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Ethyl β-{2-[4-(dimethylamino)phenyliminomethyl]-1-(phenylsulfonyl)indol-3-yl}acrylate

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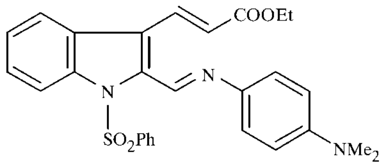
The title compound, $C_{28}H_{27}N_3O_4S$, crystallizes in the centrosymmetric space group $P2_1/n$, with one molecule in the asymmetric unit. In the indole ring, the dihedral angle between the fused rings is 3.6 (1)°. The phenyl ring of the sulfonyl substituent makes a dihedral angle of 79.2 (1)° with the best plane of the indole moiety. The phenyl ring of the dimethylaminophenyl group is orthogonal to the phenyl ring of the phenylsulfonyl group. The dihedral angle formed by the weighted least-squares planes through the pyrrole ring and the phenyl ring of the dimethylaminophenyl group is 7.8 (1)°. The molecular structure is stabilized by C—H···O and C—H···N interactions.

Comment

The indole ring system is present in a number of natural products, many of which are found to possess antibacterial (Okabe & Adachi, 1998), antitumour (Schollmeyer *et al.*, 1995), antidepressant (Papenstasion & Newmeyer, 1972), antimicrobial (El-Sayed *et al.*, 1986; Gadaginamath & Patil, 1999) and anti-inflammatory activities (Rodriguez *et al.*, 1985; Polletto *et al.*, 1974). Indoles also intercalate with DNA (Sivaraman *et al.*, 1996); intercalation between the base pairs in DNA has been implicated for their medicinal properties. The indole ring system occurs in plants (Nigović *et al.*, 2000); for example, indole-3-acetic acid is a naturally occurring plant growth hormone that controls several plant-growth activities (Moore, 1989; Fargasova, 1994). Indoles have also been proven to display high aldose reductase inhibitory activity (Rajeswaran *et al.*, 1999). Sulfonamide-containing drugs act as diuretics and sulthiame as a carbonic anhydrase inhibitor (Crawford & Kennedy, 1959; Camerman & Camerman, 1975; Tanimukai *et al.*, 1965). The sulfonamides inhibit the growth of bacterial organisms and are also useful for treating urinary and gastrointestinal infections. Against this background, and in order to obtain detailed information on its molecular conformation in the solid state, X-ray studies on the title compound, (I), have been carried out.



(I)

The indole system of (I) is not strictly planar, and the dihedral angle formed by the pyrrole and benzo planes is 3.6 (1)°. Atom S1 has a distorted tetrahedral configuration. The widening of the O1—S1—O2 angle to 120.5 (2)°, and the resultant narrowing of the C9—S1—N1 angle to 104.7 (1)°, from the ideal tetrahedral value, are attributed to the Thorpe–Ingold effect (Bassindale, 1984). The O2—S1—N1—C4 and O2—S1—C9—C14 torsion angles describe the conformation of the phenylsulfonyl group with respect to the indole system, which causes the best planes of the indole and phenyl rings to form a dihedral angle of 79.2 (1)°, as observed in similar structures (Yokum & Fronczek, 1997; Sankaranarayanan *et al.*, 2000).

The phenyl ring of the dimethylaminophenyl group is orthogonal to the phenyl ring of the phenylsulfonyl group, forming a dihedral angle of 80.1 (1)°. The dihedral angle formed by the weighted least-squares planes through the pyrrole ring and the phenyl ring of the dimethylaminophenyl group is 7.8 (1)°. Atoms C15 and C20 are out of the indole plane by 0.021 (3) and 0.212 (3) Å, respectively, on one side, while atom S1 is out of the plane by 0.727 (1) Å on the other side.

The relatively large values of the C—N distances in the indole moiety, namely N1—C4 and N1—C1, are due to the

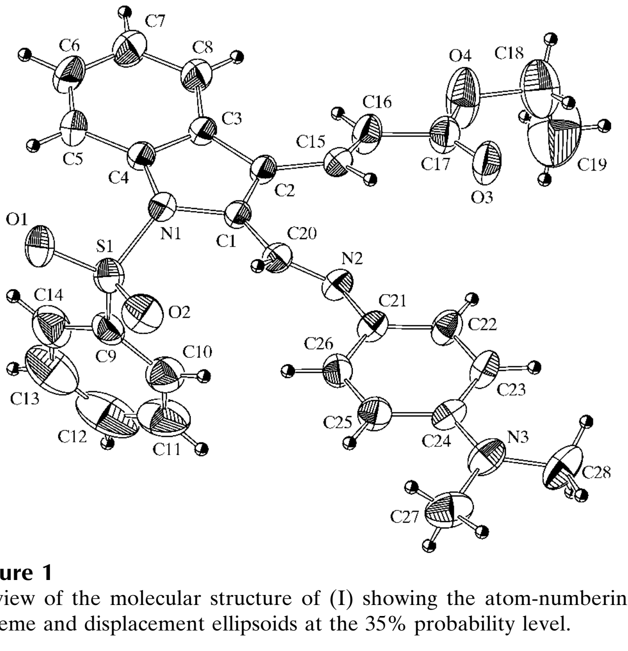


Figure 1
A view of the molecular structure of (I) showing the atom-numbering scheme and displacement ellipsoids at the 35% probability level.

