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

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.005 Å
R factor = 0.070
wR factor = 0.182
Data-to-parameter ratio = 13.9

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

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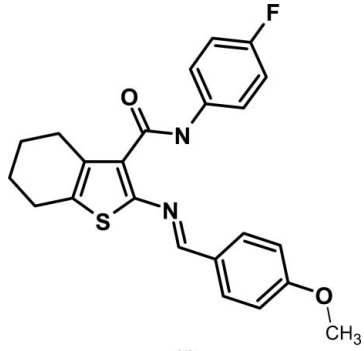
In the molecule of the title compound, $C_{24}H_{21}FN_2O_2S$, the fused six-membered ring has a half-chair conformation, with a pseudo-twofold axis passing through the mid-points of the bridgehead C—C bond and the opposite C—C bond. The dihedral angles between the planar thiophene (*B*), fluorophenyl (*C*) and methoxyphenyl (*D*) rings are *B*/*C* = 13.65 (3)°, *B*/*D* = 9.72 (2)° and *C*/*D* = 23.34 (3)°. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules into centrosymmetric dimers; these may be effective in the stabilization of the structure.

Comment

The title compound, (I), belongs to a series of Schiff bases of 3-aryl carboxamides and was found to exhibit antibacterial and antifungal activities (Mohan & Saravanan, 2003; Dzhurayev *et al.*, 1992). Solid-state conformational studies of a few of these have shown that they contain N—H···N and N—H···O hydrogen bonds (Anilkumar *et al.*, 2005). Crystal structures containing F atoms possess biological and pharmocological significance and the study of interactions involving fluorine has been a major aspect in crystal engineering (Choudhury *et al.*, 2002), as it has been demonstrated that in small organofluorine molecules the F atom plays a major role in intermolecular interactions (Choudhury *et al.*, 2004). In view of the above, the crystal structure of (I) has been determined.



(I)

In the molecule of (I) (Fig. 1), the bond lengths and angles (Table 1) are generally within normal ranges (Allen *et al.*, 1987). The ring *A* (C4–C9) has a total puckering amplitude, Q_T of 0.396 (2) Å and a half-chair conformation [q_2= 0.3051 (1) Å, φ = −88.69 (2)° and θ = 129.64 (4)°; Cremer & Pople, 1975]. Ring *A* has a pseudo-twofold axis passing through the mid-points of the C5–C6 and C8–C9 bonds, as can be deduced from the torsion angles (Table 1). Rings *B* (S1/C2/C3/C8/C9), *C* (C11–C16) and *D* (C17–C22) are, of course, planar and the dihedral angles between them are *B*/*C* =

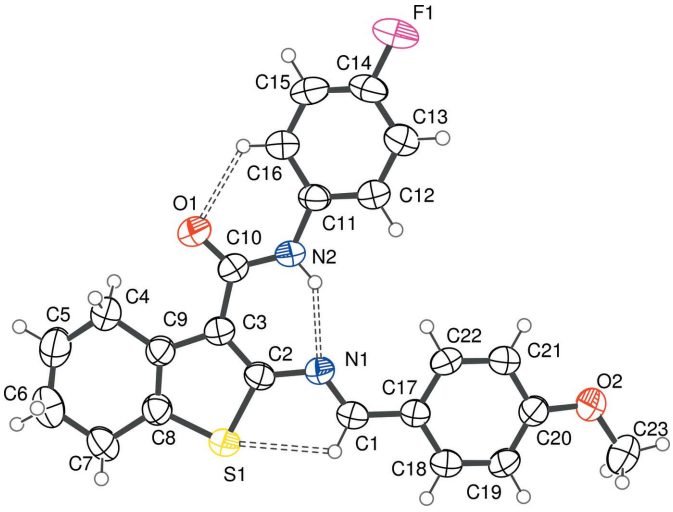


Figure 1
The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as double dashed lines.

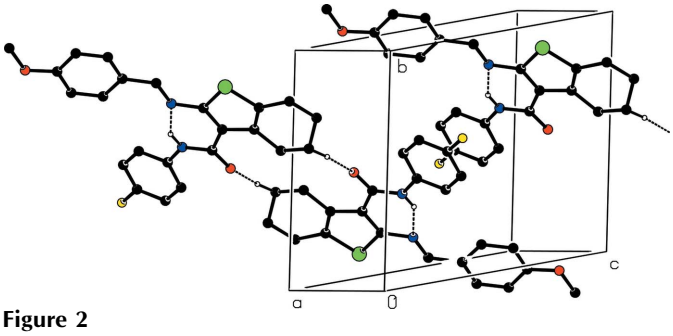


Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines and H atoms not involved in these interactions have been omitted.

13.65 (3)°, *B*/*D* = 9.72 (2)° and *C*/*D* = 23.34 (3)°.

In ring *B*, the C8—C9 bond (Table 1) is the shortest, indicating the absence of delocalization of the double bonds. This is also reflected in the C2—S1 and C8—S1 bonds, which are shorter than normal C—S bonds. The variations in C1—N1 and C11—N2 bond lengths indicate delocalization of π-bonding across the ring systems.

