



Synthesis and redetermination of the crystal structure of salicylaldehyde *N*(4)-morpholinothiosemicarbazone

Dang Tran Buu,^a Vu Duong Ba,^a Minh Khoi Nguyen Hoang,^b Trung Vu Quoc,^{c*} Linh Duong Khanh,^c Yen Oanh Doan Thi^d and Luc Van Meervelt^{e*}

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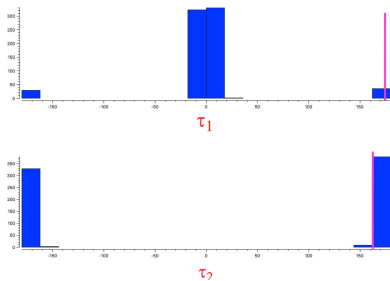
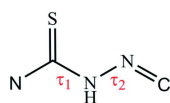
^aFaculty of Chemistry, Ho Chi Minh City University of Education, 280 An Duong Vuong Street, District No. 5, Ho Chi Minh City, Vietnam, ^bVietnam National University, Ho Chi Minh City High School for the Gifted, 153 Nguyen Chi Thanh, District 5, Ho Chi Minh City, Vietnam, ^cFaculty of Chemistry, Hanoi National University of Education, 136 Xuan Thuy, Cau Giay, Hanoi, Vietnam, ^dPublishing House for Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam, and ^eDepartment of Chemistry, KU Leuven, Biomolecular Architecture, Celestijnenlaan 200F, Leuven (Heverlee), B-3001, Belgium. *Correspondence e-mail: trungvq@hnue.edu.vn, luc.vanmeervelt@kuleuven.be

The structure of the title compound (systematic name: *N*-{[(2-hydroxyphenyl)methylidene]amino}morpholine-4-carbothioamide), C₁₂H₁₅N₃O₂S, was previously determined (Koo *et al.*, 1977) using multiple-film equi-inclination Weissenberg data, but has been redetermined with higher precision to explore its conformation and the hydrogen-bonding patterns and supramolecular interactions. The molecular structure shows intramolecular O—H···N and C—H···S interactions. The configuration of the C=N bond is *E*. The molecule is slightly twisted about the central N—N bond. The best planes through the phenyl ring and the morpholino ring make an angle of 43.44 (17)°. In the crystal, the molecules are connected into chains by N—H···O and C—H···O hydrogen bonds, which combine to generate sheets lying parallel to (002). The most prominent contribution to the surface contacts are H···H contacts (51.6%), as concluded from a Hirshfeld surface analysis.

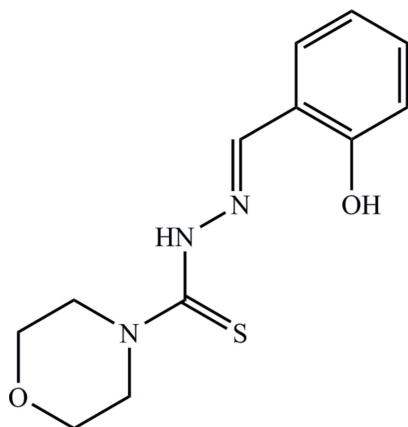
1. Chemical context

For many years, scientific studies on cancer have attracted a lot of attention, especially in the field of antitumor drugs. Cisplatin is well known as an effective therapy to prohibit the proliferation of tumor cells (Berners-Price, 2011). However, this drug has some unforeseen side effects with detrimental effects on the patient's health (Lévi *et al.*, 2000; Go & Adjei, 1999; Harbour *et al.*, 1996). In a search for antitumour drugs with fewer harmful side effects, thiosemicarbazides were examined since this organic class of thiourea derivatives was known to possess a diversity of biological activities such as antitumoral, antibacterial, and antifungal activities owing to presence of the N—N—C=S system (Dilović *et al.*, 2008; Liberta & West, 1992). Many mechanisms have been advanced to probe the role of this conjugated system. In general, thiosemicarbazones can bind to nucleotides of tumour cells by the nitrogen and sulfur atoms, which prevents the distorted DNA from translation and encryption for their growth (Dilović *et al.*, 2008).

Thiosemicarbazones are synthesized by the condensation between an aldehyde or ketone and an *N*(4)-substituted thiosemicarbazide. Many reports have demonstrated that *N*(4)-aromatic or heterocyclic substituted thiosemicarbazides are biologically more active than thiosemicarbazones without



substituted groups (Dilović *et al.*, 2008; Chen *et al.*, 2004; Shi *et al.*, 2009). In addition, salicylaldehyde is a key compound in the synthesis of a variety of potential therapeutic products (Bindu *et al.*, 1998).



The crystal and molecular structure of salicylaldehyde *N*(4)-morpholinothiosemicarbazone was published previously (Koo *et al.*, 1977) based on multiple-film equi-inclination Weissenberg data using Cu $K\alpha$ radiation and refined to an *R* value of 0.11. In this study, we present the synthesis of salicylaldehyde *N*(4)-morpholinothiosemicarbazone (**3**) together with its structural characteristics and crystal structure redetermination using present-day technology.

