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Dimethyl 1,3-dichloro-8-phenyl-5-phenylsulfanylisoquinoline-6,7-dicarboxylate

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.052
wR factor = 0.138
Data-to-parameter ratio = 18.3

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

In the title molecule, $C_{25}H_{17}Cl_2NO_4S$, one of the phenyl rings is nearly perpendicular to the isoquinoline moiety. The angle subtended at the S atom joining another phenyl ring to the isoquinoline is 102.2 (1)°. The extended structure is built from infinite molecular chains parallel to the b axis which are stabilized by C—H···O hydrogen bonds.

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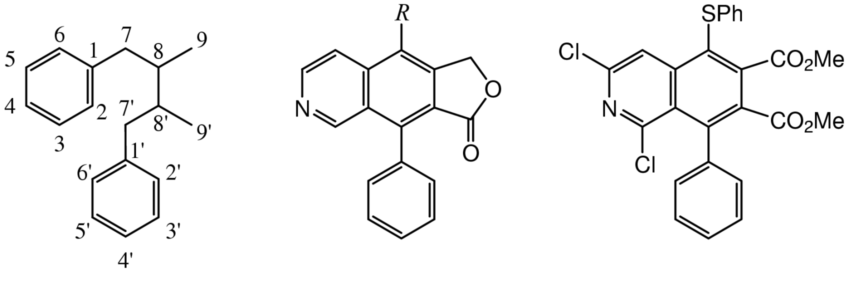
Comment

Lignans, which are characterized by the presence of two phenylpropane moieties bonded through C8—C8′, as in (I) in the Scheme below, have generated much interest in view of their widespread occurrence in nature and their biological activities (Ward, 1993). In recent years, a class of compounds having the lignan skeleton with one or two heteroatoms in the phenylpropane units has been developed in various research laboratories (Ramos *et al.*, 1999). Compounds of this class, *viz.* heterolignans, are of wide structural diversity and possess not only biological activities comparable to lignans but also display either enhanced biological activities or a variety of other properties. In view of the importance of these heterolignans, we have conducted a synthetic program in order to investigate the structure–activity relationship of lignans (II) and (III). During the course of this work, we have synthesized the substituted isoquinoline (IV) which is related to the heterolignans (II) and (III). An X-ray structure determination of (IV) was undertaken in order to elucidate the molecular conformation.



(I)

(II) R = H
(III) R = OH

(IV)

In the structure of (IV) (Fig. 1), the bond lengths and angles are normal (Allen *et al.*, 1987). Atoms Cl1 and Cl2 lie in the isoquinoline (C1–C9/N1) plane, with displacements of 0.031 (1) and 0.050 (1) Å, respectively. Both of the attached methyl carboxylates (O1/O2/C24/C25 and O3/O4/C22/C23) are planar, and the two planes are twisted out of the isoquinoline plane by 64.8 (1) and 63.0 (1)°, respectively.

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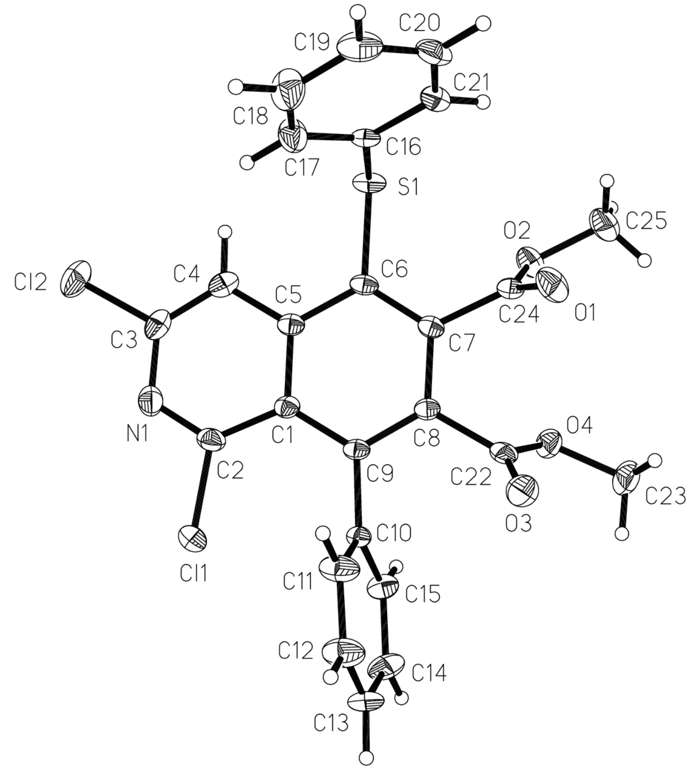

Figure 1
The structure of (IV), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The C10–C15 phenyl ring attached to atom C9 is nearly perpendicular to the isoquinoline plane, with a dihedral angle of 82.7 (1)°. The C6—S1—C16 angle between the C16–C21 phenyl ring and the isoquinoline system is 102.2 (1)°, while the dihedral angle between this phenyl ring and the isoquinoline moiety is 76.6 (1)°.