electron-withdrawing character of the phenylsulfonyl group (Govindasamy *et al.*, 1997, 1998). The C15—C2—C3 angle is wider than C15—C2—C1. The S1—N1 and S1—C9 bond distances are comparable with the respective literature values of 1.642 (24) and 1.758 (18) Å (Allen *et al.*, 1987). The significant difference in the lengths of the C17—O4 and C18—O4 bonds is attributed to a partial contribution from the O^-—C=O^+—C resonance structure of the O3=C17—O4—C18 group (Merlino, 1971). This feature, commonly observed in the carboxlic ester groups of substituents in various compounds, gives average values of 1.340 and 1.447 Å, respectively, for these bonds (Varghese *et al.*, 1986). The bond angles involving the carbonyl O atom are invariably expanded (Dunitz & Schweizer, 1982). The O4—C17—C16 and O3—C17—C16 exocyclic bond angles are comparable with the corresponding values for the structure of ethyl 2-acetyl-3-[5-(*p*-tolyl)-2-furyl]acrylate [110.2 (1) and 125.6 (1)°; Lokaj *et al.*, 1990].

In the benzene ring of the indole system of (I), the endocyclic angles at C5 and C8 are contracted to 117.5 (3) and 118.8 (3)°, respectively, while those at C6, C7 and C4 are expanded to 121.5 (3), 121.1 (4) and 122.0 (3)°, respectively. This would appear to be a real effect caused by the fusion of the smaller pyrrole ring to the six-membered benzene ring, and the strain is taken up by angular distortion rather than by bond-length distortions (Allen, 1981). A similar effect has also been observed by Varghese *et al.* (1986) and Sankaranarayanan *et al.* (2000).

The orientation of the indole substituent is influenced by a weak C5—H5···O1 interaction, defined by the torsion angles C5—C4—N1—S1 and C4—N1—S1—C9, while the orientation of the phenyl ring bound to the sulfonyl group is governed by a C14—H14···O1 interaction, defined by the torsion angle O1—S1—C9—C14. In addition to van der Waals interactions, the molecular structure of (I) is stabilized by C—H···O and C—H···N interactions (Table 2).

Experimental

To a well stirred suspension of sodium hydride (0.1 g, 4 mmol) in dry tetrahydrofuran (5 ml) under nitrogen at 273 K, a solution of diethyl [1-phenylsulfonyl-3-(β-carbethoxyvinyl)indol-2-yl]methylphosphonate (1.01 g, 2 mmol) in the same solvent (15 ml) was added slowly. After the evolution of hydrogen had ceased, 4-nitroso-*N*,*N*-dimethylaniline (0.30 g, 2 mmol) in the same solvent (10 ml) was added. The mixture was stirred for a further 3 h and then poured over ice. The bright orange–red solid which precipitated was filtered off and dried over calcium chloride. Compound (I) was crystallized from ethyl acetate.

Crystal data

$C_{28}H_{27}N_3O_4S$
M_r = 501.59
Monoclinic, $P2_1/n$
a = 15.0582 (3) Å
b = 11.3915 (3) Å
c = 15.8945 (3) Å
β = 109.595 (1)°
V = 2568.6 (1) Å^3
Z = 4
D_x = 1.297 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7574 reflections
θ = 1.6–28.4°
μ = 0.17 mm^{-1}
T = 293 (2) K
Block, orange–red
0.32 × 0.23 × 0.18 mm

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.413 (2)	N1—C1	1.420 (4)
S1—O2	1.415 (2)	N3—C24	1.374 (4)
S1—N1	1.676 (3)	O3—C17	1.185 (4)
S1—C9	1.740 (4)	O4—C17	1.335 (4)
N1—C4	1.417 (4)	O4—C18	1.475 (5)
O1—S1—N1	106.1 (1)	C6—C5—C4	117.5 (3)
O2—S1—C9	108.7 (2)	C5—C6—C7	121.5 (3)
C17—O4—C18	117.9 (3)	C8—C7—C6	121.1 (4)
C2—C1—N1	109.4 (2)	C7—C8—C3	118.8 (3)
C1—C2—C15	124.0 (3)	O3—C17—O4	123.0 (3)
C15—C2—C3	128.2 (3)	O3—C17—C16	125.9 (3)
C5—C4—C3	122.0 (3)	O4—C17—C16	111.1 (3)
O2—S1—N1—C4	−176.2 (2)	O1—S1—C9—C14	11.8 (3)
C9—S1—N1—C4	68.5 (3)	O2—S1—C9—C14	144.6 (3)
S1—N1—C4—C5	35.9 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1	0.93	2.33	2.925 (4)	121
C18—H18*B*···O3	0.97	2.30	2.692 (5)	103
C20—H20···O2	0.93	2.34	2.791 (3)	109
C15—H15···N2	0.93	2.45	3.024 (3)	119

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
17 978 measured reflections
6295 independent reflections
2749 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.094
$\theta_{\rm max}$ = 28.4°
$h = -16 \rightarrow 20$
$k = -14 \rightarrow 15$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.187$
S = 0.91
6295 reflections
329 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0829P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.41 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.37 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0034 (8)

Due to the poor quality of the crystal, the higher-angle reflections were very weak and only 44% of the reflections were found to be observed with $I > 2\sigma(I)$. This resulted in a high value for $R_{\rm int}$. All H atoms were fixed geometrically and allowed to ride on their parent atoms, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = $1.5_{\rm eq}$(C) for methyl H atoms and $1.2U_{\rm eq}$(C) for other H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1558). Services for accessing these data are described at the back of the journal.

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