



Synthesis, crystal structure and Hirshfeld surface analysis of (2*Z*,2'*E*)-2,2'-(3-methoxy-3-phenylpropane-1,2-diylidene)bis(hydrazine-1-carbothioamide) dimethylformamide monosolvate

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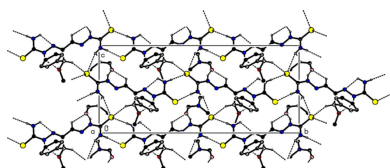
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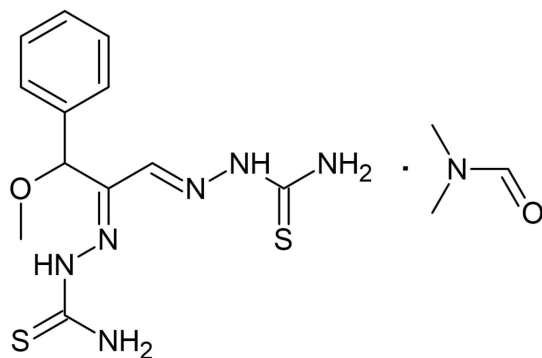
The overall molecular configuration of the title compound, C₁₂H₁₆N₆OS₂·C₃H₇NO, is stabilized in the solid state by intramolecular C—H···N, C—H···O, N—H···N and N—H···O interactions, forming *S*(5) ring motifs. In the crystal, molecules are linked to each other and solvent dimethylformamide molecules by N—H···S, N—H···O, C—H···O and C—H···S hydrogen bonds, forming a three dimensional network. The phenyl ring of the title compound is disordered over two sites with an occupancy ratio of 0.57 (4):0.43 (4). A Hirshfeld surface analysis was performed to quantify the contributions of the different intermolecular interactions, indicating that the most important contributions to the crystal packing are from H···H (38.7%), S···H / H···S (24.0%), C···H / H···C (18.5%) and N···H / H···N (9.8%) interactions.

1. Chemical context

Hydrazones are very attractive compounds in synthesis, catalysis, crystal engineering and medicinal chemistry due to their reactivity, hydrogen-bonding donor ability and broad spectrum of biological activities (Afkhami *et al.*, 2019; Gurbanov *et al.*, 2020*a,b*; Mahmoudi *et al.*, 2017*a,b,c*; Khalilov 2021; Martins *et al.*, 2017). The most common synthetic pathway for the synthesis of hydrazones is the reaction of appropriate hydrazines with different aldehydes or ketones in various organic solvents (Khalilov *et al.*, 2021). For example, hydrazinecarbothioamide has been well explored as a substrate in the synthesis of hydrazones (Safarova *et al.*, 2019; Velásquez *et al.*, 2019). The functional properties of hydrazones can be improved by attaching electron-withdrawing or -donating substituents to the hydrazone moiety (Gurbanov *et al.*, 2022*b*, 2017, 2021; Kopylovich *et al.*, 2011). In fact, due to the participation of the substituents in various sorts of intermolecular interactions (Mahmudov *et al.*, 2010, 2012, 2022; Mahmoudi *et al.*, 2019, 2021) the catalytic activity of metal complexes of hydrazones has been improved in comparison to those with unsubstituted ligands (Gurbanov *et al.*, 2022*a*). In order to continue our work in this perspective, we have synthesized a new hydrazone dimethylformamide mono-



solvate, (2*Z*,2'*E*)-2,2'-(3-methoxy-3-phenylpropane-1,2-diylidene)bis(hydrazine-1-carbothioamide)·DMF *via* reaction of hydrazinecarbothioamide with the highly reactive substrate 2-chloro-2-(diethoxymethyl)-3-phenyloxirane, which may be also replaced by 1-chloro-3,3-diethoxy-1-phenylpropan-2-one (Guseinov *et al.*, 2006, 2017, 2020).



2. Structural commentary

As shown in Fig. 1, the title compound adopts a *Z* configuration about the C5=C6 double bond with regard to the 3-methoxy-3-phenylpropane group and *E* configuration regarding the hydrazine-1-carbothioamide moieties. The bond has a length of 1.452 (3) Å. The molecular conformation of the title compound is stabilized by intramolecular C11–H11···N7, C17–H17···O18, N1–H1A···N4 and N3–H3···O18 classical and non-classical hydrogen-bonding interactions, resulting in *S*(5) ring motifs (Table 1; Bernstein *et al.*, 1995). The C12–C17 phenyl ring is disordered over two sites with occupancy factors in a 0.57 (4) to 0.43 (4) ratio. The major (C12–C17) and minor (C12A–C17A) components of the disordered phenyl ring subtend a dihedral angle of 2.0 (9)° to each other, *i.e.* they are nearly co-planar. Bond lengths and angles of the title compound are generally in agreement with

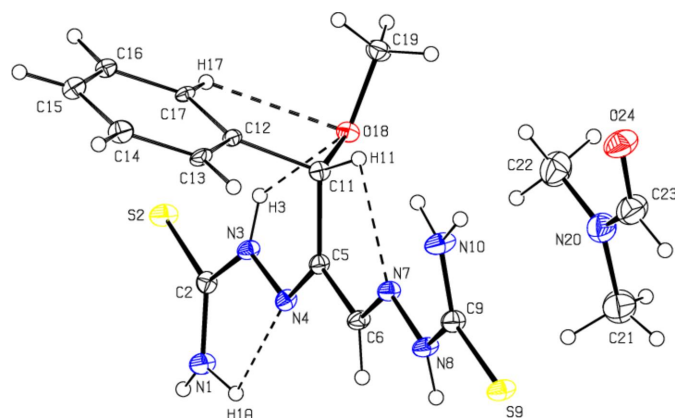


Figure 1
The molecular structure of the title compound, showing the atom labeling and displacement ellipsoids drawn at the 30% probability level. Intramolecular C11–H11···N7, C17–H17···O18, N1–H1A···N4 and N3–H3···O18 interactions are shown as dashed lines. The minor component of the disorder was omitted for clarity reasons.

