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N-(2-Chlorophenyl)-2-{[(1*E*)-(4-methoxyphenyl)-methylene]amino}-4,5,6,7-tetrahydro-1-benzothiophene-3-carboxamide

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In the title compound, $C_{24}H_{24}ClN_2O_2S$, the variations in the bond lengths and angles around the N atoms indicate delocalization of the N-atom lone pair. The molecular structure is stabilized by intramolecular N—H···N, N—H···Cl, C—H···S and C—H···O hydrogen bonds.

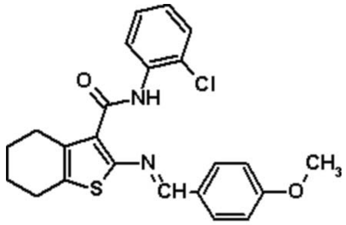
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.007 Å
R factor = 0.066
wR factor = 0.152
Data-to-parameter ratio = 14.7

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

Comment

The title compound, $C_{24}H_{24}ClN_2O_2S$, (I) belongs to a series of Schiff bases of 2-amino-3-(*N*-chlorophenyl carboxamido)-4,5,6,7-tetrahydrobenzothiophenes (Mohan & Saravanan, 2003). The majority of Schiff bases (Csaszar & Morvay, 1983; Lakshmi *et al.*, 1985; Cohen *et al.*, 1977) and their thiophene derivatives (El-Maghraby *et al.*, 1984; Dzhurayev *et al.*, 1992; Gewald *et al.*, 1966) possess antibacterial, antitubercular and antifungal activities; sulfur-containing Schiff bases are particularly effective.



(I)

The molecular structure of (I) is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. The thiophene ring is planar and exhibits normal bond lengths and angles. The six-membered cyclohexane ring adopts a half-chair conformation, with puckering parameters (Cremer &

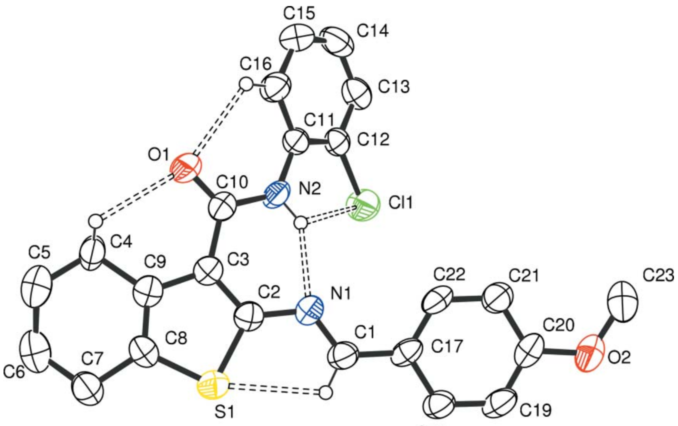


Figure 1
A drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

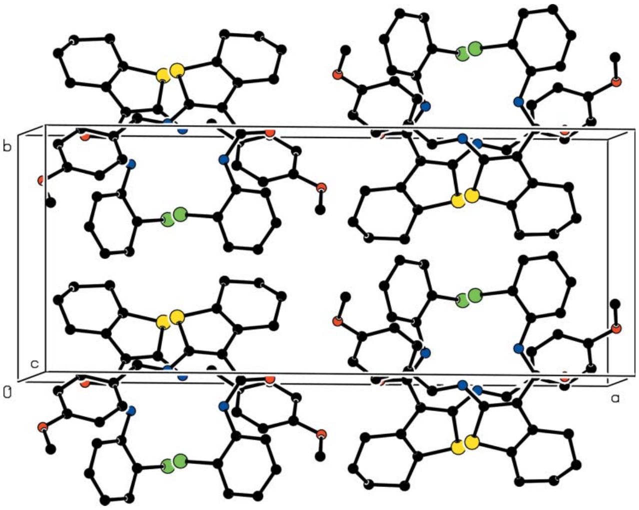


Figure 2
A packing diagram for (I). H atoms have been omitted.

Pople, 1975; Spek, 1990) of q_2 = 0.277 (3) Å, φ_2 = −95.4 (2)° and θ_2 = 52.3 (1)°.

In the thiophene ring, the C8—C9 bond length [1.353 (1) Å] is the shortest, indicating the absence of delocalization of the double bonds. This is also reflected in the C2—S1 [1.744 (4) Å] and C8—S1 [1.728 (5) Å] bonds, which are longer than normal C—S bonds (Abrahams & Lipscomb, 1952). The C1—N1 [1.287 (2) Å] bond is shorter than C11—N2 [1.410 (1) Å], which indicates greater delocalization of π-bonding across the ring systems.