2. Structural commentary

The title compound crystallizes in the orthorhombic space group $Pna2_1$ with one molecule in the asymmetric unit (Fig. 1). The N9–N10 and C11=N10 bond lengths are 1.371 (3) and 1.275 (3) Å, respectively (compared to 1.40 and 1.30 Å in the previous structure determination; Koo *et al.*, 1977). The configuration of the C11=N10 bond is *E* [the N9–N10–C11–C12 torsion angle is -179.9 (3)°], which gives rise to an intramolecular O18–H18···N10 hydrogen bond with an $S_1^1(6)$ graph-set motif (Table 1). The planes of the phenyl ring (r.m.s. deviation = 0.0020 Å) and the thiosemicarbazone function (N1/C7–C11; r.m.s. deviation = 0.0911 Å) make an angle of 16.26 (5)°. The molecule is slightly twisted about the N9–N10

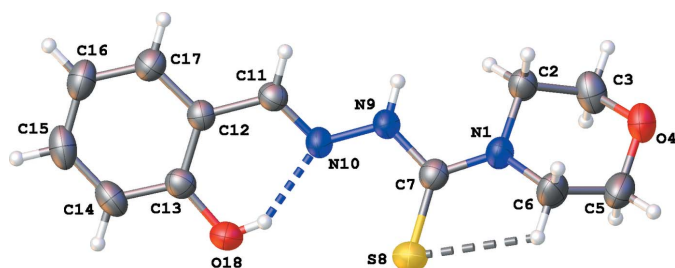


Figure 1

A view of the molecular structure of (**3**), with atom labels and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii and the intramolecular O–H···N and C–H···S interactions, respectively, by blue and grey dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N9–H9···O4 ⁱ	0.86 (3)	2.33 (3)	3.141 (3)	157 (3)
O18–H18···N10	0.80 (4)	1.91 (5)	2.597 (3)	145 (4)
C6–H6A···S8	0.97	2.62	3.121 (3)	112
C15–H15···O18 ⁱⁱ	0.93	2.48	3.404 (4)	176

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

bond [torsion angle C7–N9–N10–C11 is 162.4 (3)°; *ap* conformation].

The morpholino ring adopts a chair conformation [puckering parameters $Q = 0.554$ (3) Å, $\theta = 173.2$ (3)° and $\varphi = 214$ (3)°] with the thiosemicarbazone function in an equatorial position. The plane of the phenyl ring forms a dihedral angle of 43.44 (17)° with the best plane through the morpholino ring. A second intramolecular C6–H6A···S8 interaction is observed (Table 1).

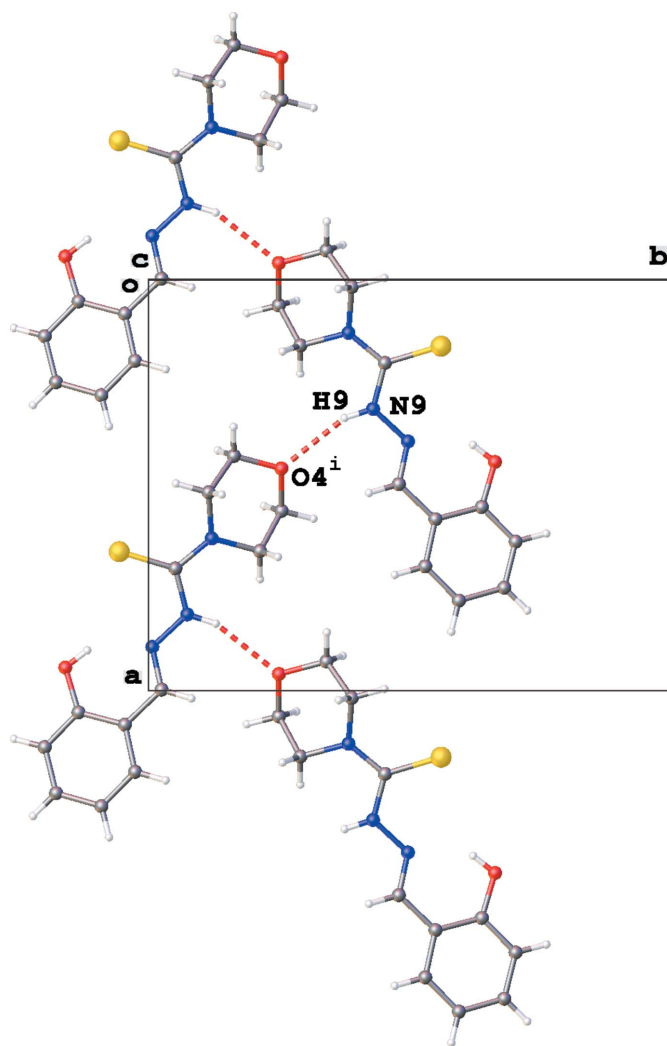


Figure 2

Partial crystal packing of (**3**), showing the N–H···O interactions (red dashed lines) resulting in chain formation in the *a*-axis direction [see Table 1; symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z$].

