Chien Ing Yeo and Edward R.T. Tiekink*

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

<https://doi.org/10.1515/ncrs-2019-0204>

Received March 19, 2019; accepted April 28, 2019; available online July 9, 2019

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, $\beta = 107.823(1)^\circ$, $V = 1309.08(2)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0266$, $wR_{ref}(F^2) = 0.0728$, $T = 100(2)$ K.

CCDC no.: 1912669

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;

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com. <https://orcid.org/0000-0003-1401-1520>

Chien Ing Yeo: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.18 × 0.09 × 0.05 mm
Wavelength:	Cu K α 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 (Å²).

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%. **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane; CDCl₃): δ [p.p.m.] 8.87 (s, br, 1H, Ph–NH), 7.67 (s, br, 1H, N–NH), 7.58 (d, 2H, N(H)C₆H₅-2,6, ³J_{HH} = 7.72 Hz), 7.35 (t, 4H, NC₆H₅-3,5 and N(H)C₆H₅-3,5, ³J_{HH} = 7.86 Hz), 7.20 (t, 1H, N(H)C₆H₅-4, ³J_{HH} = 7.42 Hz), 7.06–7.01 (m, 3H, NC₆H₅-2,4,6), 3.21 (s, 3H, NCH₃). **¹³C{¹H} NMR** (Bruker Ascend 400 MHz NMR spectrometer; CDCl₃): δ [p.p.m.] 180.0 (Cq), 148.8 (NC₆H₅, C1), 137.6 (N(H)C₆H₅, C1), 129.6 (N(H)C₆H₅, C3, C5), 128.7 (N(H)C₆H₅, C2, C6), 126.1 (N(H)C₆H₅, C4), 124.3 (NC₆H₅, C3, C5), 122.5 (NC₆H₅, C4), 114.9 (NC₆H₅, C2, C6), 41.9 (NCH₃). **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 $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. 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 $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{equiv}}(\text{N})$.

Comment

With the possibility of up to four substitutions, thiourea derivatives, *i.e.* molecules of the general formula $R^1(R^2)\text{NC}(=\text{S})\text{N}(R^3)R^4$ 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⋯S1ⁱ: H2n⋯S1ⁱ = 2.534(13) Å, N2⋯S1ⁱ = 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 {⋯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–H14a⋯Cg(C8–C13)]ⁱⁱⁱ = 2.59 Å with angle at H14a = 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 {⋯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], Me₂NN(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 (PhNO₂-4)N(H)N(H)C(=S)N(H)Ph [11].

Acknowledgements: The Research Centre for Crystalline Materials (Sunway University) is thanked for providing the X-ray data.

References

- Agilent Technologies: CrysAlis PRO. Agilent Technologies, Santa Clara, CA, USA (2017).
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
- Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
- Saeed, A.; Flörke, U.; Erben, M. F.: A review on the chemistry, coordination, structure and biological properties of 1-(acyl/aroil)-3-(substituted) thioureas. *J. Sulfur Chem.* **35** (2014) 318–355.
- Nishikawa, Y.: Recent topics in dual hydrogen bonding catalysis. *Tetrahedron Lett.* **59** (2018) 216–223.
- Kožurková, M.; Sabolová, D.; Kristian, P.: A review on acridinylthioureas and its derivatives: biological and cytotoxic activity. *J. Appl. Toxicol.* **37** (2017) 1132–1139.
- Yeo, C. I.; Tiekink, E. R. T.: 1-[N–Methyl–N–(phenyl)amino]-3-(4-methylphenyl)thiourea. *Molbank* **2019** (2019) M1052 (5 pages).
- López-Torres, E.; Dilworth, J. R.: Reactivity of thiosemicarbazides with redox active metal ions: controlled formation of coordination complexes versus heterocyclic compounds. *Chem. Eur. J.* **15** (2009) 3012–3023.
- Yeo, C. I.; Tiekink, E. R. T.: Crystal structure of 1-(4-chlorophenyl)-3-[methyl(phenyl)amino]thiourea, C₁₄H₁₄ClN₃S. *Z. Kristallogr. NCS* **234** (2019) 989–990.
- Li, Z.; Wu, F.-Y.; Guo, L.; Li, A.-F.; Jiang, Y.-B.: Enhanced anion binding of N-(anilino)thioureas. contribution of the N-anilino -NH proton acidity. *J. Phys. Chem. B* **112** (2008) 7071–7079.