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

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···N4	0.92 (3)	2.27 (4)	2.670 (3)	106 (3)
N1–H1B···S9 ⁱ	0.92 (4)	2.54 (4)	3.450 (2)	172 (4)
N3–H3···O18	0.90 (2)	2.04 (3)	2.694 (3)	129 (3)
N8–H8···O24 ⁱⁱ	0.87 (3)	2.07 (4)	2.847 (4)	149 (3)
N10–H10A···S9 ⁱⁱⁱ	0.91 (3)	2.72 (3)	3.570 (3)	156 (3)
N10–H10B···S2 ^{iv}	0.91 (4)	2.42 (4)	3.322 (3)	175 (4)
C6–H6···O24 ⁱⁱ	0.95	2.54	3.224 (4)	129
C11–H11···N7	1.00	2.42	2.853 (3)	105
C11–H11···S9 ⁱⁱⁱ	1.00	2.87	3.706 (2)	141
C17–H17···O18	0.95	2.45	2.787 (16)	101
C21–H21B···S9 ^v	0.98	2.98	3.951 (5)	171

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

those reported for related compounds, as discussed in the *Database survey* section below.

3. Supramolecular features and Hirshfeld surface analysis

Molecules in the crystal of the title compound are linked to each other and to the solvent dimethylformamide by classical and non-classical N–H···S, N–H···O, C–H···O and C–H···S hydrogen bonds (Table 1; Figs. 2, 3 and 4), resulting in a three-dimensional network. Fig. 5 shows all interactions as supplied in Table 1. In addition some offset weak C/N–H··· π interactions are observed.

Crystal Explorer 17.5 (Spackman *et al.*, 2021) was used to perform a Hirshfeld surface analysis and to generate the corresponding two-dimensional fingerprint plots, with a standard resolution of the three-dimensional d_{norm} surfaces plotted over a fixed color scale of -0.5044 (red) to $+1.5170$ (blue) a.u. (Fig. 6). The red spots symbolize short contacts and negative d_{norm} values on the surface corresponding to the N–H···S, N–H···O and C–H···O hydrogen bonds mentioned above (Table 1). The N1–H1B···S9, N8–H8···O24, N10–H10A···S9, N10–H10B···S2 and C6–H6···O24 interactions, which play a key role in the molecular packing of the title compound, are responsible for the red spots observed around S2, S9 and O24.

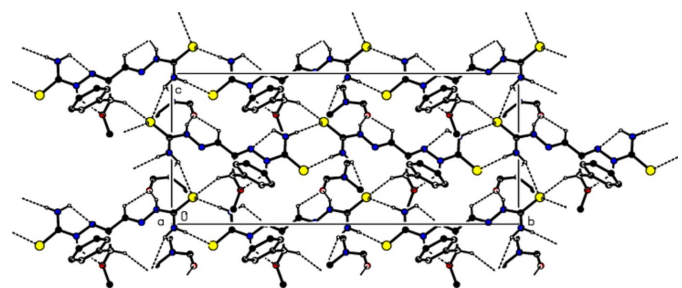


Figure 2
View of the molecular packing along the *a*-axis. Intramolecular C–H···N, C–H···O, N–H···N and N–H···O interactions and intermolecular N–H···S, N–H···O, C–H···O and C–H···S hydrogen bonds are shown as dashed lines. The minor part of the disorder and hydrogen atoms not involved in hydrogen bonding were omitted for clarity reasons.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

Contact	Distance	Symmetry operation
S2···H10B	2.42	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
H16···O24	2.73	$\frac{1}{2} + x, \frac{1}{2} + y, z$
H19A···N3	2.71	$-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$
S9···H10A	2.72	$x, 1 - y, \frac{1}{2} + z$
S9···H21B	2.98	$1 + x, 1 - y, \frac{1}{2} + z$
H6···H16A	2.49	$-\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$
N3···H15A	2.56	$-1 + x, y, z$
H8···O24	2.07	$x, 1 - y, \frac{1}{2} + z$
H19B···H22A	2.58	x, y, z
H22C···H21A	2.31	$x, 1 - y, -\frac{1}{2} + z$

The overall two-dimensional fingerprint plot for the title compound is provided in Fig. 7a, and those delineated into N–H···S, N–H···O and C–H···O contacts are shown in Fig. 7b–e, while numerical details of the different contacts are supplied in Table 2. The most important contributions to the Hirshfeld surfaces from the various interatomic contacts are H···H (38.7%), S···H/H···S (24.0%), C···H/H···C (18.5%) and N···H/H···N ((9.8%). Other, less notable contacts comprise O···H/H···O (5.0%), S···N/N···S (1.7%), S···C/C···S (0.7%), O···N/N···O (0.5%), N···C/C···N (0.4%), N···N (0.2%), C···C (0.2%) and S···O/O···S (0.1%); they have little, if any, directional influence on the molecular packing.

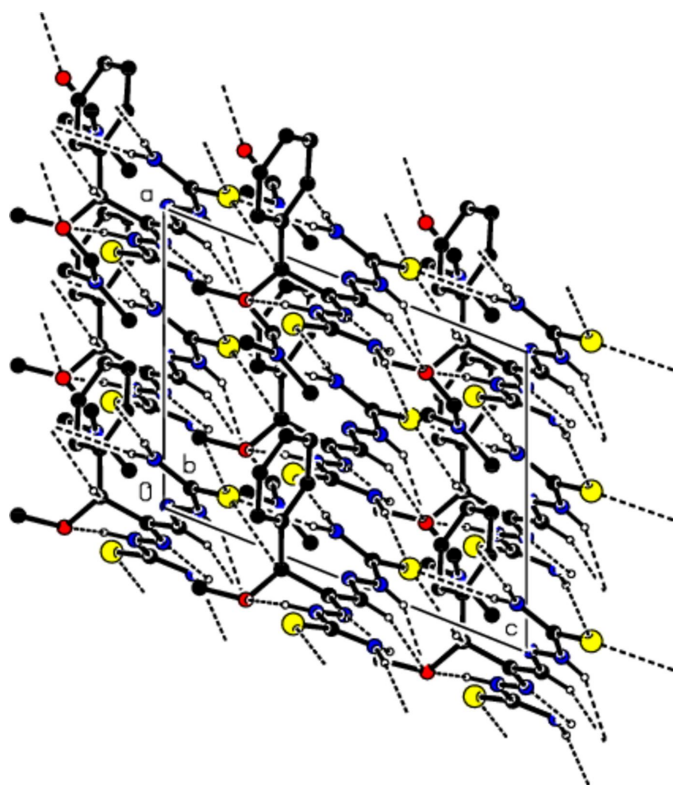


Figure 3
View of the molecular packing along the *b*-axis. Intramolecular C–H···N, C–H···O, N–H···N and N–H···O interactions and intermolecular N–H···S, N–H···O, C–H···O and C–H···S hydrogen bonds are shown as dashed lines. The minor part of the disorder and hydrogen atoms not involved in hydrogen bonding were omitted for clarity reasons.