3. Supramolecular features

The crystal packing of **(3)** is dominated by N9—H9···O4 hydrogen bonds (Table 1), resulting in the formation of chains of molecules with graph-set motif $C_1^1(7)$ propagating along the a -axis direction (Fig. 2). Furthermore, a second parallel chain of molecules with graph-set motif $C_1^1(5)$ running along the a -axis direction is formed by C15—H15···O18 interactions (Fig. 3). These two chain motifs combine to generate a sheet lying parallel to (002). No voids or π - π stackings are observed in the crystal packing of **(3)**.

A Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed in order to further investigate the supramolecular network. The Hirshfeld surface calculated using *CrystalExplorer* (Turner *et al.*, 2017) and mapped over d_{norm} is given in Fig. 4. The bright-red spots near atoms O4 and N9 in Fig. 4a refer to the N9—H9···O4 hydrogen bond, and near atoms C15 and O18 in Fig. 4b to the C15—H15···O18 hydrogen bond. The faint-red spots near atoms C5 and S8 illustrate a short contact in the crystal packing of **(3)** ($H5B\cdots S8 = 2.913 \text{ \AA}$). The fingerprint plots (Fig. 5) further indicate a major contribution by H···H

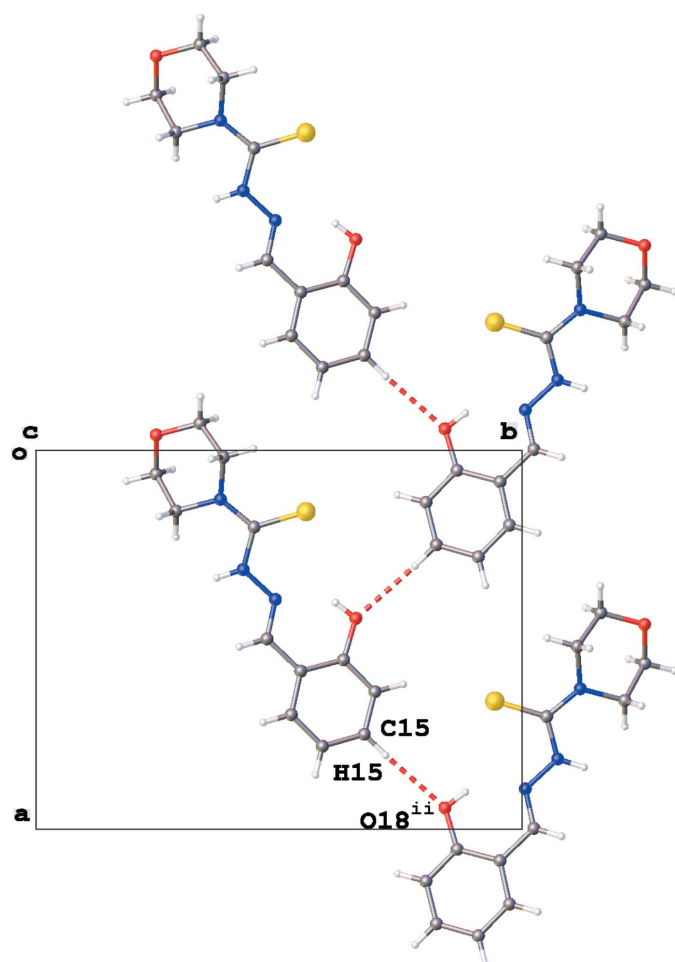


Figure 3
Partial crystal packing of **(3)**, showing the C—H···O interactions (red dashed lines) resulting in chain formation in the a -direction [see Table 1; symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$].

