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N-(2-Chlorophenyl)-2-{(1*E*)-[4-(dimethylamino)-phenyl]methyleneamino}-4,7-dihydro-1-benzothiophene-3-carboxamide

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.069
wR factor = 0.158
Data-to-parameter ratio = 14.9

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

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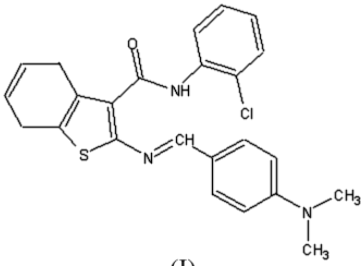
In the title compound, $C_{24}H_{22}ClN_3OS$, variations in C—N bond lengths and angles around the N atoms indicate delocalization of the N-atom lone pair. The benzothiophene moiety is essentially planar. The dimethylaminophenyl and *o*-chlorobenzene rings form dihedral angles of 41.9 (1) and 26.2 (2)°, respectively, with the benzothiophene plane. The molecular structure is stabilized by N—H···Cl, N—H···N, C—H···N, C—H···S and C—H···O hydrogen bonds. Molecules pack as layers parallel to (101).

Comment

The title compound, (I), is one of a series of Schiff bases of 2-amino-3-(*N*-chlorophenylcarboxamido)-4,5,6,7-tetrahydrobenzothiophenes (Mohan & Saravanan, 2003) and was found to exhibit antibacterial and antifungal activities. Various derivatives of thiophenes (El-Maghraby *et al.*, 1984; Dzhurayev *et al.*, 1992; Gewald *et al.*, 1966) and Schiff bases (Csaszar & Morvay, 1983; Lakshmi *et al.*, 1985; Cohen *et al.*, 1977) are known to possess different biological activities, such as antitubercular, bacteriostatic and antifungal activities. Sulfur-containing Schiff bases are the most effective. Solid-state conformational studies of a few of these have shown that they contain N—H···N and N—H···O hydrogen bonds (Vasu *et al.*, 2003). The crystal structures of halogen-containing organic compounds are stabilized by weak interactions involving halogen atoms (Desiraju & Steiner, 1999). In view of the above, the crystal structure determination of (I) was undertaken.



(I)

The bond angles around C2 and C3 deviate significantly from 120°. The widening of the N1—C2—C3 [126.9 (3)°] and C2—C3—C10 [125.3 (3)°] bond angles reduces electronic repulsions. The C—C—C bond angles at atoms C11, C17 and C20 [117.4 (3), 116.5 (3) and 117.1 (3)°] of the benzene rings are narrower than the normal 120°. The bond angles C2—N1═C1 [121.7 (3)°] and C10—N2—C11 [126.4 (3)°] around the azomethane N and amide N atoms are different, indicating the delocalization of the N-atom lone pair, and this assump-

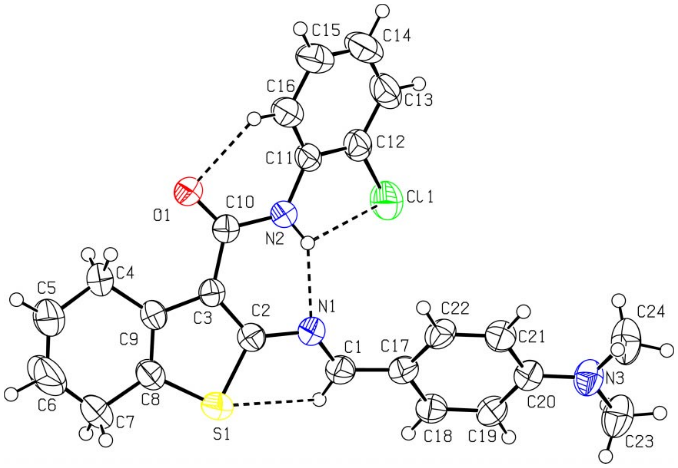


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as dashed lines.

