)

The bond lengths and angles in the title compound are in good agreement with expected values. Those values within the indole moiety (C1–C8/N1) and oxetane ring (O3/C7/C11/C12) are comparable with the corresponding values in a previously studied spiroxetane structure (Usman *et al.*, 2001). The bond lengths and angles of the oxazoline ring (C11–C13/O4/N2) are within acceptable ranges and comparable with those in a 2-oxazoline derivative (Fustero *et al.*, 1996). The planarity of the oxazoline ring is due to the conjugation of $\text{C}-\text{O}$ and $\text{C}=\text{N}$ bonds.

The heterocyclic ring of the indole moiety is not planar, being distorted towards an envelope conformation with a local

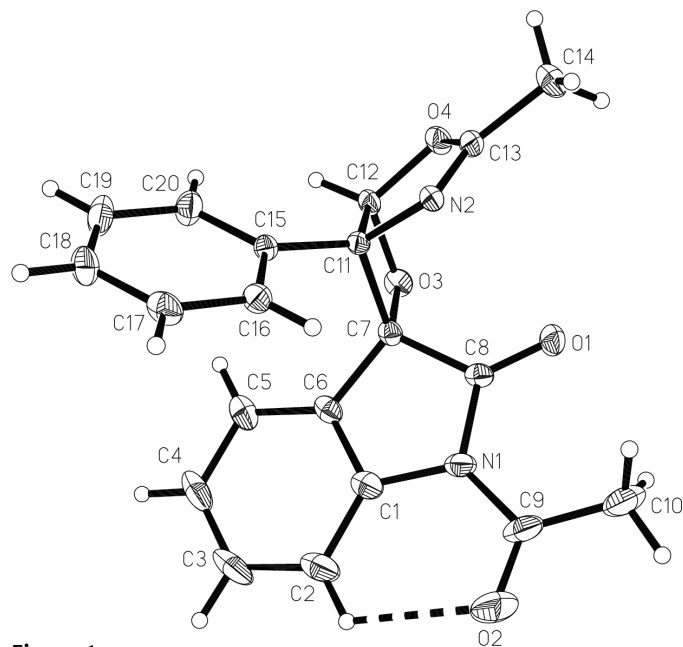


Figure 1
The structure of title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

pseudo-mirror passing through C7 and the midpoint of the C1–N1 bond. The puckering parameters for this plane are $Q_2 = 0.124(3) \text{ \AA}$ and $\varphi_2 = 57.6(1)^\circ$ (Cremer & Pople, 1975). The acetyl group attached at atom N1 is twisted around the N1–C9 bond by $7.1(1)^\circ$ from the heterocyclic ring. The dihedral angle between the mean planes of the heterocyclic and benzene rings in the indole system is $3.5(1)^\circ$.

The oxetane plane is almost perpendicular to the indole plane [dihedral angle $88.2(1)^\circ$], while the dihedral angle between the oxetane and oxazoline rings is $67.7(1)^\circ$. Atoms C7, C11 and C12 have the same chirality.

The C15–C11–C12 angle is $122.7(2)^\circ$, implying that the phenyl ring attached at the C11 atom is slightly pushed away from the oxazoline ring. The relative orientation of this phenyl ring with respect to the indole moiety is determined by the C6–C7–C11–C15 torsion angle, $4.5(3)^\circ$, corresponding to *+sp*. The conformation of the phenyl–oxazoline system relative to the indole moiety is conditioned by the tetrahedral environment of C11.

In the crystal packing of the title compound, there is an intramolecular C2–H2...O2 hydrogen bond forming a closed six-membered O2–C9–N1–C1–C2–H2 ring. This interaction adds its effect to that of the π -conjugation of the acetyl group, so that this group is coplanar with the indole system [C1–N1–C9–O2 = $-3.3(4)^\circ$]. The molecules are interconnected by two intermolecular C10–H10B...O4ⁱ and C12–H12...O2ⁱⁱ hydrogen bonds (see Table 2 for details) into chains parallel to the *b* axis (Fig. 2). An intermolecular C–H... π interaction involving the centroid of the phenyl ring (C15–C20) is also observed. In Table 2, *C_g* denotes the centroid of this phenyl ring. The packing structure is stabilized by these interactions, as well as the dipole–dipole and van der Waals interactions.

