

# 1-Acetyl-4'-ethyl-2a'-phenyl-2',2a',5',5a'-tetrahydrospiro[1H-indole-3,2'-oxeto[5,4-b]oxazol]-2(3H)-one and 1-acetyl-4',5a'-diphenyl-2',2a',5',5a'-tetrahydrospiro[1H-indole-3,2'-oxeto[5,4-b]oxazol]-2(3H)-one

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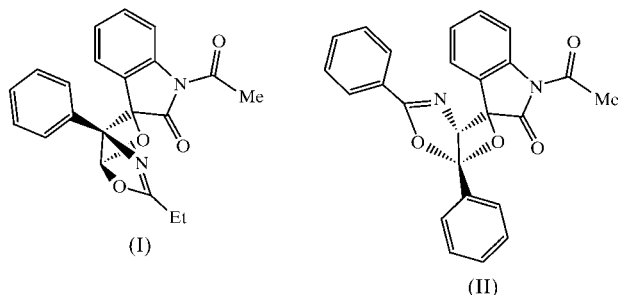
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In the title compounds,  $C_{21}H_{18}N_2O_4$  and  $C_{25}H_{18}N_2O_4$ , respectively, the five-membered ring of the indole system is almost planar. The oxetane and oxazole rings are individually planar. The orientations of the indole, oxetane, oxazole and phenyl moieties are conditioned by the  $sp^3$  nature of the spiro-C atoms. In both compounds, the relative orientation of the indole and oxazole rings is opposite.

## Comment

Recently, we have studied the photocycloaddition reactions of some  $\alpha$ -dicarbonyl compounds with oxazole derivatives (Zhang *et al.*, 2003). For the photoinduced reactions of 1-acetylisatin with oxazole derivatives, some of the separable products are the corresponding spiro[1H-indole-3,2'-oxeto[5,4-b]oxazol]-2(3H)-one derivatives. We have structurally analysed two of these derivatives, *viz.* (I) and (II), and the results are presented here.



The bond lengths and angles in compounds (I) and (II) (Figs. 1 and 2, respectively) are within normal ranges (Allen *et al.*, 1987).

The corresponding values agree with each other. Those within the indole moieties (C1–C6/N1/C7/C8) are comparable to the corresponding values in the related compound spiro[1H-indole-3,2'-oxetan]-2(3H)-one, hereafter (III) (Usman *et al.*, 2002).

An elongation of the  $Csp^3$ – $Csp^3$  bond C8–C11 of the spiro-oxetane ring (C8/C9/C11/O1) is observed, especially in compound (I), due to the bulky phenyl substituent attached at C11. This elongation is also found in compound (III).

The spiro-oxetane ring is nearly planar, with the dihedral angle between the O1/C8/C11 and O1/C9/C11 planes being  $178.6(2)^\circ$  in (I) and  $176.6(3)^\circ$  in (II). This is in contrast to the corresponding dihedral angle of  $163.0(3)^\circ$  in (III) (Usman *et al.*, 2002).

The planes through the oxetane ring and its fused oxazole ring (C9/C11/N2/C10/O2) make a dihedral angle of  $66.5(1)^\circ$  in (I) and  $67.0(2)^\circ$  in (II). This is conditioned by the eclipsed configuration of the  $sp^3$  state of the shared atoms C9 and C11. The angles around these two atoms are listed in Tables 1 and 3 for (I) and (II), respectively.

The oxetane ring and the indole system are nearly orthogonal, with dihedral angles of  $89.8(1)$  and  $83.6(1)^\circ$  between their planes in (I) and (II), respectively, and the C12–C17 phenyl rings make dihedral angles with the oxetane ring of  $56.9(1)$  and  $61.1(2)^\circ$  in (I) and (II), respectively. The relative orientation of the oxazole ring and the indole moiety in (I) is opposite compared with that in (II). This is shown by the C1–C8–C11–N2 and C7–C8–C11–N2 torsion angles which are  $-134.9(1)$  and  $-12.2(2)^\circ$ , respectively, for (I), and  $19.9(3)$  and  $141.0(2)^\circ$  for (II).