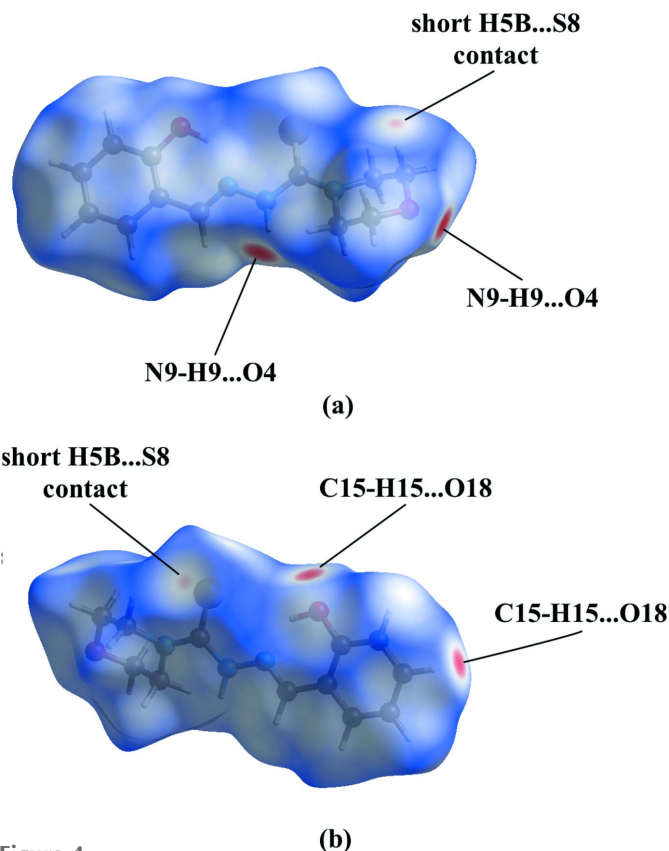


Figure 4
The Hirshfeld surface mapped over d_{norm} for **(3)** in the range -0.3153 to 1.2662 a.u.

contacts, corresponding to 51.6% of the two-dimensional fingerprint plot (Fig. 5b). Significant contributions by reciprocal O···H/H···O (13.4%) and S···H/H···S (12.5%) contacts appear as two symmetrical spikes at $d_e + d_i \simeq 2.2$ and 2.8 \AA , respectively (Fig. 5c,d). Smaller contributions are from C···H/H···C (11.7%, Fig. 5e), N···C/C···N (5.3%, Fig. 5f),

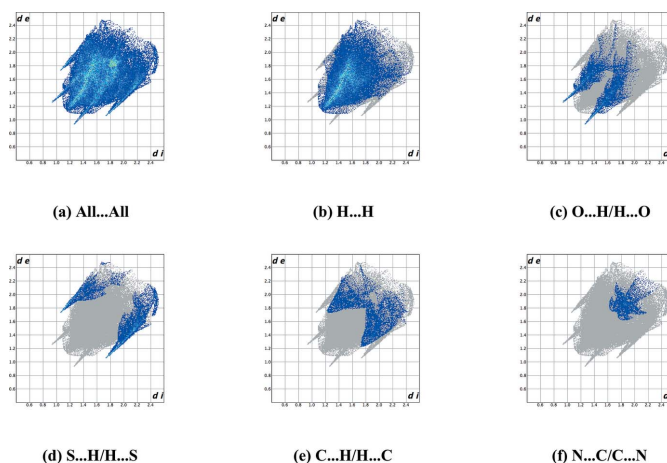


Figure 5
Full two-dimensional fingerprint plots for **(3)**, showing (a) all interactions, and delineated into (b) H···H, (c) O···H/H···O, (d) S···H/H···S, (e) C···H/H···C and (f) N···C/C···N interactions. The d_i and d_e values are the closest internal and external distances (in \AA) from a given point on the Hirshfeld surface.

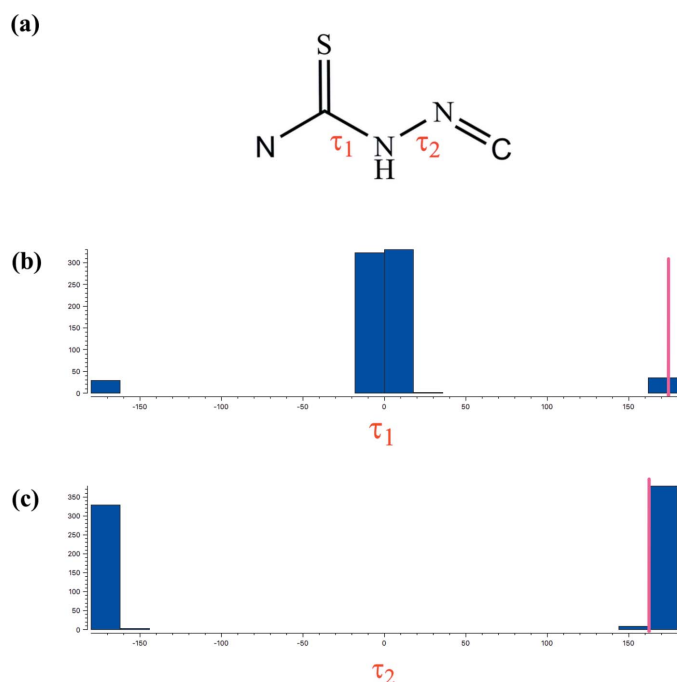


Figure 6
 (a) Fragment used for a search in the CSD. (b),(c) Histograms of torsion angles τ_1 and τ_2 . The vertical pink lines show the torsion angle observed in (3).

C...C (3.2%), N...H/H...N (1.6%), C...O/O...C (0.3%), C...S/S...C (0.3%) and O...O contacts (0.1%).

