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4′-(4-Chlorophenyl)-3″-ethyl-1′-methyl-1*H*-indole-3-spiro-2′-pyrrolidine-3′-spiro-5″-[1,3]thiazole-2(3*H*),2″(3″*H*),4″(5″*H*)-trione benzene sesquisolvate

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The title compound, $C_{22}H_{20}ClN_3O_3S\cdot1.5C_6H_6$, was synthesized by the intermolecular [3 + 2]-cycloaddition of azomethine ylide, derived from isatin and sarcosine by a decarboxylative route, and 5-(4-chlorobenzylidene)-3-ethylthiazolidine-2,4-dione. In the molecule of the title compound, an approximately planar 2-oxindole system, a pyrrolidine ring in an envelope conformation, and a planar thiazolidine ring are joined *via* two spiro-junctions. The molecules in the crystal are linked by an intermolecular N—H···N hydrogen bond [N···N = 3.071 (3) Å], forming infinite chains running along the *c* axis. One of the solvate benzene molecules occupies a special position on an inversion centre.

Comment

Spiro-compounds represent an important class of naturally occurring substances, which in many cases exhibit interesting biological properties (Kobayashi *et al.*, 1991; James *et al.*, 1991). 1,3-Dipolar cycloaddition reactions are widely used for the construction of spiro-compounds (Caramella & Grunanger, 1984). In this paper, the structure of the title compound, (I), is reported. The compound was synthesized by the intermolecular [3 + 2]-cycloaddition of azomethine ylide, derived from isatin and sarcosine by a decarboxylative route, and 5-(4-chlorobenzylidene)-3-ethylthiazolidine-2,4-dione.

(I)
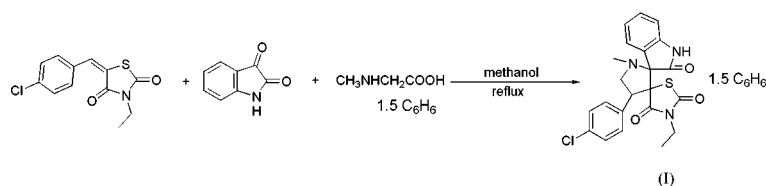
The molecular structure of (I) is shown in Fig. 1. The molecule involves 2-oxindole, pyrrolidine, and thiazolidine moieties, joined *via* two spiro-junctions. The pyrrolidine ring N2—C5—C4—C3—C6 has an envelope conformation; atom N2 is displaced by 0.618 (3) Å from the mean plane of the C5/C4/C3/C6 atoms [plane *A*; maximum deviation of atom C4 is 0.031 (3) Å]. The C5/N2/C6 plane forms a dihedral angle of 135.6 (2)° with plane *A*, whereas the dihedral angle of the latter with the mean plane of the benzene ring (C10–C15) is 76.7 (3)°. Both the bicyclic indole system and the thiazolidine ring are almost planar [maximum deviations of atoms C17 and C2 from their respective mean planes are 0.035 (3) and 0.041 (4) Å]; their planes are approximately orthogonal to plane *A*; the dihedral angles are equal to 78.3 (2) and 88.7 (3)°, respectively. Atoms O1 and O2 are displaced from the mean
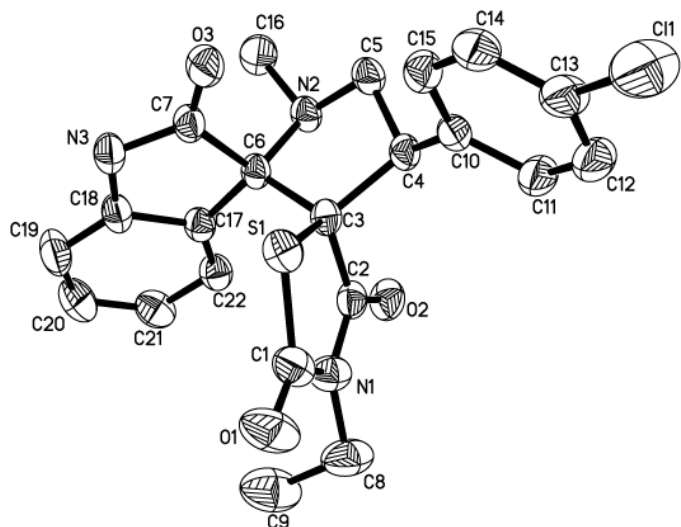
Figure 1
The molecular structure of (I); displacement ellipsoids are drawn at the 30% probability level, H atoms have been omitted and solvate benzene molecules are not shown.

plane of the thiazolidine cycle by 0.027 (2) and −0.155 (2) Å, respectively.