The bond angles around atoms C2 and C3 show significant deviation from 120°, and the widening of the bond angles N1—C2—C3 [126.1 (8)°] and C2—C3—C10 [126.2 (2)°] reduces electronic repulsion. The C10—N2—C11 bond angle [127.3 (2)°] deviates significantly from the ideal value (120°), indicating delocalization of the N-atom lone pair, which is further supported by the variation in the C—N bond lengths in the imine and carboxamide moieties. The C18—C17—C22 [118.2 (4)°] and C19—C20—C21 [119.8 (4)°] bond angles deviate significantly from the ideal value for a phenyl ring (120°), probably due to the electron-donating resonance effect of the methoxy group at C20 (Vasu *et al.*, 2004).

The variations in the bond lengths and angles of the *o*-chlorophenyl ring are due to the halogen atom attached at C12. The *p*-methoxyphenyl moiety (C17–C22/O2/C23) and the *o*-chlorophenyl ring (C11–C16/Cl1) make dihedral angles of 9.8 (3) and 40.4 (7)°, respectively, with the thiophene ring. The torsion angles C3—C10—N2—C11 [168.4 (5)°] and C2—N1—C1—C17 [−175.6 (4)°] show the *anti* conformation of the two moieties about the C10—N2 and N1—C1 bonds.

The molecular structure of (I) is stabilized by intramolecular N—H···N, N—H···Cl, C—H···S and C—H···O hydrogen bonds (Table 2). The N—H···N and C—H···O hydrogen bonds form psuedo-six-membered rings and the C—H···S bond forms a pseudo-five-membered ring, thus locking the molecular conformation and eliminating conformational flexibility. The molecules are packed in layers along the *b* axis (Fig. 2).

Experimental

The title compound, (I), was synthesized using the Gewald reaction (Gewald *et al.*, 1966). *o*-Chlorophenyl 2-cyanoacetamide (0.04 mol) was refluxed with cyclohexanone (0.98 g, 0.01 mol) in the presence of ammonium acetate (1.00 g) and glacial acetic acid (2 ml) in benzene, and was then treated with sulfur (1.28 g, 0.04 mol), dimethylamine (4 ml) and ethanol at 323 K. The product was treated with 4-methoxybenzaldehyde in an equimolar ratio, in the presence of propan-2-ol and a catalytic amount of glacial acetic acid, using microwave irradiation, yielding (I). Compound (I) was crystallized from *N*,*N*-dimethylformamide and ethanol (1:2) by slow evaporation.

Crystal data

$C_{23}H_{21}ClN_2O_2S$
M_r = 424.93
Orthorhombic, $Pca2_1$
a = 24.727 (3) Å
b = 10.2755 (13) Å
c = 8.2037 (11) Å
V = 2084.4 (5) Å^3
Z = 4
D_x = 1.354 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 470 reflections
θ = 2.0–27.8°
μ = 0.31 mm^{-1}
T = 291 (2) K
Block, red
0.31 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.912, T_{max} = 0.940
16016 measured reflections

3866 independent reflections
3126 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.5°
h = −29 → 29
k = −12 → 12
l = −9 → 9

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.152
S = 1.11
3866 reflections
263 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.7356P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), with 2009 Friedel pairs
Flack parameter: 0.08 (14)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.280 (5)	S1—C2	1.744 (4)
N2—C11	1.406 (5)	C8—C9	1.353 (6)
S1—C8	1.728 (5)		
C10—N2—C11	127.0 (3)	C22—C17—C18	118.2 (4)
C3—C2—N1	126.0 (4)	C19—C20—C21	119.8 (4)
C2—C3—C10	125.8 (4)		
C2—N1—C1—C17	−175.6 (4)	C11—N2—C10—C3	168.5 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···Cl1	0.86	2.58	2.945 (4)	107
N2—H2···N1	0.86	2.08	2.797 (5)	140
C1—H1···S1	0.93	2.56	3.019 (5)	111
C4—H4*A*···O1	0.97	2.44	2.838 (7)	104
C16—H16···O1	0.93	2.34	2.863 (6)	115

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H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93 (CH), 0.97 (CH_2) and 0.96 Å (CH_3), and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2 (1.5 for methyl) times U_{eq}(C/N). A rotating-group model was used for the methyl group. Atoms C5 and C6 of the cyclohexane ring have large vibrational degrees of freedom and this is reflected in the large atomic displacement parameters, resulting in a short C5—C6 bond length, which was restrained to 1.538 (9) Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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