Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

10″-(4-Chlorobenzylidene)-5″-(4-chlorophenyl)-4′-(2,4-dichlorophenyl)-1′-methyl-2,3,2″,3″,7″,8″,9″,10″-octahydro-1*H*,5″*H*,6″*H*-indole-3-spiro-2′-pyrrolidine-3′-spiro-2″-cycloheptено[1,2-*d*]thiazolo[3,2-*a*]pyrimidine-2,3″-dione

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Received 23 March 2005
Accepted 14 April 2005
Online 23 April 2005

Key indicators

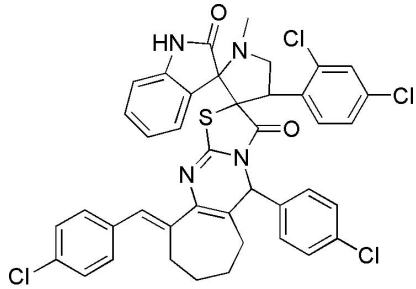
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.049
wR factor = 0.168
Data-to-parameter ratio = 13.6

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

The title compound, $C_{41}H_{32}Cl_4N_4O_2S$, was synthesized by the intermolecular [3 + 2] cycloaddition of azomethine ylide, derived from isatin and sarcosine by a decarboxylative route, and 5-(4-chloro)phenyl-10-(4-chloro)benzylidene-2-(2,4-dichloro)benzylidene-2,3,6,7,8,9-hexahydro-5*H*,10*H*-cycloheptено[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-one. In the molecule, the two spiro junctions link a planar 2-oxindole ring, a pyrrolidine ring in an envelope conformation and a 10-(arylmethylene)hexahydrocycloheptено[1,2-*d*]thiazolo-[3,2-*a*]pyrimidin-3-one ring. The packing of the molecules in the crystal structure is mainly due to N—H···O hydrogen bonds.

Comment

The intermolecular 1,3-dipolar cycloaddition reaction of azomethine ylides with olefins represents an efficient method for the construction of the pyrrolidine structural unit, whose importance in medicinal and synthetic organic chemistry is well known (Tsuge *et al.*, 1987; Garner *et al.*, 1994). The most developed approach for the synthesis of these compounds depends mainly on a cycloaddition reaction to exocyclic double bonds, which provides the spiropyrrolidine framework widely occurring in natural substances characterized by highly pronounced biological properties (Raj *et al.*, 2003; Mishriky *et al.*, 1997). 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-chloro)phenyl-10-(4-chloro)benzylidene-2-(2,4-dichloro)-benzylidene-2,3,6,7,8,9-hexahydro-5*H*,10*H*-cycloheptено[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-one (Ali *et al.*, 1979).



(I)

Fig. 1 shows the molecular structure of (I). There are two spiro junctions in the molecule, which consists of a 2-oxindole

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ring, a pyrrolidine ring and a 10-(arylmethylene)hexahydrocyclohepteno[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-one ring system. The pyrrolidine ring (N3/C4/C1/C2/C3) is not planar, with an envelope conformation. Atoms C4, C1, C2 and C3 are almost coplanar, the mean deviation from this plane being 0.001 (3) Å. Atom N3 lies 0.589 (3) Å above the C4/C1/C2/C3 plane in the pyrrolidine ring, forming the flap of the envelope. The dihedral angle between the C4/N3/C3 plane and the C4/C1/C2/C3 mean plane is 42.6 (2)°. Compared with previously reported structures, which contain the analogous spiropyrrolidine framework, (I) shows a greater degree of coplanarity (Li *et al.*, 2003). The 2,4-dichlorophenyl group is rotated by 109.8 (2)° with respect to the C4/C1/C2/C3 plane, as a result of steric hindrance. The 2-oxoindole ring (C4/C5/N4/C6/C11/C10/C9/C8/C7) is nearly planar and the mean deviation from this plane is 0.016 (3) Å. This 2-oxoindole plane makes a dihedral angle of 78.7 (2)° with the C4/C1/C2/C3 plane. As part of the 10-(arylmethylene)hexahydrocyclohepteno[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-one ring, the five-membered thiazolidine ring (S1/C20/N2/C19/C1) has an envelope conformation. The C1/C19/N2/C20 group is nearly planar and the mean deviation from this plane is 0.022 (3) Å. Atom S1 is displaced from the C1/C19/N2/C20 plane by 0.096 (3) Å. The dihedral angle between the C1/S1/C20 plane and the C1/C19/N2/C20 mean plane is 4.5 (2)°. The C1/C19/N2/C20 mean plane makes a dihedral angle of 86.9 (2)° with the adjacent C4/C1/C2/C3 plane. Atoms N2/C20/N1/C21/C22 of the six-membered dihydropyrimidine ring are almost coplanar, as a result of electron delocalization. The mean deviation from this plane is 0.011 (3) Å. Atom C23 lies 0.295 (3) Å above the N2/C20/N1/C21/C22 plane, and the dihedral angle between the N2/C23/C22 plane and the N2/C20/N1/C21/C22 plane is 19.8 (2)°. The N2/C20/N1/C21/C22 plane makes dihedral angles of 6.0 (2) and 82.7 (2)°, respectively, with the C1/C19/N2/C20 plane and the 4-chlorophenyl group (C24–C29). The seven-membered cycloheptene ring displays a boat conformation.

