Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

1-Acetyl-3′-(4-bromophenyl)-3′-chlorospiro[3*H*-indole-3,2′-oxetan]-2(1*H*)-one

Anwar Usman,[a] Ibrahim Abdul Razak,[a] Hoong-Kun Fun,[a]* Suchada Chantrapromma,[a]† Yan Zhang[b] and Jian-Hua Xu[b]

[a]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]Department of Chemistry, Nanjing University, Nanjing 210093, People's Republic of China
Correspondence e-mail: hkfun@usm.my

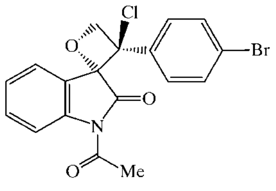
Received 12 March 2002
Accepted 27 March 2002
Online 30 April 2002

In the title compound, $C_{18}H_{13}BrClNO_3$, the heterocyclic ring of the indole is distorted from planarity towards an envelope conformation. The orientations of the indole, oxetane, chloro and bromophenyl substituents are conditioned by the sp^3 states of the spiro-junction and the Cl-attached C atoms.

Comment

1-Acetylisatin undergoes photoinduced cycloaddition reactions with a wide range of alkenes. These reactions have become one of the synthetic routes to obtain the corresponding spiroxetane derivatives (Xue *et al.*, 2001; Zhang *et al.*, 2002). The asymmetric alkenes in these reactions give syn- and anticlinal spiroxetanes as a separable mixture by column chromatography. The structure analyses of these spiroxetanes have been reported by us in previous studies (Usman *et al.*, 2001, 2002). As an extension of our systematic study into these photoinduced reactions, we have isolated the title compound, (I), which was one of the spiroxetanes resulting from such a photoinduced reaction between 1-acetylisatin and β-chloro-4-bromostyrene. An X-ray crystal structure analysis has been undertaken to elucidate its steric configuration and conformation, and the results are presented here.

The bond lengths and angles in (I) (Fig. 1) are within normal ranges (Allen *et al.*, 1987). The C8—C9 bond length of the spiroxetane (C8/C9/C10/O2) is slightly longer than the typical value for Csp^3—Csp^3, due to the bulky substituents attached to atoms C8 and C9. The spiroxetane is not planar, with atoms O2, C8, C9, and C10 deviating by 0.085 (2), −0.078 (3), 0.074 (3), and −0.080 (3) Å, respectively, from the mean plane, and the dihedral angle between the O2/C8/C10 and C8/C9/C10 planes is 163.0 (3)°.



(I)

The orientations of the indole (C1/N1/C2–C8), bromophenyl (C11–C16/Br1) and chloro (Cl1) substituents are conditioned by the Csp^3 state of atoms C8 and C9, while the relative distribution of the indole and bromophenyl substituents is described by the torsion angles C7—C8—C9—Cl1 of −25.4 (1)° and C1—C8—C9—C11 of −20.8 (3). These indicate the staggered arrangement of atoms C8 and C9 joining the two substituents. The bond angles subtended at atoms C8 and C9 are in the ranges 89.7 (2)–123.7 (3)° and 84.1 (2)–121.1 (2)°, respectively. The oxetane ring and the indole moiety are approximately orthogonal, corresponding to an angle of 81.1 (2)° between their mean planes, and the planar bromophenyl substituent makes a dihedral angle of 42.9 (2)° with respect to the mean plane of the oxetane ring.

The indole moiety is not planar, with the heterocyclic ring being distorted from planarity towards an envelope conformation. Atom C1 is displaced by 0.216 (3) Å from the N1/C2/C7/C8 plane, and the ketone atom O1 attached to C1 deviates by 0.331 (2) Å from the mean plane of the heterocyclic ring. The mean plane of the heterocyclic ring makes an angle of 7.1 (2)° with the benzene ring (C2–C7).

In (I), the acetyl group (O3/C17/C18) attached at N1 is twisted by an angle of 5.1 (1)° from the mean plane of the indole moiety. This indicates that the acetyl group tends to be coplanar with the indole moiety, as observed in 1-acetylindole (Usman *et al.*, 2002), due to the interactions of the π-conjugation of the acetyl group. The intramolecular C3—H3···O3 interaction (Table 2), which forms a six-membered closed ring, O3/C17/N1/C2/C3/H3, also participates in the π-conjugation.

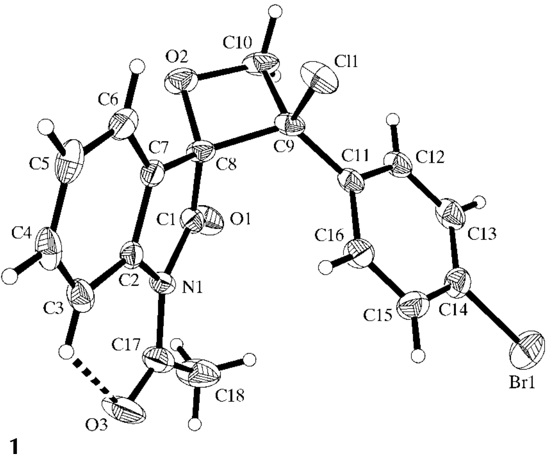


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii and the intramolecular hydrogen bond is shown as a dashed line.