The widening of the N1—C2—C3 and C2—C3—C10 bond angles reduces electronic repulsion. The widening of the C10—N2—C11 bond angle indicates delocalization of the N-atom lone pair, which is further supported by variation in the C—N bonds in the imine and carboxide units. In ring *D*, the significant deviations in the C18—C17—C22 and C19—C20—C21 bond angles from ideal values is probably due to the electron-donating resonance effect of the methoxy group at C20.

The *p*-methoxyphenyl ring (C17–C22/O2/C23) and 4-fluorophenyl ring (C11–C16/F1) make dihedral angles of 9.7 (2) and 10.4 (3)°, respectively, with ring *B*. The torsion angles C3—C10—N2—C11 and C2—N1—C1—C17 show the *anti* conformation of the two units about the C10—N2 and N1—C1 bonds.

In (I) (Fig. 1), intramolecular N—H···N and C—H···O hydrogen bonds form psuedo-six-membered rings, while the intramolecular C—H···S hydrogen bond forms a pseudo-five-membered ring (Table 2), thus locking the molecular conformation and eliminating conformational flexibility. On the other hand, as can be seen from the packing diagram (Fig. 2), the intermolecular C—H···O hydrogen bonds (Table 2) link the molecules into centrosymmetric dimers; these may be effective in the stabilization of the crystal structure. Dipole–dipole and van der Waals interactions are also effective in the molecular packing.

Experimental

The title compound was synthesized using the Gewald reaction (Gewald *et al.*, 1966). 4-Fluorophenyl-2-cyanoacetamide (7.08 g, 40 mmol) was refluxed with cyclohexanone (0.98 g, 10 mmol) in the presence of catalytic ammonium acetate (1.00 g) and glacial acetic acid (2 ml) in benzene (80 ml). The mixture was then treated with sulfur (1.28 g, 40 mmol), dimethylamine (4 ml) and ethanol (40 ml) at 323 K. The product was treated with 4-methoxybenzaldehyde in an equimolar ratio in the presence of 2-propanol (40 ml) and a catalytic amount of glacial acetic acid by microwave irradiation, which yielded (I). It was crystallized from *N*,*N*-dimethylformamide and ethanol (1:2) by slow evaporation (yield; 5.24 g, 74%, m.p. 455 K).

Crystal data

$C_{23}H_{21}FN_2O_2S$
M_r = 408.48
Triclinic, $P\overline{1}$
a = 8.6363 (11) Å
b = 11.0660 (14) Å
c = 11.8153 (15) Å
α = 67.874 (3)°
β = 81.656 (2)°
γ = 70.473 (2)°
V = 985.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 291 (2) K
0.32 × 0.26 × 0.19 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*;, Sheldrick, 1996)
T_{min} = 0.943, T_{max} = 0.965
9977 measured reflections
3656 independent reflections
2256 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.182
S = 0.99
3656 reflections
263 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.279 (4)	S1—C2	1.743 (3)
N2—C11	1.411 (4)	C8—C9	1.357 (5)
S1—C8	1.727 (4)		
C10—N2—C11	128.4 (3)	C18—C17—C22	117.3 (3)
N1—C2—C3	126.3 (3)	C19—C20—C21	119.3 (3)
C2—C3—C10	125.9 (3)		
C2—N1—C1—C17	174.6 (3)	C6—C7—C8—C9	−12.3 (6)
C9—C4—C5—C6	39.2 (6)	C7—C8—C9—C4	−0.6 (6)
C4—C5—C6—C7	−54.6 (6)	C5—C4—C9—C8	−11.6 (5)
C5—C6—C7—C8	38.5 (6)	C11—N2—C10—C3	−175.6 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1	0.86	2.06	2.791 (4)	142
C1—H1···S1	0.93	2.54	3.010 (4)	111
C5—H5A···O1^{i}	0.97	2.56	3.438 (6)	150
C16—H16···O1	0.93	2.23	2.817 (5)	120

Symmetry code: (i) $-x, -y+1, -z$.

H atoms were positioned geometrically, with N—H = 0.86 and C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,N), where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 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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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Anilkumar, G. N., Kokila, M. K., Puttaraja,, Mohan, S. & Manjunath Shetty, K. S. (2005). *Acta Cryst.* E**61**, o3038–o3040.
Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
Choudhury, A. R., Nagarajan, K. & Guru Row, T. N. (2004). *Acta Cryst.* C**60**, o644–o647.
Choudhury, A. R., Urs, U. K., Guru Row, T. N. & Nagarajan, K. (2002). *J. Mol. Struct.*, **605**, 71–77.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dzhurayev, A. D., Karimkulov, K. M., Makhsumov, A. G. & Amanov, N. (1992). *Khim. Farm. Zh.* **26**, 73–75. (In Russian.)
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gewald, K., Schinke, E. & Botcher, H. (1966). *Chem. Ber.* **99**, 94–100.
Mohan, S. & Saravanan, J. (2003). *Asian J. Chem.* **15**, 67–70.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.