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, update of May 2019; Groom *et al.*, 2016) for the central N—C(=S)—NH—N=C moiety (Fig. 6a) present in the title compound gave 583 hits. Fig. 6b,c illustrate the histograms of the distribution of torsion angles τ_1 and τ_2 . The histogram of τ_1 shows a major preference for the $-sp/+sp$ (or *cis*) conformation and a minor preference for the $-ap/+ap$ (or *trans*) conformation. For torsion angle τ_2 , only one region is preferred: a narrow spread in the region $-ap/+ap$ (or *trans*). For (3), the torsion angles τ_1 and τ_2 are both in the $+ap$ region [$\tau_1 = 173.8$ (3) and $\tau_2 = 162.4$ (3)].

The most similar compound present in the CSD is the 2-hydroxynaphthaldehyde-based thiosemicarbazone (refcode IDEQAM; Aneesrahman *et al.*, 2018). The asymmetric unit contains two molecules (one morpholino ring shows disorder). The mean plane of the non-disordered morpholino ring makes an angle of 36.9 (7) $^\circ$ with the naphthalene ring system. The

torsion angles τ_1 [175.89 (15) and -175.97 (15) $^\circ$] and τ_2 [166.51 (16) and -174.99 (16) $^\circ$] are similar to those observed for the title compound. An intramolecular hydrogen bond similar to O18—H18...N10 is also observed.

5. Synthesis and crystallization

The reaction scheme for the synthesis of (3) is given in Fig. 7.

Synthesis of 2-((morpholine-4-carbonothioyl)thio)acetic acid (1):

A mixture consisting of carbon disulfide (0.2 mol) and concentrated ammonia (25 mL) was stirred to form a homogeneous solution at 278 K. Then, morpholine (0.2 mol) was added dropwise to this solution. The yellow solid that separated from the solution was filtered off and immediately dissolved in deionized water (300 mL) at room temperature to generate a yellow solution. Sodium chloroacetate (0.2 mol) was added to this solution and the reaction mixture maintained for 6 h at room temperature. The yellowish solution was acidified with concentrated hydrochloric acid and the resulting white precipitate was filtered off and recrystallized from ethanol.

Synthesis of N(4)-morpholiniothiosemicarbazide (2):

A mixture composed of (1) (50 mmol), deionized water (10 mL) and hydrazine hydrate (25 mL) was refluxed for 30 minutes at 353 K. The white solid which precipitated from the transparent solution was filtered off and recrystallized from ethanol to give (2).

Synthesis of salicylaldehyde N(4)-morpholiniothiosemicarbazone (3):

After dissolving (2) in hot ethanol, the solution was added to an equivalent amount of salicylaldehyde. The final solution was refluxed at 353 K for 2 h in the presence of acetic acid as a catalyst. The resulting solution was gradually reduced in volume at room temperature overnight. The needle-shaped crystals that formed were filtered off and recrystallized from ethanol to give (3) in the form of transparent crystals (yield 60%), m.p. 461–463 K. FT-IR (cm^{-1}): 3436 (O—H), 3279 (N—H), 1617 ($\text{C}_{\text{Ar}}-\text{H}$), 1540 (C=N), 1061 (N—N), 1348 and 959 (C=S). ^1H NMR [Bruker 500 MHz, d_6 -DMSO, δ (ppm), J (Hz)]: 3.67 (4H, *t*, H2 and H6); 3.92 (4H, *t*, H3 and H5); 6.90 (2H, *m*, H14 and H16); 7.28 (1H, *m*, $J = 7.5$, H15); 7.41 (1H, *d*, $J = 7.0$, H17); 8.47 (1H, *s*, H11); 11.49 (1H, *br*, N—H); 11.55 (1H, *br*, O—H). ^{13}C NMR [Bruker 125 MHz, d_6 -DMSO, δ (ppm)]: 49.4 (C2 and C6), 66.2 (C3 and C5), 117.0 (C14), 118.9 (C12), 119.5 (C16), 130.4 (C17), 131.3 (C15), 146.9 (C13), 157.6 (C11), 180.1 (C7). UV-Vis (ethanol, nm): 200 ($\pi \rightarrow \pi^*$); 300 and 350 ($n \rightarrow \pi^*$).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Both H atoms H9 and H18 were located from difference electron density maps and refined freely. The other H atoms were placed in idealized positions and included as riding contributions with $U_{\text{iso}}(\text{H})$ values $1.2U_{\text{eq}}$ of the parent atoms, with C—H distances of 0.93

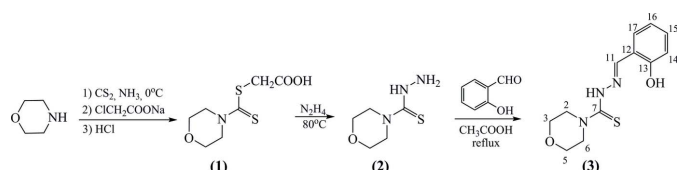


Figure 7
 Reaction scheme for the synthesis of (3).

(aromatic, CH=N) and 0.97 Å (CH₂). In the final cycles of refinement, 4 outliers were omitted.

Acknowledgements

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References

Aneesrahman, K. N., Rohini, G., Bhuvanesh, N. S. P., Sundararaj, S., Musthafa, M. & Sreekanth, A. (2018). *ChemistrySelect* **3**, 8118–8130.