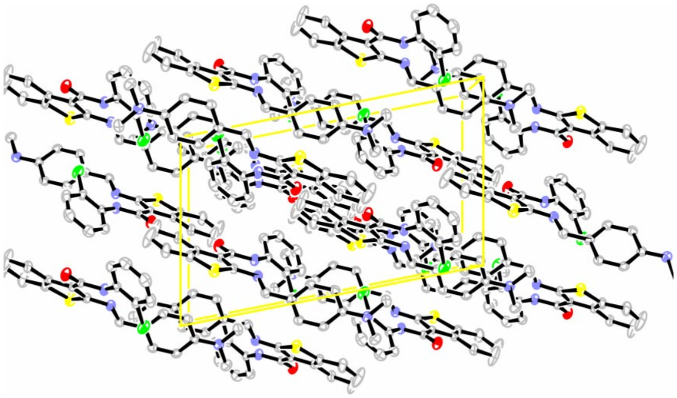


Figure 2
Packing of (I), viewed along the *b* axis. For clarity H atoms have been omitted.

tion is further supported by the variation in C—N bond distances [N2—C10 = 1.369 (4) Å and N2—C11 = 1.401 (4) Å]. The N3—C20 [1.360 (4) Å] distance also indicates the delocalization.

The benzothiophene moiety is almost planar; the dihedral angle between the benzene and thiophene rings is 3.6 (2)°. The dimethylaminophenyl ring (C17–C22) and *o*-chlorobenzene ring (C11–C16) make dihedral angles of 41.9 (1) and 26.2 (2)°, respectively, with the benzothiophene moiety. The C2—N1—C1—C17 and C3—C10—N2—C11 torsion angles of −171.8 (3) and −177.6 (3)° indicate that both the *o*-chlorobenzene and the dimethylaminophenyl moiety are *trans* oriented with respect to the benzothiophene ring. The molecular structure is stabilized by intramolecular N2—H2···Cl1, N2—H2···N1, C1—H1···S1 and C16—H16···O1 hydrogen bonds (Fig. 1 and Table 1). The N—H···N and C—H···O hydrogen bonds form six-membered rings, whereas the other hydrogen bonds form five-membered rings. Only a very weak C—H···Cl [H13($2 - x$, $1 - y$, $1 - z$)···Cl1 = 2.96 Å] interaction can be seen between the molecules, and Cl···Cl interactions are absent. In the crystal structure, the molecules are packed in layers parallel to (101) (Fig. 2).

Experimental

The title compound was synthesized using the Gewald reaction by refluxing *o*-chlorophenyl cyanoacetamide (0.04 mol) with cyclohexanone (0.98 g, 0.01 mol) in the presence of ammonium acetate (1 g) and glacial acetic acid (2 ml) in benzene. This was then treated with sulfur (1.28 g 0.04 mol), diethylamine (4 ml) and ethanol at 325 K. The product was reacted with *p*-(dimethylamino)benzaldehyde in an equimolar ratio in the presence of 2-propanol and a catalytic amount of glacial acetic acid by a microwave irradiation method, which yielded (I) (50%). This was then purified and crystallized from *N*,*N*-dimethylformamide and ethanol (1:2) solution by slow evaporation.

Crystal data

$C_{24}H_{22}ClN_3OS$
$M_r = 435.97$
Monoclinic, $P2_1/c$
$a = 9.9850$ (8) Å
$b = 13.6440$ (11) Å
$c = 16.3425$ (14) Å
$\beta = 101.292$ (1)°
$V = 2183.3$ (3) Å^3
$Z = 4$
$D_x = 1.326$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 541 reflections
$\theta = 2.0$–27.2°
$\mu = 0.29$ mm^{-1}
$T = 296$ (2) K
Block, red
0.23 × 0.18 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.939$, $T_{\max} = 0.966$
16 005 measured reflections
4061 independent reflections
3506 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25.5°$
$h = -10 \rightarrow 12$
$k = -14 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.158$
$S = 1.24$
4061 reflections
273 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 1.4409P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

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

	D—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.86	2.58	2.939 (3)	106
N2—H2···N1	0.86	2.01	2.743 (4)	143
C1—H1···S1	0.93	2.70	3.066 (3)	104
C16—H16···O1	0.93	2.41	2.893 (4)	113

H atoms were placed in idealized positions [C—H = 0.93–0.97 Å and N—H = 0.86 Å] and constrained to ride on their parent atoms [$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom) or 1.5$U_{\rm eq}$($C_{\rm methyl}$)]. A rotating group model was used for the methyl groups.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

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ORTEP-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PARST* (Nardelli, 1995), *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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