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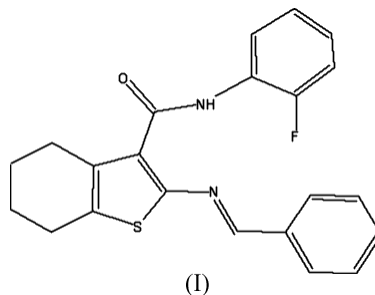
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.046
 wR factor = 0.128
Data-to-parameter ratio = 14.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-[(*E*)-Benzylideneamino]-*N*-(2-fluorophenyl)-
4,5,6,7-tetrahydro-1-benzothiophene-3-
carboxamide

The crystal structure of the title compound, $\text{C}_{22}\text{H}_{19}\text{FN}_2\text{OS}$, has been determined in order to study the role of organic fluorine in crystal engineering. There is an intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond, but the packing is controlled by $\text{C}-\text{H}\cdots\text{F}$ intermolecular interactions, forming dimers which are then linked by $\text{C}-\text{H}\cdots\text{O}$ interactions to form tetramers.

Comment

Crystal engineering *via* manipulation of hydrogen bonding has been the subject of much interest in the recent literature (Aakeröy, 1997; Desiraju, 2000; Hunter *et al.*, 2001). It has been shown that fluorine does not readily accept hydrogen bonding, and hence F behaves differently from Cl and Br (Howard *et al.*, 1996; Shimoni & Glusker, 1994; Desiraju & Parthasarathi, 1989). The introduction of F has been found to influence solid-state photochemical reactions (Vishnumurthy *et al.*, 1996). This feature is not observed in the title compound, (I).



In the molecule of (I), the $\text{C}2-\text{C}1-\text{N}2-\text{C}16$ and $\text{N}2-\text{C}16-\text{C}17-\text{C}18$ torsion angles are 177.1 (2) and -4.5 (3)°, respectively, indicating that the [*E*]-phenylmethylene]amino moiety is nearly coplanar with the thiophene ring. The $\text{C}9-\text{N}1-\text{C}10-\text{C}11$ torsion angle is 151.8 (2)°, showing that the phenyl ring is twisted in order to minimize steric repulsion between the atom H18 and the F atoms. The variations in $\text{C}-\text{N}$ bond lengths (Table 1) reflect the different hybridization states of these N atoms.

There is an intramolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond (Table 2, Fig. 1). The crystal structure is stabilized by $\text{C}-\text{H}\cdots\text{F}$ intermolecular interactions, forming dimers, along with $\text{C}-\text{H}\cdots\text{O}$ interactions, which link these dimers together, leading to the formation of tetramers, which provide stability to the overall packing (Fig. 2).

Experimental

The title compound was synthesized according to the procedure of Gewald *et al.*, 1966). 2-Fluoroaniline (1 mol) and ethylcyanoacetate

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(1 mol) were taken in a molar ratio of 1:1 and heated to 430–440 K. To the resulting mixture, cyclohexanone (0.04 mol) was added in the presence of ammonium acetate–acetic acid buffer in benzene as solvent, and stirred for 10 h. Sulfur (0.04 mol, 1.28 g) was then added in the presence of ethanol (40 ml) and diethylamine (4 ml), followed by the final addition of benzaldehyde (1 mol) in the presence of propanol (30 ml), and the mixture was warmed with microwave radiation for 1 min to yield the final compound (yield 60%). Single crystals of suitable size and quality were grown using the slow evaporation method, by dissolving the compound in ethanol and warming the resulting solution in a steam bath. After 7 d, crystals of (I), of block morphology, were obtained.