Berners-Price, S. J. (2011). *Angew. Chem. Int. Ed.* **50**, 804–805.

Bindu, P., Kurup, M. R. P. & Satyakeerty, T. R. (1998). *Polyhedron*, **18**, 321–331.

Chen, J., Huang, Y. W., Liu, G., Afrasiabi, Z., Sinn, E., Padhye, S. & Ma, Y. (2004). *Toxicol. Appl. Pharmacol.* **197**, 40–48.

Dilović, I., Rubčić, M., Vrdoljak, V., Kraljević Pavelić, S., Kralj, M., Piantanida, I. & Cindrić, M. (2008). *Bioorg. Med. Chem.* **16**, 5189–5198.

Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.

Go, R. S. & Adjei, A. A. (1999). *J. Clin. Oncol.* **17**, 409–422.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst. B* **72**, 171–179.

Harbour, J. W., Murray, T. G., Hamasaki, D., Ciciarelli, N., Hernández, E., Smith, B., Windle, J. & O'Brien, J. M. (1996). *Invest. Ophthalmol. Vis. Sci.* **37**, 1892–1898.

Koo, C. H., Kim, H. S. & Ahn, C. H. (1977). *J. Korean Chem. Soc.* **21**, 3–15.

Lévi, F., Metzger, G., Massari, C. & Milano, G. (2000). *Clin. Pharmacokinet.* **38**, 1–21.

Liberta, A. E. & West, D. X. (1992). *Biometals*, **5**, 121–126.

McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* 3814–3816.

Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst. B* **69**, 249–259.

Rigaku OD (2018). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, UK.

Sheldrick, G. M. (2015a). *Acta Cryst. A* **71**, 3–8.

Sheldrick, G. M. (2015b). *Acta Cryst. C* **71**, 3–8.

Shi, L., Mao, W. J., Yang, Y. & Zhu, H. L. (2009). *J. Coord. Chem.* **62**, 3471–3477.

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₅ N ₃ O ₂ S
<i>M_r</i>	265.33
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.7579 (4), 15.0584 (5), 7.1103 (3)
<i>V</i> (Å ³)	1258.92 (8)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	0.26
Crystal size (mm)	0.5 × 0.2 × 0.1
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Single source at offset/far, Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T_{min}</i> , <i>T_{max}</i>	0.483, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	12278, 2565, 2314
<i>R_{int}</i>	0.025
(sin θ/λ) _{max} (Å ⁻¹)	0.625
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.034, 0.087, 1.07
No. of reflections	2565
No. of parameters	171
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.17, -0.17
Absolute structure	Flack <i>x</i> determined using 938 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.02 (3)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.

Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *CrystalExplorer17*. University of Western Australia. <http://hirshfeldsurface.net>

supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

N-{[(2-Hydroxyphenyl)methylidene]amino}morpholine-4-carbothioamide

Crystal data

C₁₂H₁₅N₃O₂S

M_r = 265.33

Orthorhombic, *Pna*2₁

a = 11.7579 (4) Å

b = 15.0584 (5) Å

c = 7.1103 (3) Å

V = 1258.92 (8) Å³

Z = 4

F(000) = 560

D_x = 1.400 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 5842 reflections

θ = 3.2–27.3°

μ = 0.26 mm⁻¹

T = 293 K

Block, colourless

0.5 × 0.2 × 0.1 mm

Data collection

Rigaku Oxford Diffraction SuperNova, Single source at offset/far, Eos diffractometer

Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source

Mirror monochromator

Detector resolution: 15.9631 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)

T_{min} = 0.483, *T_{max}* = 1.000

12278 measured reflections

2565 independent reflections

2314 reflections with *I* > 2σ(*I*)

R_{int} = 0.025

θ_{max} = 26.4°, θ_{min} = 2.7°

h = -14→14

k = -18→18

l = -8→8

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.034

wR(*F*²) = 0.087

S = 1.07

2565 reflections

171 parameters

1 restraint

Primary atom site location: dual space

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.1653P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Flack x determined using
938 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*,
2013)

