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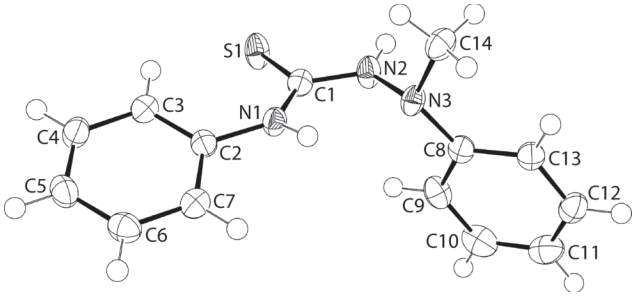
Crystal structure of 3-[methyl(phenyl)amino]-1-phenylthiourea, $C_{14}H_{15}N_3S$



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Abstract

$C_{14}H_{15}N_3S$, monoclinic, $P2_1/c$ (no. 14), $a = 10.4801(1)$ Å, $b = 10.8132(1)$ Å, $c = 12.1341(1)$ Å, $\beta = 107.823(1)°$, $V = 1309.08(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0266$, $wR_{ref}(F^2) = 0.0728$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Phenyl isothiocyanate (Merck; 1.19 mL, 0.01 mol) in ethanol (10 mL) was added dropwise to an equivalent molar amount of 1-methyl-1-phenylhydrazine (Merck; 1.18 mL, 0.01 mol) in ethanol (10 mL). The resulting mixture was stirred for 2 h and left for evaporation at room temperature, yielding colourless crystals after 2 weeks. ***M.pt.*** (Biobase automatic melting point apparatus MP450): 426–427 K. **Elem. Anal.** (Leco TruSpec Micro CHN Elemental Analyser): Calc. for $C_{14}H_{15}N_3S$: C, 65.34; H, 5.87; N, 16.33%. Found: C, 65.14;

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.18 × 0.09 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	2.07 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16316, 2338, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2266
$N(param)_{refined}$:	170
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
S1	0.34126(3)	0.36235(3)	0.50973(2)	0.02291(11)
N1	0.27734(9)	0.28022(9)	0.28687(8)	0.0174(2)
H1N	0.2881(14)	0.2973(13)	0.2205(9)	0.021*
N2	0.41261(10)	0.44811(9)	0.33649(8)	0.0197(2)
H2N	0.4662(12)	0.4958(12)	0.3887(10)	0.024*
N3	0.41405(10)	0.45604(9)	0.22106(8)	0.0175(2)
C1	0.34249(11)	0.35979(10)	0.37083(10)	0.0172(2)
C2	0.19660(11)	0.17545(11)	0.28940(10)	0.0166(2)
C3	0.20148(12)	0.10995(11)	0.38922(10)	0.0204(3)
H3	0.2585	0.1367	0.4623	0.024*
C4	0.12241(12)	0.00505(11)	0.38144(11)	0.0223(3)
H4	0.1246	−0.0388	0.4498	0.027*
C5	0.04058(12)	−0.03621(11)	0.27532(11)	0.0221(3)
H5	−0.0124	−0.1084	0.2707	0.027*
C6	0.03667(12)	0.02894(11)	0.17573(11)	0.0221(3)
H6	−0.0189	0.0008	0.1026	0.027*
C7	0.11320(12)	0.13459(11)	0.18224(10)	0.0195(3)
H7	0.1090	0.1793	0.1139	0.023*
C8	0.35658(11)	0.56884(10)	0.16702(9)	0.0170(2)
C9	0.24293(12)	0.61596(11)	0.18976(11)	0.0223(3)
H9	0.2097	0.5770	0.2456	0.027*
C10	0.17873(12)	0.71932(12)	0.13098(12)	0.0270(3)
H10	0.1012	0.7504	0.1465	0.032*
C11	0.22629(13)	0.77820(12)	0.04964(11)	0.0268(3)
H11	0.1814	0.8487	0.0092	0.032*
C12	0.33986(12)	0.73283(11)	0.02827(10)	0.0225(3)
H12	0.3732	0.7728	−0.0271	0.027*
C13	0.40599(12)	0.62918(11)	0.08701(10)	0.0182(3)
H13	0.4847	0.5996	0.0725	0.022*
C14	0.54288(12)	0.41597(11)	0.20906(10)	0.0216(3)
H14A	0.5677	0.3358	0.2474	0.032*
H14B	0.6120	0.4772	0.2450	0.032*
H14C	0.5350	0.4081	0.1268	0.032*