Fig. 2 shows the crystal packing of (I). The packing is characterized by a layer parallel to the *ab* plane. In space group $I\overline{4}$, with $Z = 8$, four molecules are connected by intermolecular N—H···O hydrogen bonds around the center of the unit cell and present a saddle-like cavity through the *ab* plane. The atoms of the 4-chlorophenyl group and a part of the 4-chlorobenzylidene group (C32–C37/Cl4 and the relevant H atoms) are disordered over two sites, and the atoms (C30/C38–C40 and the relevant H atoms) of the cycloheptene are disordered over three sites.

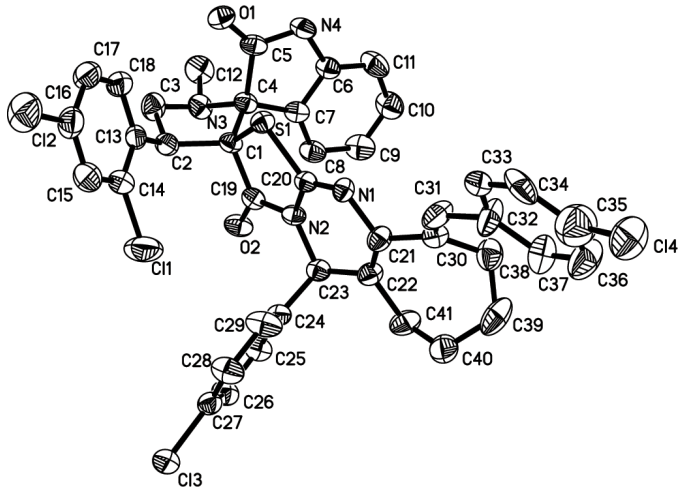

Figure 1
The molecular structure of (I), with the atom numbering, showing 30% probability displacement ellipsoids for the non-H atoms. H atoms have been omitted for clarity. Only the major disorder components are shown.