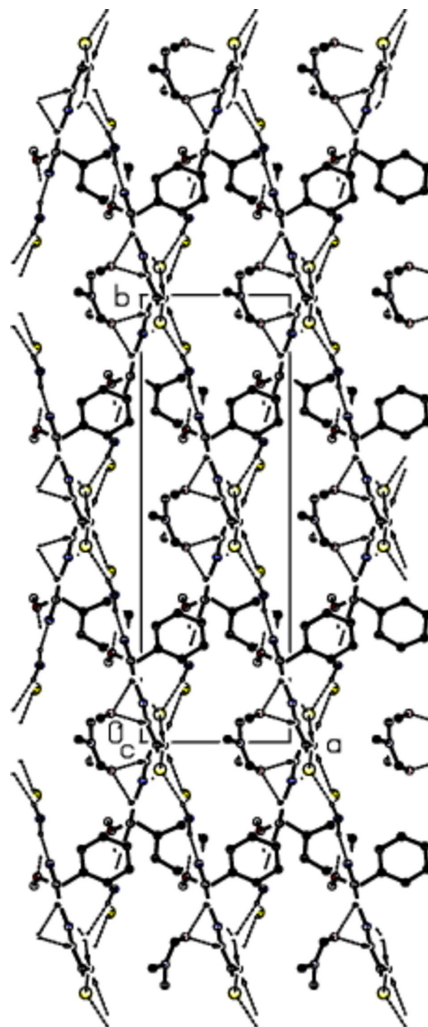


Figure 4
View of the molecular packing along the *c*-axis. Intramolecular C–H···N, C–H···O, N–H···N and N–H···O interactions and intermolecular N–H···S, N–H···O, C–H···O and C–H···S hydrogen bonds are shown as dashed lines. The minor part of the disorder and hydrogen atoms not involved in hydrogen bonding were omitted for clarity reasons.

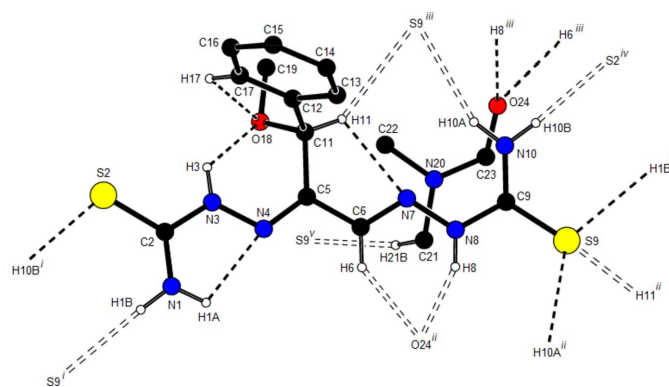
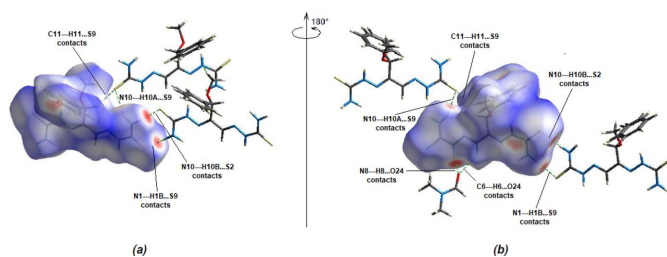


Figure 5
A general view of the possible intra- and intermolecular hydrogen bonds of the molecule. The minor disorder component was omitted for clarity. Symmetry codes: (i) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $x, -y + 1, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (v) $x - 1, -y + 1, z - \frac{1}{2}$.


Figure 6

(a) Front and (b) back sides of the three-dimensional Hirshfeld surface of the title compound mapped over d_{norm} .

4. Database survey

A database search was carried out using *ConQUEST* (Bruno *et al.*, 2002), part of the software for version 2023.2.0 of the Cambridge Structural Database (Groom *et al.*, 2016). A search for the keyword ‘hydrazinecarbothioamide’ resulted in nearly