Crystal data

$C_{22}H_{19}FN_2OS$
 $M_r = 378.46$
 Triclinic, $P\bar{1}$
 $a = 8.447$ (5) Å
 $b = 10.821$ (7) Å
 $c = 11.759$ (7) Å
 $\alpha = 67.224$ (9)°
 $\beta = 70.794$ (9)°
 $\gamma = 77.127$ (9)°
 $V = 930.2$ (10) Å³

$Z = 2$
 $D_x = 1.351$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 660 reflections
 $\theta = 1.7$ – 25.2 °
 $\mu = 0.20$ mm⁻¹
 $T = 293$ (2) K
 Block, yellow
 $0.52 \times 0.29 \times 0.26$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan, (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.855$, $T_{\max} = 0.950$
 9614 measured reflections

3715 independent reflections
 3189 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 26.4$ °
 $h = -10 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.128$
 $S = 1.04$
 3714 reflections
 257 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.2811P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.59$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S1–C8	1.724 (2)	N1–C9	1.348 (2)
S1–C1	1.7351 (19)	N1–C10	1.402 (2)
O1–C9	1.210 (2)	N2–C16	1.273 (2)
F1–C11	1.356 (2)	N2–C1	1.390 (2)
C2–C1–N2–C16	177.09 (17)	N2–C16–C17–C18	−4.5 (3)
C1–N2–C16–C17	173.91 (16)	C9–N1–C10–C11	151.7 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1–H1 ⁱ ⋯N2	0.79 (2)	2.10 (2)	2.786 (2)	147 (2)
C21–H21 ⁱ ⋯O1 ⁱ	0.93	2.40	3.285 (3)	158
C7–H7B ⁱⁱ ⋯F1 ⁱⁱ	0.97	2.52	3.415 (4)	154

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

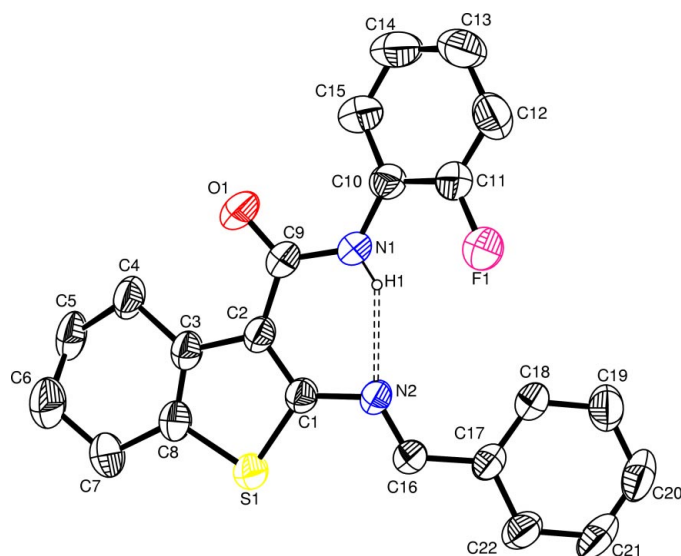


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate the N–H⋯N hydrogen bond.

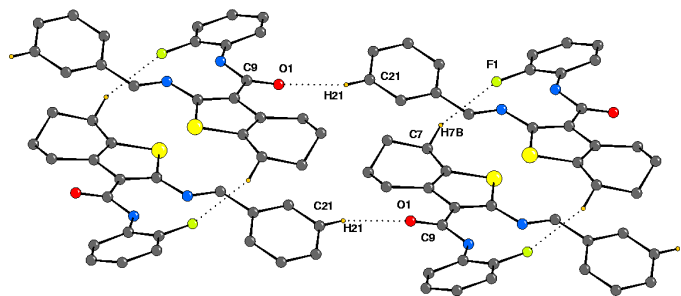


Figure 2

Diagram highlighting the formation of a tetramer. H atoms have been omitted. Dashed lines indicate hydrogen bonds.

The amino H atom was located in a difference Fourier map and refined isotropically. The methyl H atoms were constrained to an ideal geometry, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C–C bond. All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. A large residual electron density close to atom C5 was modelled by introducing a disordered distribution of atom C5 over two sites, with occupancy factors in the ratio 0.77 (4):0.23 (2).

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); 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: PLATON (Spek, 2003).

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