In (I) and (II), the orientations and the relative distributions of the indole moiety and the C12–C17 phenyl ring are conditioned by the eclipsed configuration of the atom pairs

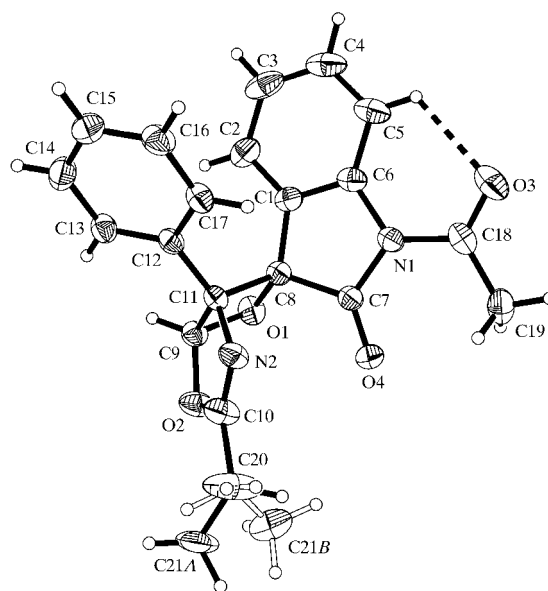


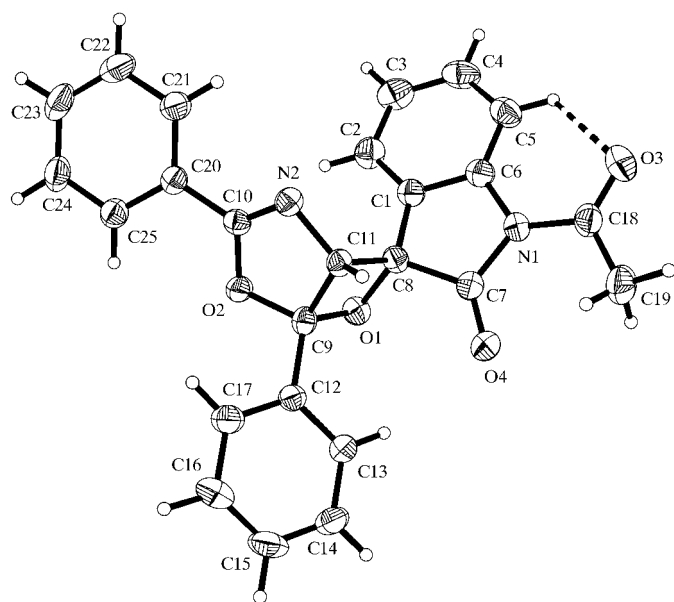
Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The major and minor components of the disorder are shown for atom C21.

C8—C11 and C9—C11. These are supported by the torsion angles involving C8—C11 and C9—C11 (see Tables 1 and 3).

In both compounds, the indole moiety is almost planar, with the five-membered ring adopting a conformation intermediate between envelope and half-chair in (I) and a half-chair conformation in (II). The  $Q_2$  puckering amplitude is 0.129 (2) Å for (I) and 0.150 (3) Å for (II). The dihedral angle between the five-membered ring and the fused benzene ring is 4.2 (1)° in (I) and 4.6 (2)° in (II). Ketone atom O4 attached at C7 deviates from the mean plane of the five-membered ring by 0.280 (1) Å in (I) and 0.308 (2) Å in (II).

In (I) and (II), the acetyl group (O3/C18/C19) attached at N1 is twisted by angles of 8.9 (1) and 11.6 (1)°, respectively, from the mean plane of the indole moiety. This indicates that the acetyl group tends to be coplanar with the indole moiety, as is usually observed for 1-acetylindole derivatives due to the interactions of the  $\pi$ -conjugation of the acetyl group. In (I) and (II), the C—H...O intramolecular interaction which forms an O3—C18—N1—C6—C5—H5 *S*(6) graph ring (Etter *et al.*, 1990) also participates in the  $\pi$ -conjugation (Tables 2 and 4).



**Figure 2**  
The structure of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

In (I), the ethyl group (C20/C21) attached to C10 shows a positional disorder, so that the major and minor component (C21A and C21B) are displaced in opposite directions, by 0.421 (8) and 0.993 (4) Å, respectively, from the oxazole plane. In (II), the C20—C25 phenyl ring attached to C10 is twisted by an angle of 21.1 (2)° with respect to the oxazole plane.

For (I) and (II), the asymmetric units (Figs. 1 and 2) have atom C8 as an *S* chiral center. However, while atoms C9 and C11 of (I) are *S* chiral centers, these atoms are *R* chiral centers in (II) in Fig. 2. Moreover, since both compounds crystallized in centrosymmetric space groups, the samples used in this study are racemic crystals.