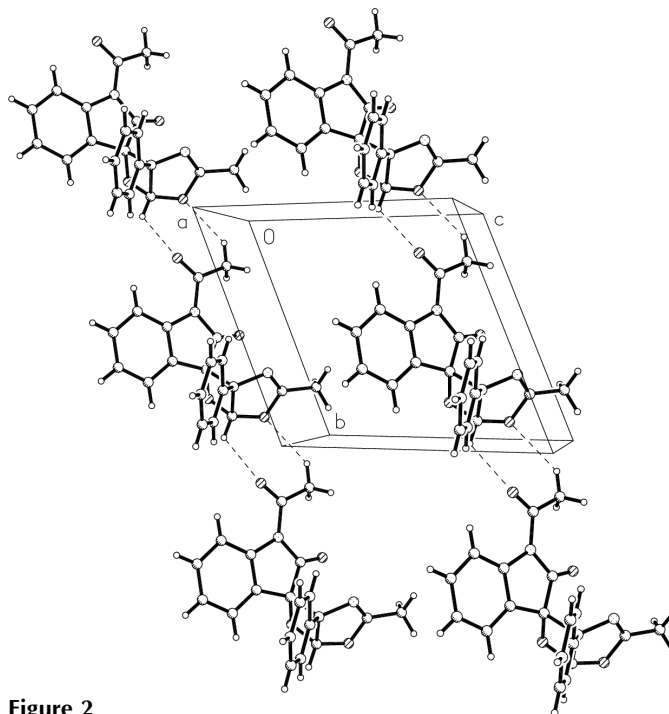


Figure 2
The packing of the title compound viewed down the *a* axis, showing the formation of molecular chains.

Experimental

The title compound was prepared by a photoinduced cycloaddition reaction between 1-acetyl-satin and an excess amount of 2-methyl-4-phenyloxazole in benzene solution. It was isolated using a silica-gel column chromatographic separation of the reaction mixture. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of an acetone–petroleum ether solution.

Crystal data

C₂₀H₁₆N₂O₄
M_r = 348.35
 Triclinic, *P* $\bar{1}$
a = 9.2852 (2) \AA
b = 9.5994 (4) \AA
c = 10.6206 (5) \AA
 α = 67.323 (1) $^\circ$
 β = 73.287 (1) $^\circ$
 γ = 84.761 (1) $^\circ$
V = 836.36 (6) \AA^3

Z = 2
D_x = 1.383 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 3902 reflections
 θ = 2.7–28.3 $^\circ$
 μ = 0.10 mm⁻¹
T = 183 (2) K
 Block, colorless
 0.40 \times 0.40 \times 0.36 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.962$, $T_{\max} = 0.966$
 4078 measured reflections

2870 independent reflections
 2245 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\max} = 25.0^\circ$
 $h = -9 \rightarrow 11$
 $k = -11 \rightarrow 8$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.073$
 $wR(F^2) = 0.192$
 $S = 0.99$
 2870 reflections
 238 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1195P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.078 (14)

Table 1
Selected interatomic distances (Å).

O4—C13	1.376 (3)	N2—C11	1.467 (3)
O4—C12	1.420 (3)	C11—C12	1.539 (3)
N2—C13	1.277 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C2—H2···O2	0.93	2.28	2.822 (4)	116
C10—H10B···O4 ⁱ	0.96	2.60	3.413 (4)	143
C12—H12···O2 ⁱⁱ	0.98	2.57	3.246 (4)	126
C10—H10C···Cg ⁱⁱⁱ	0.96	2.68	3.538 (4)	148

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

The H atoms were geometrically positioned and were treated as riding on their parent C atoms, with C—H distances in the range 0.93–0.98 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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References

- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Fustero, S., Navarro, A., Díaz, D., de la Torre, M. G., Asensio, A., Sanz, F. & González, M. L. (1996). *J. Org. Chem.* **61**, 8849–8859.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Usman, A., Razak, I. A., Fun, H.-K., Chantrapromma, S., Zhang, Y. & Xu, J.-H. (2001). *Acta Cryst.* **E57**, o852–o854.
- Xue, J., Zhang, Y., Wang, X.-L., Fun, H.-K. & Xu, J.-H. (2000). *Org. Lett.* pp. 2583–2586.
- Xue, J., Zhang, Y., Wu, T., Fun, H.-K. & Xu, J.-H. (2001). *J. Chem. Soc. Perkin Trans.* **1**, pp. 183–191.