

Data collection

Siemens P4 diffractometer	$\theta_{\max} = 27.49^\circ$
θ - 2θ scans	$h = -1 \rightarrow 15$
Absorption correction: none	$k = -1 \rightarrow 19$
1532 measured reflections	$l = -1 \rightarrow 5$
1311 independent reflections	3 standard reflections
921 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.014$	intensity decay: 2.0%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$\Delta\rho_{\max} = 0.126 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.119$	$\Delta\rho_{\min} = -0.138 \text{ e } \text{\AA}^{-3}$
$S = 1.056$	Extinction correction: none
1311 reflections	Scattering factors from
141 parameters	<i>International Tables for</i>
H atoms not refined	<i>Crystallography</i> (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.1331P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Selected torsion angles ($^\circ$)

C15—C14—C17—O18	-13.4 (5)	C13—C14—C17—O17	-15.7 (5)
C13—C14—C17—O18	162.9 (4)	C18—N18—C21—C22	-123.6 (4)
C15—C14—C17—O17	168.0 (3)	N18—C21—C22—N23	65.7 (5)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N23—H23A...O17 ⁱ	0.89	1.895 (4)	2.748 (4)	159.86 (16)
N23—H23B...O17 ⁱⁱ	0.89	1.890 (5)	2.766 (5)	167.78 (11)
N23—H23C...O18 ⁱⁱⁱ	0.89	1.876 (5)	2.732 (5)	160.72 (13)
O11—H11...N18	0.82	1.874 (5)	2.596 (5)	146.25 (11)
O3...O11			2.675 (17)	
O3...O18 ^{iv}			2.921 (18)	

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, 1-y, \frac{1}{2}+z$; (iii) $-x, 1-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{3}{2}-y, z-1$.

All non-H atoms were refined with anisotropic displacement parameters. The H atoms were located in a difference map, positioned with idealized geometry, and refined with displacement parameters $1.2U_{\text{eq}}$ of the parent atom using a riding model. Late in the refinement, a peak in the difference map with a height of $0.58 \text{ e } \text{\AA}^{-3}$ was observed. This peak was in a position at a reasonable distance for a water molecule with a hydrogen bond to O18. The peak was modeled as a water molecule with a site occupancy factor that refined to 0.28 (1). No H atoms were placed on the water molecule. The absolute structure could not be determined with the present data.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: XS in SHELXTL (Sheldrick, 1994). Program(s) used to refine structure: XL in SHELXTL. Molecular graphics: XP in SHELXTL.

The authors wish to thank Montclair State University for supporting this work. This paper is dedicated to the memory of Peggy Etter (1943–1992).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1066). Services for accessing these data are described at the back of the journal.

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N—H...S and N—H...Ph Hydrogen Bonding in 1-(2-Fluorophenyl)thiourea

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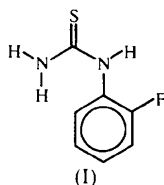
Abstract

In the title compound, $\text{C}_7\text{H}_7\text{FN}_2\text{S}$, the dominant hydrogen-bond motif is formed by ribbons of the thiourea moieties, which are linked by pairs of N—H...S=C hydrogen bonds. In addition, there is a distorted N—H...Ph hydrogen bond.

Comment

The crystal structure of the title compound, (I), was determined in order to elucidate the hydrogen-bond interactions. The initial interest was caused by the molecular constitution of (I). The molecule contains three strong N—H hydrogen-bond donors, but only moderate and weak hydrogen-bond acceptors. S=C is known to have much weaker acceptor properties than the O=C analogue (Allen *et al.*, 1997), but it is still the strongest acceptor in (I). The next-weakest acceptor is the phenyl ring, and the weakest of all is the F atom. Organic F is known to accept hydrogen bonds only very rarely (Howard *et al.*, 1996; Dunitz & Taylor, 1997), but examples with F— C_{sp^3} and F— C_{sp^2} have recently been reported (Borwick *et al.*, 1997; Weiss *et al.*, 1997). In this context, it is of interest to see which kinds of hydrogen bonds would be formed in crystalline (I), where different weak acceptors compete for three strong donors.