Absolute structure parameter: 0.02 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.12956 (17)	0.37994 (13)	0.5311 (5)	0.0441 (5)
C2	0.1602 (2)	0.28850 (18)	0.4815 (5)	0.0438 (7)
H2A	0.174911	0.254390	0.594672	0.053*
H2B	0.228621	0.288274	0.405192	0.053*
C3	0.0625 (3)	0.2474 (2)	0.3728 (5)	0.0552 (8)
H3A	0.050961	0.280351	0.257136	0.066*
H3B	0.081833	0.186795	0.339747	0.066*
O4	-0.04027 (17)	0.24774 (14)	0.4794 (3)	0.0545 (6)
C5	-0.0710 (2)	0.3379 (2)	0.5178 (7)	0.0615 (9)
H5A	-0.141436	0.338728	0.588879	0.074*
H5B	-0.084419	0.368531	0.399814	0.074*
C6	0.0177 (3)	0.3860 (2)	0.6249 (6)	0.0597 (9)
H6A	-0.003873	0.447934	0.636901	0.072*
H6B	0.023218	0.361089	0.750398	0.072*
C7	0.2028 (2)	0.44909 (15)	0.5299 (5)	0.0388 (6)
S8	0.16206 (6)	0.55578 (4)	0.54532 (17)	0.0552 (2)
N9	0.31482 (18)	0.42656 (14)	0.5168 (4)	0.0406 (6)
H9	0.337 (2)	0.3724 (19)	0.521 (6)	0.044 (8)*
N10	0.39379 (18)	0.49289 (14)	0.4965 (3)	0.0384 (6)
C11	0.4978 (2)	0.47549 (15)	0.5317 (5)	0.0366 (5)
H11	0.519030	0.418814	0.569994	0.044*
C12	0.5829 (2)	0.54502 (15)	0.5115 (4)	0.0353 (6)
C13	0.5532 (2)	0.63316 (17)	0.4666 (4)	0.0394 (6)
C14	0.6374 (3)	0.69733 (19)	0.4546 (5)	0.0512 (8)
H14	0.617815	0.755628	0.426000	0.061*
C15	0.7497 (3)	0.6758 (2)	0.4845 (4)	0.0542 (8)
H15	0.805097	0.719608	0.475521	0.065*
C16	0.7811 (2)	0.5896 (2)	0.5277 (6)	0.0537 (7)
H16	0.857037	0.575138	0.547403	0.064*
C17	0.6977 (2)	0.52566 (18)	0.5408 (6)	0.0466 (6)
H17	0.718495	0.467720	0.570242	0.056*
O18	0.44378 (18)	0.65822 (14)	0.4336 (4)	0.0513 (6)
H18	0.402 (3)	0.617 (3)	0.446 (6)	0.073 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0326 (10)	0.0409 (10)	0.0590 (14)	-0.0031 (9)	0.0038 (14)	-0.0046 (15)
C2	0.0354 (13)	0.0407 (13)	0.0551 (19)	-0.0024 (11)	0.0056 (13)	-0.0046 (13)
C3	0.0576 (18)	0.0553 (18)	0.0528 (19)	-0.0181 (15)	0.0075 (16)	-0.0038 (15)
O4	0.0436 (11)	0.0530 (11)	0.0670 (16)	-0.0148 (9)	0.0020 (11)	0.0020 (11)
C5	0.0376 (14)	0.0584 (17)	0.088 (3)	-0.0044 (13)	-0.0064 (19)	0.014 (2)
C6	0.0370 (16)	0.0545 (17)	0.088 (3)	-0.0016 (14)	0.0139 (17)	-0.0090 (18)
C7	0.0360 (12)	0.0418 (12)	0.0387 (14)	-0.0009 (10)	-0.0011 (15)	0.0015 (15)
S8	0.0481 (4)	0.0396 (3)	0.0780 (6)	0.0056 (3)	0.0010 (5)	-0.0010 (5)
N9	0.0333 (11)	0.0329 (10)	0.0556 (16)	-0.0031 (8)	0.0009 (12)	0.0040 (12)
N10	0.0336 (11)	0.0359 (10)	0.0458 (15)	-0.0050 (9)	-0.0004 (10)	0.0032 (10)
C11	0.0388 (13)	0.0329 (10)	0.0380 (13)	-0.0003 (9)	-0.0010 (14)	0.0021 (14)
C12	0.0353 (12)	0.0354 (11)	0.0353 (16)	-0.0029 (9)	0.0002 (12)	-0.0007 (12)
C13	0.0418 (14)	0.0356 (12)	0.0408 (15)	0.0001 (11)	0.0026 (12)	-0.0019 (12)
C14	0.0605 (19)	0.0351 (13)	0.0581 (19)	-0.0111 (13)	0.0005 (16)	0.0001 (14)
C15	0.0534 (17)	0.0585 (17)	0.0507 (19)	-0.0249 (15)	-0.0003 (15)	-0.0007 (15)
C16	0.0363 (14)	0.0681 (17)	0.0567 (18)	-0.0104 (13)	-0.0022 (17)	0.0016 (19)
C17	0.0389 (14)	0.0465 (13)	0.0545 (16)	-0.0001 (11)	-0.0039 (18)	0.0019 (18)
O18	0.0448 (11)	0.0349 (10)	0.0744 (15)	0.0042 (9)	-0.0019 (11)	0.0049 (10)

Geometric parameters (Å, °)