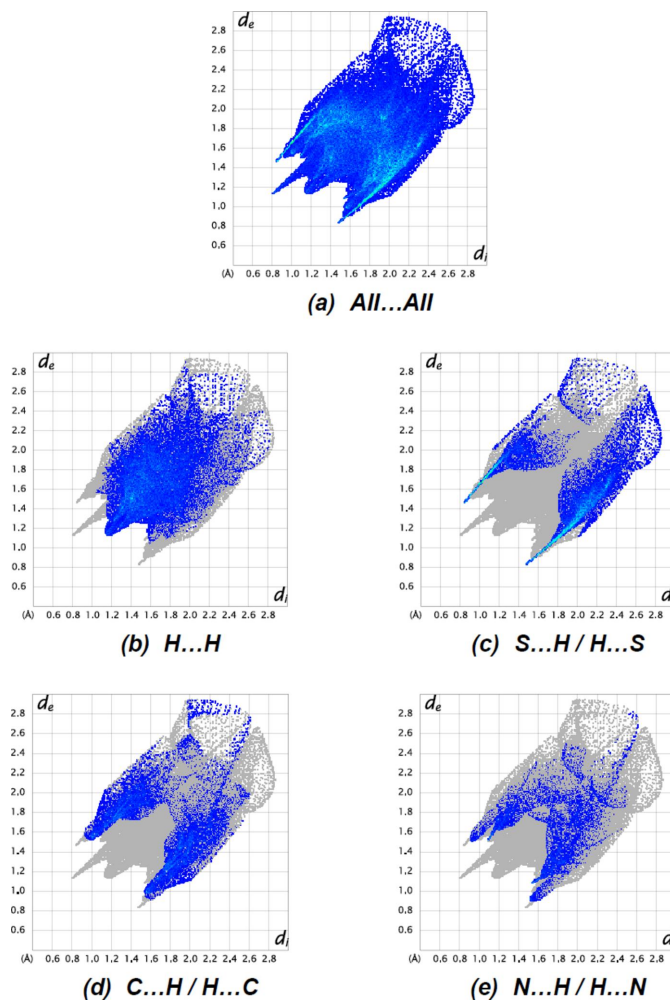
600 hits. A search for the structural bis-hydrazinecarbothioamide motif without considering hydrogen atoms narrowed that down to 45. For a more detailed analysis, four of those compounds were chosen as relatively more closely related to the title compound, yet with a variation of the substituent(s) numbers and position on the bis-hydrazinecarbothioamide backbone. These are: (*E,E*)-*N,N*-dimethyl-2-[3-[(methylcarbamothioyl)hydrazono]butan-2-ylidene]hydrazinecarbothioamide (CD refcode ERABIJ; Paterson *et al.*, 2010), diacetyl-2-(4-*N*-ethyl-3-thiosemicarbazone)-3-(4-*N*-allyl-3-thiosemicarbazone) dimethylsulfoxide solvate (JEXXOA; Holland *et al.*, 2007), 2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone) (KEBASC10; Gabe *et al.*, 1969) and *N*,1-dimethyl-2-[3-[2-(methylcarbamothioyl)hydrazinylidene]butan-2-ylidene]hydrazine-1-carbothioamide (RECKAP; Alonso *et al.*, 2022).

In the crystal of ERABIJ (monoclinic space group: $P2_1/c$, $Z = 4$), the molecule adopts an (*E, E*)-configuration about the imine double bonds. The arm bearing a dimethyl substituent has a slightly shorter C–S [1.6802 (19) Å] bond length and a longer C–N [1.341 (2) Å] bond length than the arm with a single methyl substituent [1.693 (2) and 1.323 (3) Å, respectively]. These bond lengths indicate that there is some extensive delocalization throughout the molecule while one tautomeric form still dominates.

In the crystal of JEXXOA (monoclinic space group: $P2_1/c$, $Z = 2$), the unsymmetrical bis(thiosemicarbazone) lies on a crystallographic center of inversion. The carbon–carbon bond length between C5 and C6 is 1.478 (3) Å, which is exactly the same as the average bond length expected for a single bond between two sp^2 -hybridized carbon atoms. Other bond lengths are indicative of the presence of a conjugated system here as well.

In the crystal of KEBASC10 (monoclinic space group: $P2_1/c$, $Z = 8$), there are two molecules per asymmetric unit. The bis-hydrazinecarbothioamide motif is outstretched (*i.e.* not bent) and extends from one sulfur atom to the other as head and tail atoms. The molecule is approximately planar except for the side chain. The bond distances and angles are very similar in the two molecules of the asymmetric unit. There is an intramolecular N–H...O hydrogen bond, which stabilizes the molecular structure, similar to what is observed in the title compound. The packing of the molecule seems dominated by the formation of N–H...S hydrogen bonds. There is also one very short C–H...S intermolecular distance between the two molecules in the asymmetric unit, which may be strong enough to cause some distortion, in one molecule more than in the other. The tendency of molecules that are crystallographically independent but have opposite absolute configurations to associate may explain why they have co-crystallized in this case and why there are, hence, two independent molecules in the asymmetric unit.

In the crystal of RECKAP (triclinic space group: $P\bar{1}$, $Z = 2$), the compound is in the thione form yet resonant, which is supported by the C–S bond distances, which are intermediate between those of single and double bonds (1.82 and 1.56 Å, respectively) and the presence of the hydrazinic hydrogen H2.


Figure 7

The two-dimensional fingerprint plots of the title compound, showing (a) all interactions, and those delineated into (b) H...H, (c) S...H/H...S, (d) C...H/H...C and (e) N...H/H...N interactions. [d_e and d_i represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

The azomethine bonds both have a length of 1.29 Å, which is in accordance with double bonds. The N—N bonds are both shorter than 1.44 Å, which agrees well with those of similar thiosemicarbazones. The two arms of the molecule adopt the *E* configuration with respect to the central C3—C4 single bond and both azomethine nitrogen atoms N3 and N4 are in an *E* configuration relative to the thione sulfur atoms. The ligand is not planar and the two arms form an angle of 73.51°. The molecules are held together in the crystal through an extended network of intermolecular hydrogen bonds involving the amine nitrogen atoms N1 and N6 and the sulfur atoms.

All the molecules discussed here, including the title compound, adopt an *E* configuration of the hydrazine moieties attached to the central C—C bond. The differences in substitution do not affect this. However, the latter gives rise to a variation in the intermolecular interactions and can also result in distinct molecular shapes from the more common (almost) planar arrangement of the bis-hydrazinecarbothioamide motif to a substantial twisting to nearly perpendicular.