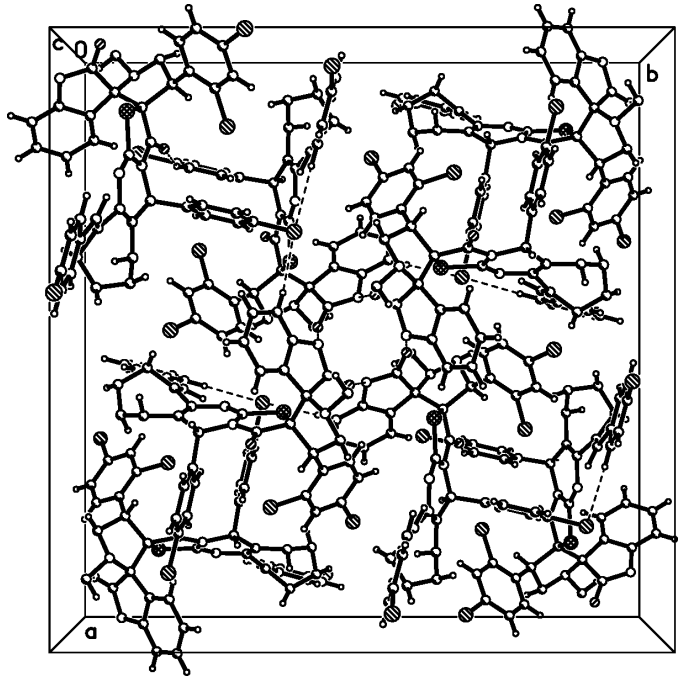

Figure 2
The crystal packing of (I), viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

Experimental

A mixture of 5-(4-chlorophenyl)-10-(4-chloro)benzylidene-2-(2,4-dichloro)benzylidene-2,3,6,7,8,9-hexahydro-5*H*,10*H*-cyclohepteno[1,2-*d*]thiazolo[3,2-*a*]pyrimidin-3-one (1 mmol), isatin (1.2 mmol) and sarcosine (1.2 mmol) were refluxed in acetonitrile (80 ml) until the disappearance of the starting materials, as evidenced by thin layer chromatography. After the reaction was over, 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. M.p. 487 K. IR (KBr, cm^{-1}): 3316.4 (–NH), 1723.4, 1707.2 (C═O), 1373.1 ($-CH_3$); ^{1}H NMR (p.p.m.): δ 1.55–2.56 (*m*, 8H, cycloheptyl), 2.21 (*s*, 3H, N—CH_3), 3.49 (*dd*, $J = 7.5$ and 8.7 Hz, 1H, –CH), 4.08 (*dd*, $J = 8.7$ and 9.9 Hz, 1H, –CH), 4.67 (*dd*, $J = 7.5$ and 9.9 Hz, 1H, –CH), 5.18 (*s*, 1H, –CH), 6.55–7.82 (*m*, 16H, ArH and –CH), 8.68 (*bs*, 1H, –NH). Compound (I) (20 mg) was dissolved in acetone (15 ml); the solution was kept at room temperature for 6 d, allowing natural evaporation to give colorless single crystals of (I), suitable for X-ray analysis.

Crystal data

$C_{41}H_{32}Cl_4N_4O_2S$
M_r = 786.6
Tetragonal, $I\overline{4}$
a = 25.035 (2) Å
c = 11.929 (2) Å
V = 7476.6 (16) Å^3
Z = 8
D_x = 1.396 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2525 reflections
θ = 2.5–20.9°
μ = 0.42 mm^{-1}
T = 293 (2) K
Block, colorless
0.40 × 0.36 × 0.24 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
T_{min} = 0.826, T_{max} = 0.905
21 971 measured reflections
7655 independent reflections
4391 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 26.4°
$h = -29 \rightarrow 31$
$k = -31 \rightarrow 29$
$l = -14 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.168
S = 1.00
7655 reflections
562 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2 + 0.1414P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 3609 Friedel pairs
Flack parameter: −0.10 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O1^{i}	0.86	2.43	2.952 (6)	120
N4—H4···O1^{ii}	0.86	2.54	3.282 (5)	145

Symmetry codes: (i) $y+1, -x+1, -z+2$; (ii) $-x+2, -y, z$.

H atoms were positioned geometrically and refined in the riding-model approximation [C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C)]. The disordered benzene ring was constrained to have the geometry of a regular hexagon. The other disordered atoms were restrained with C—Cl bond lengths of 1.75 (1) Å, C—C bond lengths of 1.52 (1) Å and C═C bond lengths of 1.34 (1) Å. The atoms of the 4-chlorophenyl group, a moiety of the 4-chlorobenzylidene group (C32–C37 and Cl4, and the relevant H atoms) are disordered over two sites, the ratio of the occupancies being 0.5:0.5. Also, atoms (C30 and C38–C40, and the relevant H atoms) of the cycloheptene ring are disordered over three sites, the ratio of occupancies being 0.5:0.3:0.2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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