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The molecular conformation of (I), as observed in the crystal structure, is shown in Fig. 1. Relevant torsion angles are $S-C1-N1-C2 = -171.0(1)$ and $C1-N1-C2-C3 = 116.8(2)^\circ$. The sums of covalent angles around the N atoms are $359(2)^\circ$ for N1 and $359(3)^\circ$ for N2, *i.e.* there is no indication of pyramidalization. The molecular conformation is, therefore, as would be expected.

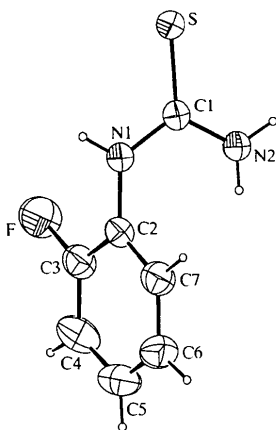


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids.

In the crystal lattice, molecules are arranged in layers parallel to the yz plane, as shown in Fig. 2. The intermolecular interactions are obviously dominated by pairs of $N-H \cdots S=C$ hydrogen bonds, which link the thiourea moieties into infinite ribbons. Analogous ribbons are also formed in thiourea itself (Truter, 1967). If H-atom positions are normalized to N—H distances of 1.04 \AA , the hydrogen-bond distances are $H(N1) \cdots S = 2.48 \text{ \AA}$ and $H(N2) \cdots S = 2.31 \text{ \AA}$. These distances are typical for $N-H \cdots S=C$ hydrogen bonding (Allen *et al.*, 1997). The other H atom bonded to N2 does not hydrogen bond with an S atom, but with the phenyl ring of a neighbouring molecule (Fig. 2). Whereas in $X-H \cdots Ph$ hydrogen bonds the $X-H$ vector ideally points to the centre of the aromatic ring (Levitt & Perutz, 1988), the $N-H \cdots Ph$ interaction in (I) is very off-centre [range of $H \cdots C$ distances $2.61-4.26 \text{ \AA}$, $H \cdots M$ (midpoint) = 3.23 \AA , shortest distance to C5; data for normalized H-atom positions]. However, on the basis of IR spectroscopy and neutron-diffraction data, hydrogen-bond nature could be shown for similarly off-centre $O-H \cdots Ph$ interactions (Steiner *et al.*, 1997). Therefore, it is not unreasonable to conclude that the

$N-H \cdots Ph$ contact in (I) also represents a hydrogen bond, albeit a weak one. The F atom in (I) does not act as an acceptor of $N-H \cdots F$ hydrogen bonds; the intramolecular contact with $N1-H$, which might appear to have hydrogen-bond geometry in Fig. 1, is in fact long and bent, with $H \cdots F = 2.79 \text{ \AA}$ and $N-H \cdots F = 75^\circ$ (for a normalized H-atom position).

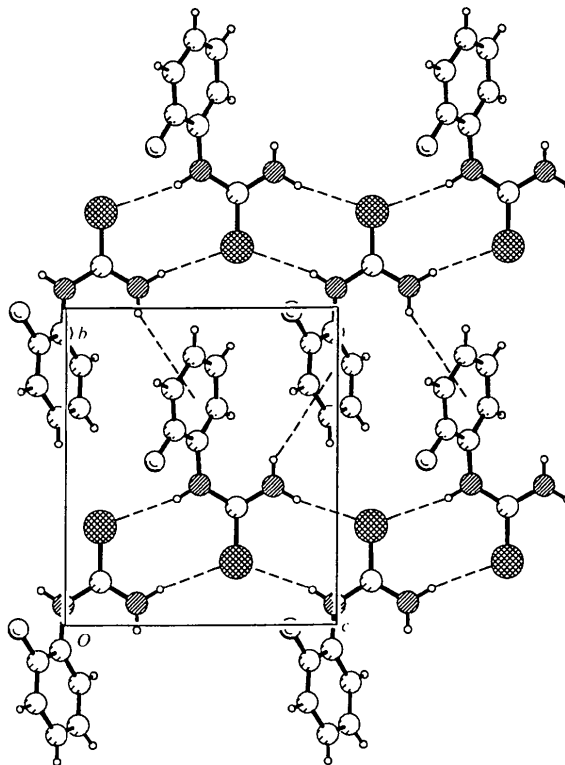


Fig. 2. Packing diagram for (I), viewed down the a axis. Hydrogen bonds are indicated by dashed lines.

