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3-Phenyl-1-(2-pyridyl)thiourea†

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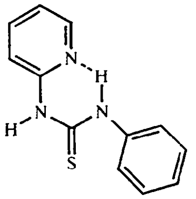
Abstract

The title compound, $C_{12}H_{11}N_3S$, contains an intramolecular N3—H···N_{py} hydrogen bond, which stabilizes the coplanarity of the thiourea moiety and the pyridine (py) ring. The molecules form centrosymmetric hydrogen-bonded dimers, with the S atom forming bifurcated intermolecular hydrogen bonds involving the N2—H group of the thiourea moiety and the C3—H group of the pyridyl ring.

Comment

Although ^{1}H NMR analysis has correctly predicted intramolecular hydrogen bonding involving the pyridyl N atom (N_{py}) and the N3—H group (Kascheres & Ueno, 1991), no structures have been reported for 1-(2-pyridyl)-3-arylthioureas, which are biologically significant molecules (Hall *et al.*, 1996). We report here the crystal structure and lattice arrangement of 3-phenyl-1-(2-pyridyl)thiourea, (I), in order to compare its intramolecular hydrogen bonding with that of benzoylthioureas (Dago *et al.*, 1987, 1988; Zhang *et al.*, 1996; Cao *et al.*, 1996) and its intermolecular hydrogen bonding with that of 1,3-substituted thioureas (Ramnathan *et al.*, 1995*a*; Ramnathan, Sivakumar, Subramanian, Meerarani *et al.*, 1996; Ramnathan, Sivakumar, Janarthanan *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Srinivasan *et al.*, 1996).



(I)

The unit cell of (I) with the atomic numbering scheme and the intra- and intermolecular hydrogen bonding is shown in Fig. 1. Selected bond distances and angles are given in Table 1. The S1—C7 bond distance [1.682 (3) Å] is essentially identical to that of 1,3-diphenylthiourea [1.681 (5) Å; Ramnathan *et al.*, 1995*b*], but longer than that of 1-benzoyl-3-*p*-nitrophenylthiourea [1.658 (2) Å; Zhang *et al.*, 1996] and 1-benzoyl-3-*p*-methoxyphenylthiourea [1.659 (3) Å; Cao *et al.*, 1996]. In contrast, the N2—C7 bond distance [1.371 (4) Å] is considerably longer than found for 1,3-diphenylthiourea [1.349 (4) Å; Ramnathan *et al.*, 1995*b*], but shorter than that of both 1-benzoyl-3-*p*-nitrophenylthiourea [1.393 (3) Å; Zhang *et al.*, 1996] and 1-benzoyl-3-*p*-methoxyphenylthiourea [1.392 (4) Å; Cao *et al.*, 1996]. The N3—C7 bonds in (I), in the three thioureas mentioned above and in nine other substituted thioureas whose structures have been solved (Dago *et al.* 1987, 1988, 1989; Koch *et al.*, 1995; Ramnathan *et al.*, 1995*a*; Ramnathan, Sivakumar, Subramanian, Meerarani *et al.*, 1996; Ramnathan, Sivakumar, Janarthanan *et al.*, 1996; Ramnathan, Sivakumar, Subramanian, Srinivasan *et al.*, 1996), all have bond distances of about 1.335 (7) Å.

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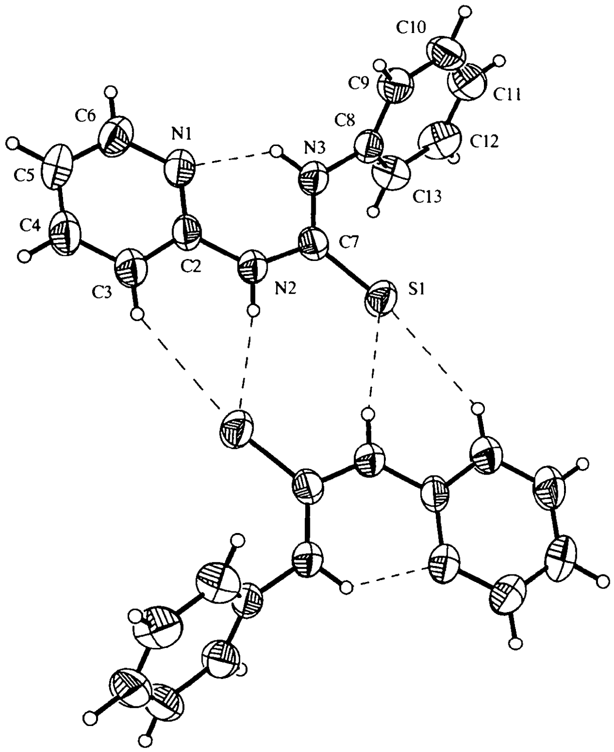

Fig. 1. The unit cell of the title compound showing the atom-numbering scheme and the centrosymmetric dimeric units. Non-H atoms are shown as 50% probability ellipsoids and H atoms are shown as small spheres of an arbitrary radius.

The N3—C7—S1 angle [124.6 (2)°] is smaller than found for the intramolecularly hydrogen-bonded compound 1-benzoyl-3-*p*-nitrophenylthiourea [126.6 (2)°; Zhang *et al.*, 1996]. The other bond angles involving C7 are reasonably close to the angles found for the intramolecularly hydrogen-bonded benzoylthioureas (Zhang *et al.*, 1996; Cao *et al.*, 1996).