There is one 'active' H atom in the molecule which participates in the intermolecular N3—H3···N2^i hydrogen bond [symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$] (Table 1). This hydrogen bond links the molecules of (I) in to infinite chains running along the c axis (Fig. 2).
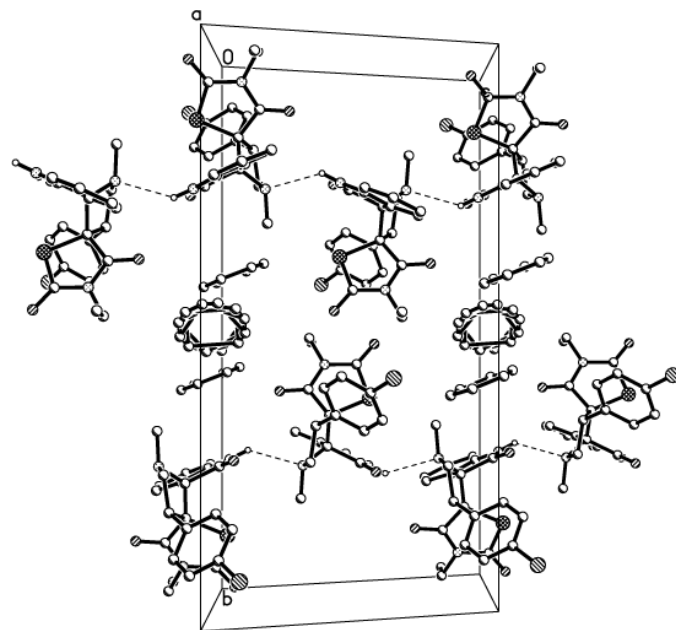
Experimental

A mixture of 5-(4-chlorobenzylidene)-3-ethylthiazolidine-2,4-dione (2 mmol), prepared according to Lo *et al.* (1958), isatin (2 mmol), and sarcosine (2 mmol) was refluxed in dioxane (30 ml) until the disappearance of the starting material (as monitored by thin-layer chromatography). When the reaction was complete, the solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, petroleum ether/ethyl acetate 5:1) to give the title compound, (I). M.p. 476 K; IR (KBr): 3358.3 (–NH), 1750.2, 1718.7, 1685.9 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, p.p.m.): 0.87 (*t*, 3H, CH$_3$), 2.26 (*s*, 3H, N—CH3), 3.40–3.50 (*m*, 2H, —CH2), 3.61 (*dd*, *J* = 9.3, 7.8 Hz, 1H, Hc), 4.03 (*dd*, *J* = 10.2, 9.3 Hz, 1H), 4.58 (*dd*, *J* = 10.2, 7.8 Hz, 1H), 6.82–7.38 (*m*, 8H, Ar—H), 7.41 (*br*, 1H, —NH); ^{13}C NMR (p.p.m.): 12.68, 35.18, 36.95, 51.33, 58.29, 72.12, 79.90, 110.31, 123.13, 123.22, 127.01, 128.81, 130.61, 131.46,133.69,136.16, 142.39, 169.38, 175.42, 177.50. 20 mg of (I) were dissolved in 15 ml of benzene and the solution was kept at room temperature for 15 d. Slow evaporation of the solvent afforded colorless single crystals of (I) suitable for X-ray analysis.

Crystal data

C$_{22}$H$_{20}$ClN$_3$O$_3$S·1.5C$_6$H$_6$	$D_x = 1.266$ Mg m^{-3}
$M_r = 559.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 886
$a = 11.132$ (3) Å	reflections
$b = 22.785$ (7) Å	$\theta = 2.7$–23.1°
$c = 12.515$ (4) Å	$\mu = 0.24$ mm^{-1}
$\beta = 112.477$ (5)°	$T = 293$ (2) K
$V = 2933.2$ (15) Å^3	Parallelepiped, colorless
$Z = 4$	0.42 × 0.40 × 0.34 mm

Figure 2
The crystal packing diagram for (I), viewed along the a axis. All H atoms, with the exception of atom H3, participating in the hydrogen bond, have been omitted. Hydrogen bonds are shown as dashed lines.

Data collection

Bruker SMART CCD area detector diffractometer	5070 independent reflections
	2701 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.046$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$\theta_{max} = 25.0°$
	$h = -12 \rightarrow 13$
$T_{min} = 0.796$, $T_{max} = 0.923$	$k = -27 \rightarrow 15$
14461 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.057$	$w = 1/[\sigma^2(F_o^2) + (0.084P)^2]$
$wR(F^2) = 0.155$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
5070 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
370 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···N2^i	0.86	2.39	3.071 (3)	136

Symmetry code: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were placed in calculated positions, with C—H distances ranging from 0.93 to 0.98 Å and an N—H distance of 0.86 Å. They were included in the refinement in the riding-model approximation, with $U_{iso} = 1.2$ (1.5 for methyl) times U_{eq} of the carrier atom. Both solvate benzene molecules refined poorly. In the final model, the benzene molecule in the general position was included with the fixed geometry of a regular hexagon (C—C = 1.39 Å). The solvate benzene molecule located about an inversion centre was represented as two-component disorder with approximately equal occupancy factors, which refined to 0.49 (3) and 0.51 (3). The bond lengths in both components of the disordered benzene were constrained to 1.39 (1) Å.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve

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structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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