## Experimental

Compounds (I) and (II) were prepared by the photoinduced reactions of 1-acetylindatin with an excess of 2-ethyl-4-phenyloxazole and 2,5-diphenyloxazole, respectively, in benzene, and were separated by silica-gel column chromatography with petroleum ether–ethyl acetate as eluant in each case. Single crystals of (I) and (II) were obtained by slow evaporation from petroleum ether–acetone solutions.

### Compound (I)

#### Crystal data

$C_{21}H_{18}N_2O_4$   
 $M_r = 362.37$   
Monoclinic,  $P2_1/n$   
 $a = 10.8569$  (6) Å  
 $b = 12.4129$  (6) Å  
 $c = 12.9849$  (6) Å  
 $\beta = 97.386$  (1)°  
 $V = 1735.4$  (2) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.387$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 6010 reflections  
 $\theta = 2.3$ – $28.3$ °  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 213$  (2) K  
Block, colorless  
0.48 × 0.44 × 0.42 mm

#### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.899$ ,  $T_{\max} = 0.960$   
10 582 measured reflections  
4238 independent reflections

3439 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 $\theta_{\text{max}} = 28.3$ °  
 $h = -14 \rightarrow 6$   
 $k = -16 \rightarrow 16$   
 $l = -17 \rightarrow 17$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.142$   
 $S = 1.07$   
4238 reflections  
257 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0644P)^2 + 0.7497P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.34$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.43$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

O1—C9	1.427 (2)	C9—C11	1.541 (2)
O2—C9	1.422 (2)	C10—C20	1.491 (3)
N2—C10	1.263 (2)	C11—C12	1.498 (2)
N2—C11	1.465 (2)	C20—C21B	1.306 (5)
C8—C11	1.595 (2)	C20—C21A	1.355 (5)
O2—C9—O1	113.5 (1)	N2—C11—C8	113.4 (1)
N2—C11—C12	112.8 (1)	C12—C11—C8	116.6 (1)
O2—C9—C11—N2	3.5 (2)	C1—C8—C11—C12	−1.3 (2)
O1—C9—C11—C8	1.0 (1)		

**Table 2**

Hydrogen-bonding geometry (Å, °) for (I).

<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>
C5—H5...O3	0.93	2.27	2.819 (3)	117

## Compound (II)

## Crystal data

$C_{25}H_{18}N_2O_4$   
 $M_r = 410.41$   
 Monoclinic,  $P2_1/n$   
 $a = 12.7908$  (10) Å  
 $b = 8.7717$  (7) Å  
 $c = 17.8346$  (13) Å  
 $\beta = 94.515$  (2)°  
 $V = 1994.8$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.367$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 3856 reflections  
 $\theta = 2.8$ – $28.3$ °  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Needle, colorless  
 $0.50 \times 0.34 \times 0.16$  mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 9586 measured reflections  
 3505 independent reflections  
 2826 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.026$   
 $\theta_{max} = 25.0$ °  
 $h = -14 \rightarrow 15$   
 $k = -10 \rightarrow 10$   
 $l = -21 \rightarrow 18$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.066$   
 $wR(F^2) = 0.134$   
 $S = 1.19$   
 3505 reflections  
 341 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 1.5031P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.19$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.20$  e Å<sup>-3</sup>

Table 3

Selected geometric parameters (Å, °) for (II).

O1–C9	1.439 (3)	C8–C11	1.563 (4)
O2–C9	1.430 (3)	C9–C12	1.494 (4)
N2–C11	1.449 (3)	C9–C11	1.537 (4)
O2–C9–O1	111.1 (2)	O1–C9–C12	113.9 (2)
O2–C9–C12	110.0 (2)	N2–C11–C8	114.6 (2)
O2–C9–C11–N2	−0.3 (3)	C1–C8–C11–N2	19.9 (3)
O1–C9–C11–C8	−2.3 (2)		

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C5–H5 $\cdots$ O3	0.92 (3)	2.36 (3)	2.872 (4)	115 (3)

The H atoms of (I) were fixed geometrically and treated as riding on their parent C atoms, with C–H distances in the range 0.93–0.98 Å and  $U_{iso}(H) = 1.2$ – $1.5U_{eq}(C)$ . For (II), the H atoms were located from difference maps and were refined isotropically [C–H = 0.91 (3)–1.02 (4) Å], except for those attached to the methyl C atoms, which were fixed geometrically and treated as riding. Rotating group refinement was used for the methyl groups of (I) and (II).

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, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1612). Services for accessing these data are described at the back of the journal.

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