N1—C2	1.466 (3)	N9—H9	0.86 (3)
N1—C6	1.478 (4)	N9—N10	1.371 (3)
N1—C7	1.351 (3)	N10—C11	1.275 (3)
C2—H2A	0.9700	C11—H11	0.9300
C2—H2B	0.9700	C11—C12	1.456 (3)
C2—C3	1.516 (4)	C12—C13	1.409 (3)
C3—H3A	0.9700	C12—C17	1.396 (4)
C3—H3B	0.9700	C13—C14	1.386 (4)
C3—O4	1.426 (3)	C13—O18	1.361 (3)
O4—C5	1.432 (4)	C14—H14	0.9300
C5—H5A	0.9700	C14—C15	1.376 (4)
C5—H5B	0.9700	C15—H15	0.9300
C5—C6	1.481 (5)	C15—C16	1.383 (4)
C6—H6A	0.9700	C16—H16	0.9300
C6—H6B	0.9700	C16—C17	1.377 (4)
C7—S8	1.680 (2)	C17—H17	0.9300
C7—N9	1.364 (3)	O18—H18	0.80 (4)
C2—N1—C6	112.7 (2)	N1—C7—N9	115.1 (2)
C7—N1—C2	124.4 (2)	N9—C7—S8	121.17 (18)
C7—N1—C6	121.5 (2)	C7—N9—H9	121.8 (18)
N1—C2—H2A	110.0	C7—N9—N10	118.7 (2)
N1—C2—H2B	110.0	N10—N9—H9	119.5 (18)
N1—C2—C3	108.6 (2)	C11—N10—N9	118.6 (2)

H2A—C2—H2B	108.4	N10—C11—H11	120.3
C3—C2—H2A	110.0	N10—C11—C12	119.5 (2)
C3—C2—H2B	110.0	C12—C11—H11	120.3
C2—C3—H3A	109.3	C13—C12—C11	121.9 (2)
C2—C3—H3B	109.3	C17—C12—C11	120.0 (2)
H3A—C3—H3B	107.9	C17—C12—C13	118.1 (2)
O4—C3—C2	111.7 (3)	C14—C13—C12	119.5 (3)
O4—C3—H3A	109.3	O18—C13—C12	122.3 (2)
O4—C3—H3B	109.3	O18—C13—C14	118.1 (3)
C3—O4—C5	108.6 (2)	C13—C14—H14	119.6
O4—C5—H5A	109.1	C15—C14—C13	120.7 (3)
O4—C5—H5B	109.1	C15—C14—H14	119.6
O4—C5—C6	112.6 (2)	C14—C15—H15	119.6
H5A—C5—H5B	107.8	C14—C15—C16	120.8 (3)
C6—C5—H5A	109.1	C16—C15—H15	119.6
C6—C5—H5B	109.1	C15—C16—H16	120.6
N1—C6—C5	111.4 (3)	C17—C16—C15	118.7 (3)
N1—C6—H6A	109.4	C17—C16—H16	120.6
N1—C6—H6B	109.4	C12—C17—H17	118.9
C5—C6—H6A	109.4	C16—C17—C12	122.1 (3)
C5—C6—H6B	109.4	C16—C17—H17	118.9
H6A—C6—H6B	108.0	C13—O18—H18	110 (3)
N1—C7—S8	123.73 (19)		
N1—C2—C3—O4	-58.7 (4)	N9—N10—C11—C12	-179.9 (3)
N1—C7—N9—N10	173.8 (3)	N10—C11—C12—C13	4.5 (5)
C2—N1—C6—C5	-50.2 (4)	N10—C11—C12—C17	-176.9 (3)
C2—N1—C7—S8	167.6 (3)	C11—C12—C13—C14	178.1 (3)
C2—N1—C7—N9	-13.0 (5)	C11—C12—C13—O18	-2.1 (4)
C2—C3—O4—C5	62.2 (4)	C11—C12—C17—C16	-178.5 (4)
C3—O4—C5—C6	-59.5 (4)	C12—C13—C14—C15	0.6 (5)
O4—C5—C6—N1	53.7 (4)	C13—C12—C17—C16	0.2 (5)
C6—N1—C2—C3	51.7 (4)	C13—C14—C15—C16	-0.2 (5)
C6—N1—C7—S8	-27.0 (5)	C14—C15—C16—C17	-0.2 (5)
C6—N1—C7—N9	152.5 (3)	C15—C16—C17—C12	0.2 (6)
C7—N1—C2—C3	-141.7 (3)	C17—C12—C13—C14	-0.6 (4)
C7—N1—C6—C5	142.7 (3)	C17—C12—C13—O18	179.3 (3)
C7—N9—N10—C11	162.4 (3)	O18—C13—C14—C15	-179.3 (3)
S8—C7—N9—N10	-6.7 (4)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N9—H9 \cdots O4 ⁱ	0.86 (3)	2.33 (3)	3.141 (3)	157 (3)
O18—H18 \cdots N10	0.80 (4)	1.91 (5)	2.597 (3)	145 (4)

C6—H6A···S8	0.97	2.62	3.121 (3)	112
C15—H15···O18 ⁱⁱ	0.93	2.48	3.404 (4)	176

Symmetry codes: (i) $x+1/2, -y+1/2, z$; (ii) $x+1/2, -y+3/2, z$.