In the crystal structure of (IV), the molecules are linked by $\mathrm{C23{-}H23}B\cdots\mathrm{O1}^{\mathrm{i}}$ hydrogen bonds (Table 1) to form an infinite chain along the *b* axis (Fig. 2). The molecular chains form sheets perpendicular to the *a* axis. An intermolecular C—H···π interaction is observed involving the centroid of the C16–C21 phenyl ring; in Table 1, the centroid is denoted Cg(*A*).

Experimental

To a stirred solution of 3,5-dichloro-1-phenyl-8-phenylsulfanyl-11-oxa-4-azatricyclo[6.2.2.0^{2,7}]undeca-2(7),3,5-triene-9,10-dicarboxylic acid dimethyl ester (75 mg, 0.14 mol), prepared from the Pummerer reaction of (4-benzenesulfinylmethyl-2,6-dichloropyridin-3-yl)-phenylmethanone (Sarkar *et al.*, 2002) in dry toluene (12 ml), was added 1,8-diazabicyclo[5.4.0]undec-7-ene (0.21 ml, 1.45 mmol) at room temperature. The mixture was refluxed for 1.5 h. After cooling to room temperature, water was added to the mixture. The toluene layer was separated and the aqueous layer extracted with ether. The combined organic layers were then washed with water, brine, dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel, and finally recrystallized from an ethyl acetate–petroleum ether (333–353 K) solution to give yellow crystals (m.p. 452–452 K).

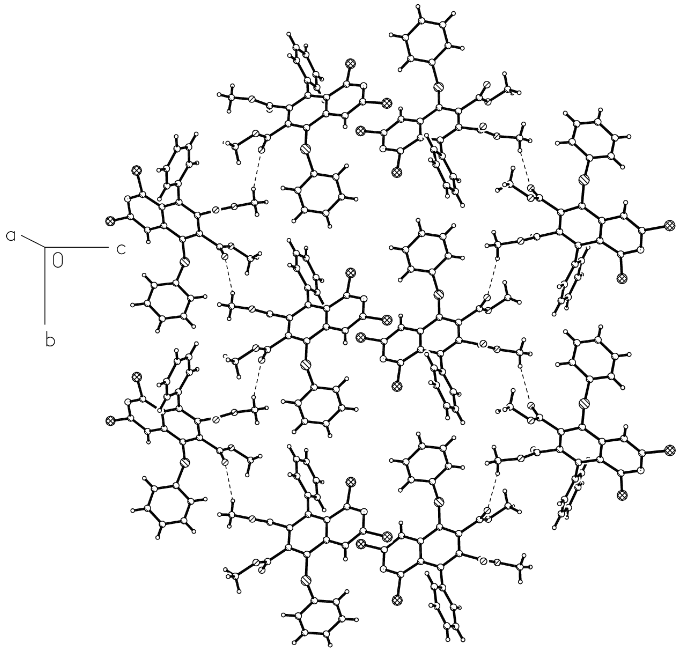

Figure 2
The structure of (IV) viewed down the *a* axis, showing the molecular chains along the *b* axis.

Crystal data

$C_{25}H_{17}Cl_2NO_4S$
$M_r = 498.36$
Orthorhombic, *Pbca*
$a = 10.8487$ (1) Å
$b = 12.6944$ (1) Å
$c = 32.6567$ (3) Å
$V = 4497.4$ (1) Å^3
$Z = 8$
$D_x = 1.472$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6457 reflections
$\theta = 2.6$–28.3°
$\mu = 0.42$ mm^{-1}
$T = 183$ (2) K
Slab, yellow
0.40 × 0.32 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.851$, $T_{\max} = 0.952$
25577 measured reflections
5513 independent reflections
3836 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.093$
$\theta_{\max} = 28.3°$
$h = -14 \rightarrow 13$
$k = -16 \rightarrow 10$
$l = -39 \rightarrow 43$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.138$
$S = 0.97$
5513 reflections
301 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0052 (6)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
$\mathrm{C23{-}H23}B\cdots\mathrm{O1}^{\mathrm{i}}$	0.96	2.52	3.447 (3)	161
$\mathrm{C12{-}H12}\cdots\mathrm{Cg}(A)^{\mathrm{ii}}$	0.93	2.67	3.524 (3)	153

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

After confirming their presence in a difference map, all H atoms were placed at geometrically calculated positions and were refined as riding-model atoms.

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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