Experimental

The title compound is commercially available (Aldrich), and was recrystallized from methanol. Crystals are stable under ambient conditions. A rod-shaped specimen was used for data collection, glued to a glass pin.

Crystal data

C₇H₇FN₂S
 $M_r = 170.27$
 Monoclinic
 $P2_1/c$
 $a = 9.573(2) \text{ \AA}$
 $b = 9.778(2) \text{ \AA}$
 $c = 8.562(2) \text{ \AA}$
 $\beta = 97.49(3)^\circ$
 $V = 794.6(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.423 \text{ Mg m}^{-3}$
 D_n , not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 15-16^\circ$
 $\mu = 0.356 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Rod
 $0.6 \times 0.1 \times 0.1 \text{ mm}$
 Colourless

Data collection

Rigaku AFC-5 diffractometer	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 27.51^\circ$
Absorption correction: none	$h = -12 \rightarrow 12$
3704 measured reflections	$k = -12 \rightarrow 2$
1821 independent reflections	$l = -11 \rightarrow 11$
1571 reflections with $I > 2\sigma(I)$	3 standard reflections every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.036$	$\Delta\rho_{\text{max}} = 0.302 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.100$	$\Delta\rho_{\text{min}} = -0.206 \text{ e } \text{\AA}^{-3}$
$S = 1.113$	Extinction correction: none
1821 reflections	Scattering factors from International Tables for Crystallography (Vol. C)
128 parameters	
All H atoms refined	
$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.1496P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...S ⁱ	0.83 (3)	2.69 (2)	3.481 (2)	162 (1)
N2—H22...S ⁱⁱ	0.85 (3)	2.50 (2)	3.337 (2)	169 (1)
N2—H21...C5 ⁱⁱⁱ	0.83 (3)	2.74 (3)	3.318 (3)	128 (2)

Symmetry codes: (i) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$.

Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1996a). Program(s) used to refine structure: *SHELXL96* (Sheldrick, 1996b). Molecular graphics: *PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL96*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1278). Services for accessing these data are described at the back of the journal.

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2',4'-Dihydroxy-2-[3-(4-methylphenyl)-isoxazol-5-yl]acetophenone†

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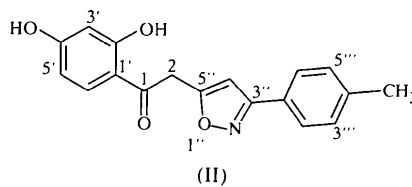
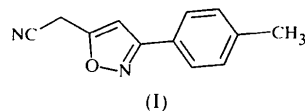
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Abstract

The synthesis and structure of the title compound, $\text{C}_{18}\text{H}_{15}\text{NO}_4$, are reported. The dihydroxyphenyl and methylphenyl groups are inclined at angles of 84.98 (4) and 9.18 (10)°, respectively, to the plane of the isoxazole ring. Both intra- and intermolecular hydrogen-bonding interactions are identified.

Comment

Due to the known various biological activities of isoxazoles (an important example being antispasmodic; Naruto *et al.*, 1982, 1983), we have synthesized a series of isoxazoles for further testing. Recently, we reported (Kumar *et al.*, 1996) the synthesis and X-ray structure of [3-(4-methylphenyl)-5-isoxazolyl]acetonitrile, (I); in the process of its derivatization (for structure–activity studies), we condensed it with resorcinol under Hoesch reaction conditions to produce the corresponding β -resorcinol derivative (II). Such compounds have not been reported previously. This X-ray investigation was undertaken in order to unambiguously assign its constitution.



† IUPAC name: 2,4-dihydroxyphenyl 3-(4-methylphenyl)isoxazol-5-ylmethyl ketone.