5. Synthesis and crystallization

Hydrazinecarbothioamide (0.380 g, 6.25 mmol) and 2-chloro-2-(diethoxymethyl)-3-phenyloxirane (1.600 g, 6.25 mmol) in 20 mL of methanol was refluxed for 2 h. After complete dissolution of hydrazinecarbothioamide, the mixture was stirred at room temperature for 24 h. The progress of the reaction was monitored by TLC in the system 9:1 chloroform:methanol $R_f = 0.53$. After completion of the reaction, the solvent was evaporated. The title compound was isolated by column chromatography in a 20:1 chloroform:methanol $R_f = 0.17$ system. The compound was obtained as a white solid in a yield of 0.689 g (34%); m.p. 421–423 K (with decomposition). Analysis calculated for $C_{12}H_{16}N_6OS_2$ ($M = 324.42$) C 44.43, H 4.97, N 25.91; found: C 44.35, H 4.90, N 25.94. 1H NMR (300 MHz, DMSO- d_6) δ 3.52 (3H, CH₃), 6.35 (1H, CH), 7.37–7.45 (5H, Ar), 8.15–8.68 (2H, NH), 10.74 (2H, NH₂), 10.80 (*s*, 2H, NH₂). ^{13}C NMR (200 MHz, DMSO- d_6) δ 57.13, 78.52, 126.22, 128.45, 136.79, 138.92, 144.20, 177.67, 178.18. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the DMF:methanol solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The C12(C12A)–C17(C17A) atoms in the C12–C17 phenyl ring are disordered over two sites with occupancies of 0.57 (4) and 0.43 (4), respectively. The N-bound hydrogen atoms were located in difference maps [$N1-H1A = 0.92$ (2), $N1-H1B = 0.92$ (2), $N3-H3 = 0.90$ (2), $N8-H8 = 0.88$ (2), $N10-H10A = 0.91$ (2) and $N10-H10B = 0.90$ (2) Å] and refined by constraining the N—H distances with SADI. All carbon-bound hydrogen atoms were positioned geometrically (C—H = 0.95–1.00 Å) and were included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{16}N_6OS_2 \cdot C_3H_7NO$
M_r	397.52
Crystal system, space group	Monoclinic, <i>Cc</i>
Temperature (K)	100
a, b, c (Å)	8.4573 (1), 23.5853 (3), 11.0072 (1)
β (°)	111.749 (2)
V (Å ³)	2039.29 (5)
Z	4
Radiation type	Cu $K\alpha$
μ (mm ⁻¹)	2.57
Crystal size (mm)	0.32 × 0.12 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Gaussian (<i>CrysAlis PRO</i> ; Rigaku OD, 2023)
T_{min}, T_{max}	0.658, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11141, 2776, 2751
R_{int}	0.030
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.634
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.088, 1.07
No. of reflections	2776
No. of parameters	317
No. of restraints	377
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.30, -0.27
Absolute structure	Classical Flack method preferred over Parsons because s.u. lower
Absolute structure parameter	0.000 (16)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2023), *SHELXT2019I* (Sheldrick, 2015a), *SHELXL2019I* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *PLATON* (Spek, 2020).

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The authors' contributions are as follows. Conceptualization, FIG, MA and AB; synthesis, AVK, EVS and KIK; X-ray analysis, AIS and ZA; writing (review and editing of the manuscript) FIG, MA and AB; supervision, FIG, MA and AB.

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supporting information

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Synthesis, crystal structure and Hirshfeld surface analysis of (2*Z*,2'*E*)-2,2'-(3-methoxy-3-phenylpropane-1,2-diylidene)bis(hydrazine-1-carbothioamide) dimethylformamide monosolvate

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Computing details

Data collection: *CrysAlis PRO* 1.171.42.91a (Rigaku OD, 2023); cell refinement: *CrysAlis PRO* 1.171.42.91a (Rigaku OD, 2023); data reduction: *CrysAlis PRO* 1.171.42.91a (Rigaku OD, 2023); program(s) used to solve structure: *SHELXT2019/1* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/1* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2020).

\ (2*Z*,2'*E*)-2,2'-(3-Methoxy-3-phenylpropane-1,2-diylidene)\ bis(2-methylhydrazine-1-carbothioamide) dimethylformamide monosolvate

Crystal data

$C_{12}H_{16}N_6OS_2 \cdot C_3H_7NO$
 $M_r = 397.52$
 Monoclinic, *Cc*
 $a = 8.4573$ (1) Å
 $b = 23.5853$ (3) Å
 $c = 11.0072$ (1) Å
 $\beta = 111.749$ (2)°
 $V = 2039.29$ (5) Å³
 $Z = 4$

$F(000) = 840$
 $D_x = 1.295$ Mg m⁻³
 Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
 Cell parameters from 9940 reflections
 $\theta = 3.7\text{--}77.6^\circ$
 $\mu = 2.57$ mm⁻¹
 $T = 100$ K
 Plate, colourless
 0.32 × 0.12 × 0.02 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
 diffractometer
 Radiation source: micro-focus sealed X-ray
 tube, PhotonJet (Cu) X-ray Source
 Mirror monochromator
 ω scans
 Absorption correction: gaussian
 (CrysAlisPro; Rigaku OD, 2023)
 $T_{\min} = 0.658$, $T_{\max} = 1.000$

11141 measured reflections
 2776 independent reflections
 2751 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\text{max}} = 77.8^\circ$, $\theta_{\text{min}} = 3.8^\circ$
 $h = -10 \rightarrow 10$
 $k = -29 \rightarrow 29$
 $l = -9 \rightarrow 13$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.088$ $S = 1.07$

2776 reflections

317 parameters

377 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.7217P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Absolute structure: Classical Flack method