---

† Permanent address: Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

DOI: 10.1107/S0108270102005681

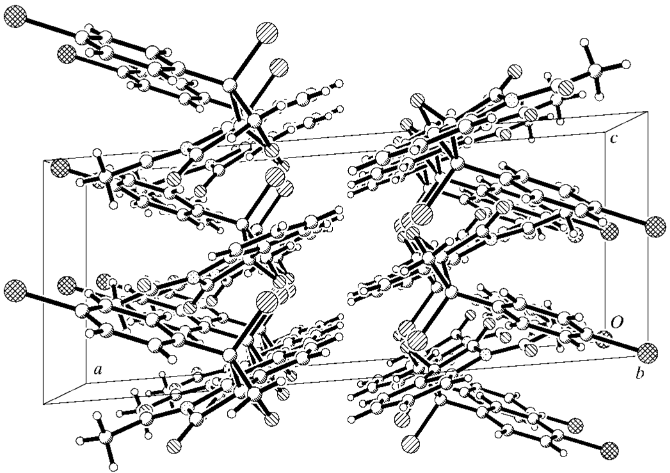


Figure 2
A packing diagram for (I) viewed down the *b* axis.

As seen in Fig. 1, in the molecule chosen for the asymmetric unit, atom C8 is the *S* chiral centre and atom C9 is the *R* chiral centre. However, the centrosymmetric crystal space group indicates that the photoinduced cycloaddition reaction of both achiral 1-acetylisatin and β-chloro-4-bromostyrene gives the racemate spiroxetane mixture of (I).

The molecules of (I) pack into columns along the *b* direction (Fig. 2). Weak intermolecular $\pi\cdots\pi$ interactions are observed in the crystal, involving the centroid of the indole benzene ring. The $\pi\cdots\pi^{\rm i}$ [symmetry code: (i) $x, -\frac{1}{2} - y, z - \frac{1}{2}$] and $\pi\cdots\pi^{\rm ii}$ [symmetry code: (ii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$] distances are 3.825 (5) Å for both interactions, and the perpendicular distances are 3.392 (5) and 3.535 (5) Å, respectively.

Experimental

A solution of 1-acetylisatin (0.05 *M*) in the presence of an excess of β-chloro-4-bromostyrene in benzene solution was irradiated with light of wavelength longer than 400 nm. After completion of the reaction, the solvent was removed *in vacuo* and the residue was separated using silica-gel column chromatography to afford (I). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an acetone–petroleum ether (3:1, *v*/*v*) solution.

Crystal data

$C_{18}H_{13}BrClNO_3$
$M_r = 406.65$
Monoclinic, $P2_1/c$
$a = 18.5810 (5)$ Å
$b = 12.5906 (4)$ Å
$c = 7.4709 (2)$ Å
$\beta = 94.645 (1)^\circ$
$V = 1742.05 (9)$ Å^3
$Z = 4$
$D_x = 1.551$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4889 reflections
$\theta = 2.7$–28.4°
$\mu = 2.53$ mm^{-1}
$T = 233 (2)$ K
Slab, colourless
0.36 × 0.28 × 0.16 mm

Table 1
Selected interatomic distances (Å).

Br1—C14	1.900 (3)	C8—C9	1.587 (4)
Cl1—C9	1.805 (3)	C9—C11	1.505 (4)
C1—C8	1.526 (4)	C9—C10	1.535 (4)
C7—C8	1.479 (4)		

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C3—H3$\cdots$O3	0.93	2.36	2.890 (4)	116

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.463$, $T_{\rm max} = 0.688$
10 113 measured reflections
4173 independent reflections
2016 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.080$
$\theta_{\rm max} = 28.3^\circ$
$h = -23 \rightarrow 24$
$k = -16 \rightarrow 13$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.120$
$S = 0.81$
4173 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0153P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.45$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.76$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.0091 (10)

The H atoms were fixed geometrically and treated as riding on their parent C atoms, with C—H = 0.93–0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. The highest peak and deepest hole were found near atom Br1, at distances of 0.94 and 0.86 Å, respectively.

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: AV1106). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Usman, A., Razak, I. A., Fun, H.-K., Chantrapromma, S., Zhang, Y. & Xu, J.-H. (2001). *Acta Cryst.* E**57**, o852–o854.
Usman, A., Razak, I. A., Fun, H.-K., Chantrapromma, S., Zhang, Y. & Xu, J.-H. (2002). *Acta Cryst.* C**58**, o59–o62.
Xue, J., Zhang, Y., Wu, T., Fun, H.-K. & Xu, J.-H. (2001). *J. Chem. Soc. Perkin Trans.* 1, pp. 183–191.
Zhang, Y., Gao, Y., Fun, H.-K. & Xu, J.-H. (2002). *J. Chem. Soc. Perkin Trans.* 1, pp. 345–353.