The mean-plane deviation of the thiourea moiety (N2, N3, C7 and S1) is 0.0038 Å and its dihedral angle with the plane of the pyridine ring (mean plane deviation 0.0053 Å) is 5.4 (1)°. The near planarity of the two moieties is expected because of the intramolecular N3—H···N_{py} hydrogen bond. In contrast, the dihedral angle between the phenyl ring and the thiourea moiety is 58.0 (1)° (Nardelli, 1995).

The separation between the pyridyl-N atom and N3 is 2.646 (4) Å, and the geometry of the molecular hydrogen bonding is N3—H3*A* 0.894 (3), H3*A*···N1 1.95 (3) Å and N3—H3*A*···N1 133 (3)°.

The molecules form centrosymmetric hydrogen-bonded dimers, with the S atom participating in a bifurcated hydrogen bond with N2—H2 and C3—H3 (Table 2). The C3···S1^{i} separation is 3.644 (4) Å and the C3—H3···S1^{i} bond angle is 146.7 (3)° [symmetry code: (i) $-x$, $1-y$, $1-z$], within the accepted range for this kind of hydrogen bonding (Taylor & Kennard, 1982). The N2···S1 separation is 3.414 (3) Å. The structure of *N*-benzoyl-*N'*-propylthiourea is also a dimer with N—H···S intermolecular hydrogen bonds (Dago *et al.*, 1989).

Experimental

2-Aminopyridine and phenyl isothiocyanate were purchased from Aldrich and used as received. The two were mixed in a 1:1 molar ratio in anhydrous ethanol and the mixture refluxed for a minimum of 1 h. A suitable crystal was formed on cooling and slow evaporation (313 K).

Crystal data

$C_{12}H_{11}N_3S$
$M_r = 229.30$
Monoclinic
$P2_1/n$
$a = 5.869\ (1)$ Å
$b = 22.530\ (3)$ Å
$c = 8.753\ (1)$ Å
$\beta = 98.67\ (1)°$
$V = 1144.2\ (3)$ Å^3
$Z = 4$
$D_x = 1.331$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 53 reflections
$\theta = 5.03–24.81°$
$\mu = 0.257$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.46 × 0.22 × 0.16 mm
Colorless

Data collection

Siemens *P*4/PC diffractometer
ω–2θ scans
Absorption correction: analytical (face-indexed numerical)
$T_{min} = 0.891$, $T_{max} = 0.960$
2205 measured reflections
2002 independent reflections

1391 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 26$
$l = -10 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.149$
$S = 1.072$
2002 reflections
152 parameters
H-atom parameters not refined, except for H2 and H3*A* on N2 and N3
$w = 1/[\sigma^2(F_o^2) + (0.0742P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.307$ e Å^{-3}
$\Delta\rho_{min} = -0.224$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C7	1.682 (3)	N2—C2	1.402 (4)
N1—C2	1.328 (4)	N3—C7	1.336 (4)
N1—C6	1.346 (5)	N3—C8	1.425 (4)
N2—C7	1.371 (4)	C2—C3	1.389 (5)
C2—N1—C6	117.3 (3)	N3—C7—N2	116.8 (3)
C7—N2—C2	130.0 (3)	N3—C7—S1	124.6 (2)
C7—N3—C8	125.7 (3)	N2—C7—S1	118.6 (2)

N1—C2—C3	122.7 (3)	C13—C8—N3	121.0 (3)
N1—C2—N2	118.7 (3)	C9—C8—N3	118.8 (3)
C3—C2—N2	118.6 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^i	0.89 (1)	2.54 (1)	3.414 (3)	168 (3)
C3—H3···S1^i	0.93 (1)	2.83 (1)	3.644 (4)	146.7 (3)
N3—H3*A*···N1	0.89 (1)	1.95 (3)	2.646 (4)	133 (3)

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1068). Services for accessing these data are described at the back of the journal.

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7-Hydroxy-4-(4-methoxyphenyl)-3,4-dihydrocoumarin

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Abstract

The heterocyclic ring of the title compound, $C_{16}H_{14}O_4$, is in a half-chair conformation. The best planes through the two phenyl rings make an angle of 61.0(1)°. The packing of the molecules is stabilized by intermolecular O—H···O and C—H···O hydrogen bonds.

Comment

Direct condensation between phenols and free cinnamic acids has been studied using concentrated hydrochloric acid (Simpson & Stephen, 1956), boron trifluoride (Main & Venkataraman, 1954), polyphosphoric acid (Reichel & Proksch, 1971; Talapatra *et al.*, 1986), trifluoroacetic acid (Chaturvedi & Mulchandani, 1990) and zinc chloride–oxotriphosphorus chloride (Suresh *et al.*, 1986) as the condensation reagent. Careful perusal of the reported results clearly indicates that the outcome of the reaction between the chalcone and 4-phenylcoumarin is highly dependent on the reagent, nature of the phenol and the acid (substitution). This report is primarily concerned with the reaction product obtained from the reaction between resorcinol and cinnamic acid in the presence of trifluoroacetic acid (TFA) as the condensation reagent. Two structures, (I) and (II), are possible for this product (see scheme). Its IR spectrum