preferred over Parsons because s.u. lower

Absolute structure parameter: 0.000 (16)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S2	0.28482 (9)	0.88049 (2)	0.35678 (8)	0.02715 (16)	
S9	0.62361 (9)	0.43859 (2)	0.67836 (8)	0.02788 (17)	
O18	0.3029 (2)	0.69867 (7)	0.22627 (17)	0.0208 (4)	
N1	0.3182 (3)	0.82853 (9)	0.5810 (2)	0.0250 (4)	
H1A	0.321 (5)	0.7946 (11)	0.623 (4)	0.035 (10)*	
H1B	0.277 (5)	0.8600 (14)	0.609 (4)	0.050 (12)*	
N3	0.3551 (3)	0.77463 (9)	0.4201 (2)	0.0193 (4)	
H3	0.338 (4)	0.7707 (16)	0.335 (2)	0.030 (9)*	
N4	0.3832 (3)	0.72789 (9)	0.4985 (2)	0.0194 (4)	
N7	0.5105 (3)	0.58678 (9)	0.5112 (2)	0.0206 (4)	
N8	0.5322 (3)	0.54302 (9)	0.5966 (2)	0.0237 (4)	
H8	0.494 (4)	0.5441 (15)	0.660 (3)	0.025 (8)*	
N10	0.6502 (3)	0.49254 (10)	0.4741 (3)	0.0304 (5)	
H10A	0.637 (4)	0.5197 (13)	0.412 (3)	0.028 (8)*	
H10B	0.689 (5)	0.4610 (13)	0.447 (4)	0.042 (10)*	
C2	0.3196 (3)	0.82596 (10)	0.4617 (3)	0.0196 (5)	
C5	0.4275 (3)	0.68202 (10)	0.4549 (2)	0.0178 (5)	
C6	0.4552 (3)	0.63348 (11)	0.5415 (3)	0.0211 (5)	
H6	0.432845	0.636140	0.619743	0.025*	
C9	0.6017 (3)	0.49391 (11)	0.5749 (3)	0.0245 (5)	
C11	0.4518 (3)	0.67600 (10)	0.3245 (2)	0.0180 (4)	
H11	0.462814	0.634948	0.306311	0.022*	
C12	0.6115 (14)	0.7087 (7)	0.3235 (18)	0.017 (2)	0.57 (4)
C13	0.7717 (16)	0.6857 (6)	0.3961 (17)	0.019 (2)	0.57 (4)
H13	0.781040	0.650478	0.440053	0.023*	0.57 (4)
C14	0.9181 (14)	0.7156 (8)	0.4026 (14)	0.025 (2)	0.57 (4)
H14	1.027777	0.700727	0.451350	0.030*	0.57 (4)
C15	0.9025 (17)	0.7670 (7)	0.3378 (13)	0.024 (2)	0.57 (4)

H15	1.001690	0.787616	0.343977	0.029*	0.57 (4)
C16	0.7452 (17)	0.7882 (6)	0.2650 (14)	0.0204 (19)	0.57 (4)
H16	0.736384	0.822536	0.217843	0.025*	0.57 (4)
C17	0.5977 (16)	0.7599 (7)	0.2590 (16)	0.0155 (19)	0.57 (4)
H17	0.488928	0.775672	0.211265	0.019*	0.57 (4)
C12A	0.618 (2)	0.7024 (9)	0.339 (2)	0.017 (3)	0.43 (4)
C13A	0.771 (2)	0.6743 (9)	0.411 (2)	0.022 (3)	0.43 (4)
H13A	0.769780	0.639161	0.452901	0.026*	0.43 (4)
C14A	0.9259 (19)	0.6998 (9)	0.4195 (19)	0.023 (2)	0.43 (4)
H14A	1.030313	0.681309	0.467394	0.027*	0.43 (4)
C15A	0.9282 (19)	0.7516 (9)	0.3588 (17)	0.020 (2)	0.43 (4)
H15A	1.033708	0.767984	0.365263	0.025*	0.43 (4)
C16A	0.780 (2)	0.7788 (8)	0.290 (2)	0.023 (3)	0.43 (4)
H16A	0.781356	0.814671	0.251521	0.028*	0.43 (4)
C17A	0.625 (2)	0.7534 (9)	0.277 (2)	0.021 (3)	0.43 (4)
H17A	0.521200	0.771477	0.225499	0.025*	0.43 (4)
C19	0.2808 (3)	0.67848 (12)	0.0984 (3)	0.0257 (5)	
H19A	0.191339	0.700524	0.032715	0.039*	
H19B	0.248038	0.638391	0.091007	0.039*	
H19C	0.387790	0.682681	0.084046	0.039*	
O24	0.2984 (3)	0.43619 (10)	0.2226 (3)	0.0449 (6)	
N20	0.1627 (4)	0.49731 (13)	0.3120 (3)	0.0405 (6)	
C21	0.0784 (5)	0.50587 (19)	0.4044 (5)	0.0551 (10)	
H21A	0.075716	0.469985	0.448488	0.083*	
H21B	-0.038264	0.519122	0.357418	0.083*	
H21C	0.140992	0.534251	0.469463	0.083*	
C22	0.1605 (5)	0.54375 (17)	0.2284 (4)	0.0503 (9)	
H22A	0.259076	0.541176	0.202153	0.075*	
H22B	0.165269	0.579467	0.275069	0.075*	
H22C	0.055571	0.542499	0.150377	0.075*	
C23	0.2273 (5)	0.44708 (17)	0.3000 (4)	0.0456 (8)	
H23	0.218115	0.417283	0.355074	0.055*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S2	0.0435 (3)	0.0159 (3)	0.0262 (3)	0.0076 (2)	0.0178 (3)	0.0043 (2)
S9	0.0488 (3)	0.0145 (3)	0.0281 (3)	0.0061 (2)	0.0234 (3)	0.0048 (2)
O18	0.0219 (7)	0.0219 (8)	0.0180 (9)	0.0023 (7)	0.0067 (6)	0.0003 (7)
N1	0.0383 (11)	0.0165 (9)	0.0250 (11)	0.0039 (8)	0.0172 (9)	0.0016 (9)
N3	0.0264 (9)	0.0145 (9)	0.0198 (10)	0.0028 (7)	0.0117 (8)	0.0030 (8)
N4	0.0233 (8)	0.0140 (9)	0.0230 (10)	0.0021 (7)	0.0112 (8)	0.0016 (8)
N7	0.0298 (9)	0.0144 (9)	0.0200 (10)	0.0022 (8)	0.0120 (8)	0.0017 (8)
N8	0.0390 (11)	0.0148 (10)	0.0236 (11)	0.0044 (9)	0.0191 (9)	0.0029 (9)
N10	0.0538 (14)	0.0157 (10)	0.0324 (13)	0.0092 (10)	0.0287 (11)	0.0052 (9)
C2	0.0205 (9)	0.0158 (11)	0.0232 (12)	0.0015 (8)	0.0090 (9)	-0.0009 (9)
C5	0.0221 (10)	0.0135 (10)	0.0192 (11)	0.0007 (8)	0.0093 (9)	0.0007 (8)
C6	0.0307 (11)	0.0158 (11)	0.0208 (11)	0.0010 (9)	0.0141 (9)	0.0012 (10)