H, 5.76; N, 15.95%. **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane; $CDCl_3$): δ [p.p.m.] 8.87 (s, br, 1H, Ph—NH), 7.67 (s, br, 1H, N—NH), 7.58 (d, 2H, N(H)C_6H_5-2,6, $^3J_{HH} = 7.72$ Hz), 7.35 (t, 4H, NC_6H_5-3,5 and N(H)C_6H_5-3,5, $^3J_{HH} = 7.86$ Hz), 7.20 (t, 1H, N(H)C_6H_5-4, $^3J_{HH} = 7.42$ Hz), 7.06–7.01 (m, 3H, NC_6H_5-2,4,6), 3.21 (s, 3H, NCH_3). **^{13}C{^{1}H} NMR** (Bruker Ascend 400 MHz NMR spectrometer; $CDCl_3$): δ [p.p.m.] 180.0 (Cq), 148.8 (NC_6H_5, C1), 137.6 (N(H)C_6H_5, C1), 129.6 (N(H)C_6H_5, C3, C5), 128.7 (N(H)C_6H_5, C2, C6), 126.1 (N(H)C_6H_5, C4), 124.3 (NC_6H_5, C3, C5), 122.5 (NC_6H_5, C4), 114.9 (NC_6H_5, C2, C6), 41.9 (NCH_3). **IR** (Bruker Vertex 70v FTIR spectrophotometer, cm^{-1}): 3265 (*m*) ν(N—H), 1485 (*vs*) ν(C—N), 1255 (*vs*) ν(C=S).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$. The N-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint of N—H = 0.88±0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{equiv}(N)$.

Comment

With the possibility of up to four substitutions, thiourea derivatives, *i.e.* molecules of the general formula $R^1(R^2)NC(=S)N(R^3)R^4$ for R^{1-4} = alkyl/aryl, comprise a rich diversity of chemical species [5]. The primary interest in these molecules relate to their use as dual hydrogen bonding catalysis for asymmetric synthesis [6] and for their utility as potential pharmaceutical agents [7]. In continuation of recent studies in this area [8], herein the crystal and molecular structures of the title compound, PhN(Me)N(H)C(=S)N(H)Ph, are described.

The molecule is shown in the figure (70% displacement ellipsoids) and comprises a strictly planar core with the r.m.s. deviation of the C1, N1, N2 and S1 atoms being 0.0059 Å, and with the appended N3 [0.0538(16) Å] and C2 [0.0284(19) Å] atoms lying to either side of the least-squares plane. The dihedral angles between the central plane and the N1- and N3-bound phenyl rings are 21.40(6) and 83.43(3)°, respectively, showing the overall molecule to be twisted; the dihedral angle between the phenyl rings is 83.99(4)°. The amine-H atoms lie to opposite sides of the central plane which allows for the formation of an intramolecular amine-N1—H1n···N3(amine) hydrogen bond [H1n···N3 = 2.164(14) Å, N1···N3 = 2.6467(14) Å with angle at H1n = 114.8(10)°] which closes an S(5) loop.

In the crystal, centrosymmetrically related molecules are connected by amine-N2—H···S1(thione) hydrogen bonds [N2—H2n···S1^i: H2n···S1^i = 2.534(13) Å, N2···S1^i = 3.3749(10) Å with angle at H2n = 161.5(11)° for symmetry operation $1 - x$, $1 - y$, $1 - z$]. This mode of association results in the formation of eight-membered $\{\cdots HNCS\}_2$ synthons. The dimeric aggregates are connected into a three-dimensional architecture by phenyl- and methyl-C—π(phenyl) interactions whereby the C8—C13 phenyl ring accepts both contacts. [C4—H4···*Cg*(C8—C13)^{ii} = 2.62 Å with angle at H4 = 139° and C14—H14*a*···*Cg*(C8—C13)^{iii} = 2.59 Å with angle at H14*a* = 159° for symmetry operations ii: x, 1/2 – y, 1/2 + z and iii: 1 – x, −1/2 + y, 1/2 – z].

The conformation of the molecule and the formation of $\{\cdots HNCS\}_2$ synthons in the molecular packing of the title compound is found in each of the closely related literature precedents PhN(Me)N(H)C(=S)N(H)(PhMe-4) [8], $Me_2NN(H)C(=S)N(H)Ph$ [9], PhN(Me)N(H)C(=S)N(H)(PhCl-4) [10], (PhCN-4)N(H)N(H)C(=S)N(H)Ph [11] and ($PhNO_2$-4)N(H)N(H)C(=S)N(H)Ph [11].

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