C9	0.0345 (12)	0.0169 (12)	0.0248 (12)	0.0016 (9)	0.0141 (10)	0.0011 (10)
C11	0.0199 (9)	0.0165 (10)	0.0186 (11)	0.0023 (8)	0.0081 (8)	0.0007 (9)
C12	0.014 (3)	0.023 (5)	0.013 (4)	-0.002 (3)	0.005 (2)	0.002 (3)
C13	0.028 (3)	0.015 (4)	0.017 (4)	0.001 (2)	0.011 (2)	0.007 (3)
C14	0.020 (2)	0.031 (5)	0.023 (4)	0.004 (3)	0.007 (2)	0.004 (4)
C15	0.025 (4)	0.025 (5)	0.024 (4)	0.000 (3)	0.011 (3)	0.003 (3)
C16	0.025 (4)	0.021 (4)	0.017 (4)	-0.002 (3)	0.009 (3)	0.002 (3)
C17	0.019 (3)	0.016 (4)	0.013 (4)	0.000 (3)	0.008 (3)	0.004 (2)
C12A	0.033 (5)	0.013 (4)	0.011 (5)	0.004 (3)	0.014 (3)	0.000 (3)
C13A	0.019 (3)	0.028 (6)	0.020 (5)	0.004 (3)	0.008 (3)	0.005 (4)
C14A	0.023 (3)	0.025 (6)	0.021 (5)	0.003 (4)	0.008 (3)	0.004 (4)
C15A	0.018 (3)	0.022 (6)	0.020 (5)	0.002 (4)	0.006 (3)	-0.004 (4)
C16A	0.030 (5)	0.021 (5)	0.018 (5)	-0.004 (4)	0.009 (4)	0.003 (4)
C17A	0.022 (4)	0.020 (5)	0.019 (6)	0.008 (4)	0.006 (4)	0.001 (4)
C19	0.0297 (11)	0.0270 (13)	0.0184 (12)	0.0000 (10)	0.0065 (10)	-0.0003 (10)
O24	0.0539 (13)	0.0453 (14)	0.0487 (15)	0.0031 (11)	0.0343 (12)	0.0024 (11)
N20	0.0429 (13)	0.0399 (15)	0.0428 (16)	-0.0030 (11)	0.0206 (12)	-0.0034 (13)
C21	0.056 (2)	0.060 (2)	0.060 (3)	-0.0086 (19)	0.0335 (19)	-0.013 (2)
C22	0.0547 (19)	0.0407 (18)	0.059 (2)	-0.0030 (16)	0.0248 (17)	0.0019 (18)
C23	0.0524 (18)	0.0432 (18)	0.050 (2)	-0.0031 (15)	0.0299 (17)	-0.0010 (16)

Geometric parameters (Å, °)

S2—C2	1.680 (3)	C15—C16	1.368 (9)
S9—C9	1.697 (3)	C15—H15	0.9500
O18—C11	1.426 (3)	C16—C17	1.394 (9)
O18—C19	1.430 (3)	C16—H16	0.9500
N1—C2	1.319 (4)	C17—H17	0.9500
N1—H1A	0.92 (2)	C12A—C17A	1.390 (14)
N1—H1B	0.92 (2)	C12A—C13A	1.407 (13)
N3—N4	1.365 (3)	C13A—C14A	1.413 (13)
N3—C2	1.366 (3)	C13A—H13A	0.9500
N3—H3	0.90 (2)	C14A—C15A	1.398 (12)
N4—C5	1.294 (3)	C14A—H14A	0.9500
N7—C6	1.288 (3)	C15A—C16A	1.361 (12)
N7—N8	1.362 (3)	C15A—H15A	0.9500
N8—C9	1.360 (3)	C16A—C17A	1.401 (13)
N8—H8	0.88 (2)	C16A—H16A	0.9500
N10—C9	1.318 (4)	C17A—H17A	0.9500
N10—H10A	0.91 (2)	C19—H19A	0.9800
N10—H10B	0.90 (2)	C19—H19B	0.9800
C5—C6	1.452 (3)	C19—H19C	0.9800
C5—C11	1.530 (3)	O24—C23	1.238 (4)
C6—H6	0.9500	N20—C23	1.332 (5)
C11—C12A	1.492 (19)	N20—C22	1.426 (5)
C11—C12	1.558 (13)	N20—C21	1.456 (5)
C11—H11	1.0000	C21—H21A	0.9800
C12—C17	1.384 (10)	C21—H21B	0.9800

C12—C13	1.402 (10)	C21—H21C	0.9800
C13—C14	1.404 (10)	C22—H22A	0.9800
C13—H13	0.9500	C22—H22B	0.9800
C14—C15	1.387 (9)	C22—H22C	0.9800
C14—H14	0.9500	C23—H23	0.9500
C11—O18—C19	112.21 (18)	C15—C16—H16	119.6
C2—N1—H1A	117 (3)	C17—C16—H16	119.6
C2—N1—H1B	121 (3)	C12—C17—C16	119.3 (8)
H1A—N1—H1B	119 (4)	C12—C17—H17	120.3
N4—N3—C2	120.8 (2)	C16—C17—H17	120.3
N4—N3—H3	120 (2)	C17A—C12A—C13A	119.3 (13)
C2—N3—H3	118 (2)	C17A—C12A—C11	121.0 (13)
C5—N4—N3	116.6 (2)	C13A—C12A—C11	119.7 (13)
C6—N7—N8	116.0 (2)	C12A—C13A—C14A	118.2 (12)
C9—N8—N7	118.7 (2)	C12A—C13A—H13A	120.9
C9—N8—H8	119 (2)	C14A—C13A—H13A	120.9
N7—N8—H8	123 (2)	C15A—C14A—C13A	121.2 (10)
C9—N10—H10A	128 (2)	C15A—C14A—H14A	119.4
C9—N10—H10B	124 (3)	C13A—C14A—H14A	119.4
H10A—N10—H10B	107 (4)	C16A—C15A—C14A	120.2 (10)
N1—C2—N3	117.3 (2)	C16A—C15A—H15A	119.9
N1—C2—S2	125.8 (2)	C14A—C15A—H15A	119.9
N3—C2—S2	116.9 (2)	C15A—C16A—C17A	119.5 (11)
N4—C5—C6	114.5 (2)	C15A—C16A—H16A	120.3
N4—C5—C11	125.7 (2)	C17A—C16A—H16A	120.3
C6—C5—C11	119.8 (2)	C12A—C17A—C16A	121.7 (12)
N7—C6—C5	119.3 (2)	C12A—C17A—H17A	119.2
N7—C6—H6	120.3	C16A—C17A—H17A	119.2
C5—C6—H6	120.3	O18—C19—H19A	109.5
N10—C9—N8	117.3 (2)	O18—C19—H19B	109.5
N10—C9—S9	123.8 (2)	H19A—C19—H19B	109.5
N8—C9—S9	118.9 (2)	O18—C19—H19C	109.5
O18—C11—C12A	117.2 (9)	H19A—C19—H19C	109.5
O18—C11—C5	106.77 (19)	H19B—C19—H19C	109.5
C12A—C11—C5	108.1 (10)	C23—N20—C22	121.8 (3)
O18—C11—C12	109.5 (6)	C23—N20—C21	121.2 (3)
C5—C11—C12	112.3 (8)	C22—N20—C21	116.8 (3)
O18—C11—H11	109.4	N20—C21—H21A	109.5
C5—C11—H11	109.4	N20—C21—H21B	109.5
C12—C11—H11	109.4	H21A—C21—H21B	109.5
C17—C12—C13	120.6 (9)	N20—C21—H21C	109.5
C17—C12—C11	121.8 (9)	H21A—C21—H21C	109.5
C13—C12—C11	117.5 (9)	H21B—C21—H21C	109.5
C12—C13—C14	118.9 (8)	N20—C22—H22A	109.5
C12—C13—H13	120.6	N20—C22—H22B	109.5
C14—C13—H13	120.6	H22A—C22—H22B	109.5
C15—C14—C13	119.9 (8)	N20—C22—H22C	109.5

C15—C14—H14	120.1	H22A—C22—H22C	109.5
C13—C14—H14	120.1	H22B—C22—H22C	109.5
C16—C15—C14	120.5 (8)	O24—C23—N20	125.1 (4)
C16—C15—H15	119.8	O24—C23—H23	117.5
C14—C15—H15	119.8	N20—C23—H23	117.5
C15—C16—C17	120.8 (8)		
C2—N3—N4—C5	-175.4 (2)	C5—C11—C12—C13	73.3 (16)
C6—N7—N8—C9	-175.4 (2)	C17—C12—C13—C14	0 (3)
N4—N3—C2—N1	1.7 (3)	C11—C12—C13—C14	-176.8 (14)
N4—N3—C2—S2	-179.27 (16)	C12—C13—C14—C15	0 (2)
N3—N4—C5—C6	-179.78 (19)	C13—C14—C15—C16	-1.5 (19)
N3—N4—C5—C11	0.4 (3)	C14—C15—C16—C17	2.8 (19)
N8—N7—C6—C5	-179.5 (2)	C13—C12—C17—C16	1 (3)
N4—C5—C6—N7	-175.5 (2)	C11—C12—C17—C16	178.0 (14)
C11—C5—C6—N7	4.3 (3)	C15—C16—C17—C12	-3 (2)
N7—N8—C9—N10	2.6 (4)	O18—C11—C12A—C17A	12 (2)
N7—N8—C9—S9	-178.22 (17)	C5—C11—C12A—C17A	-109 (2)
C19—O18—C11—C12A	79.2 (11)	O18—C11—C12A—C13A	-165.2 (16)
C19—O18—C11—C5	-159.5 (2)	C5—C11—C12A—C13A	74 (2)
C19—O18—C11—C12	78.8 (8)	C17A—C12A—C13A—C14A	1 (3)
N4—C5—C11—O18	-50.3 (3)	C11—C12A—C13A—C14A	178.2 (18)
C6—C5—C11—O18	129.9 (2)	C12A—C13A—C14A—C15A	0 (3)
N4—C5—C11—C12A	76.6 (9)	C13A—C14A—C15A—C16A	0 (2)
C6—C5—C11—C12A	-103.2 (9)	C14A—C15A—C16A—C17A	-2 (2)
N4—C5—C11—C12	69.6 (6)	C13A—C12A—C17A—C16A	-3 (4)
C6—C5—C11—C12	-110.1 (6)	C11—C12A—C17A—C16A	179.8 (19)
O18—C11—C12—C17	14.8 (19)	C15A—C16A—C17A—C12A	4 (3)
C5—C11—C12—C17	-103.6 (16)	C22—N20—C23—O24	4.0 (6)
O18—C11—C12—C13	-168.3 (13)	C21—N20—C23—O24	178.9 (4)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots N4	0.92 (3)	2.27 (4)	2.670 (3)	106 (3)
N1—H1B \cdots S9 ⁱ	0.92 (4)	2.54 (4)	3.450 (2)	172 (4)
N3—H3 \cdots O18	0.90 (2)	2.04 (3)	2.694 (3)	129 (3)
N8—H8 \cdots O24 ⁱⁱ	0.87 (3)	2.07 (4)	2.847 (4)	149 (3)
N10—H10A \cdots S9 ⁱⁱⁱ	0.91 (3)	2.72 (3)	3.570 (3)	156 (3)
N10—H10B \cdots S2 ^{iv}	0.91 (4)	2.42 (4)	3.322 (3)	175 (4)
C6—H6 \cdots O24 ⁱⁱ	0.95	2.54	3.224 (4)	129
C11—H11 \cdots N7	1.00	2.42	2.853 (3)	105
C11—H11 \cdots S9 ⁱⁱⁱ	1.00	2.87	3.706 (2)	141
C17—H17 \cdots O18	0.95	2.45	2.787 (16)	101
C21—H21B \cdots S9 ^v	0.98	2.98	3.951 (5)	171

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