



Crystal structure and Hirshfeld surface analysis of two (*E*)-*N'*-(*para*-substituted benzylidene) 4-chlorobenzenesulfonohydrazides

Akshatha R. Salian,^a Sabine Foro^b and B. Thimme Gowda^{a,c,*}

Received 22 October 2018
Accepted 9 November 2018

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; hydrazones; *N'*-(arylidene)arylsulfonohydrazides; hydrogen bonding; graph-set motif; Hirshfeld surface analysis; fingerprint plots.

CCDC references: 1578709; 1578704

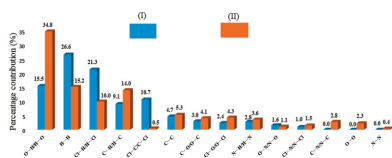
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartment of Chemistry, Mangalore University, Mangalagangotri-574 199, India, ^bInstitute of Materials Science, Darmstadt University of Technology, Alarich-Weiss-Str. 2, D-64287, Darmstadt, Germany, and ^cKarnataka State Rural Development and Panchayat Raj University, Gadag-582101, India. *Correspondence e-mail: gowdabt@yahoo.com

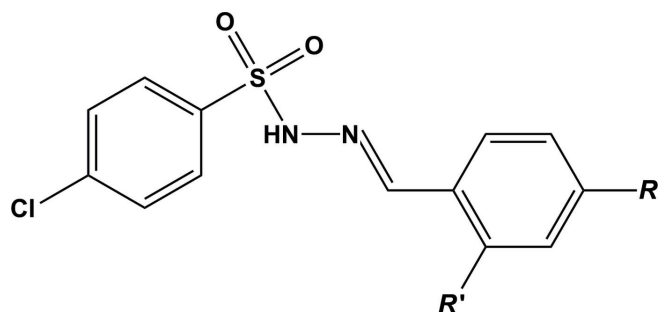
Two (*E*)-*N'*-(*p*-substituted benzylidene)-4-chlorobenzenesulfonohydrazides, namely, (*E*)-4-chloro-*N'*-(4-chlorobenzylidene)benzenesulfonohydrazide, C₁₃H₁₀Cl₂N₂O₂S, (I), and (*E*)-4-chloro-*N'*-(4-nitrobenzylidene)benzenesulfonohydrazide, C₁₃H₁₀ClN₃O₄S, (II), have been synthesized, characterized and their crystal structures studied to explore the effect of the nature of substituents on the structural parameters. Compound (II) crystallized with two independent molecules [(IIA) and (IIB)] in the asymmetric unit. In both compounds, the configuration around the C=N bond is *E*. The molecules are twisted at the S atom with C—S—N—N torsion angles of −62.4 (2)° in (I), and −46.8 (2)° and 56.8 (2)° in the molecules *A* and *B* of (II). The 4-chlorophenylsulfonyl and 4-substituted benzylidene rings form dihedral angles of 81.0 (1)° in (I), 75.9 (1)° in (IIA) and 73.4 (1)° in (IIB). In the crystal of (I), molecules are linked *via* pairs of N—H···O hydrogen bonds, forming inversion dimers with an *R*₂²(8) ring motif. The dimers are linked by C—Cl···π interactions, forming a three-dimensional structure. In the crystal of (II), molecules are linked by C—H···π interactions and N—H···O hydrogen bonds, forming *−A−B−A−B−* chains along the *c*-axis direction. The chains are linked *via* C—H···O and C—H···π interactions, forming layers parallel to the *bc* plane. Two-dimensional fingerprint plots show that the most significant contacts contributing to the Hirshfeld surface for (I) are H···H contacts (26.6%), followed by Cl···H/H···Cl (21.3%), O···H/H···O (15.5%) and Cl···C/C···Cl (10.7%), while for (II) the O···H/H···O contacts are dominant, with a contribution of 34.8%, followed by H···H (15.2%), C···H/H···C (14.0%) and Cl···H/H···Cl (10.0%) contacts.

1. Chemical context

In the field of synthetic chemistry, hydrazones are frequently used as nucleophiles and electrophiles (Ogawa *et al.*, 2004). They also play an important role in organic synthesis as one of the reaction intermediates due to their ring-closure reactions (Rollas & Küçükgülzel, 2007). Hydrazones have drawn considerable attention in the field of coordination chemistry (Weber *et al.*, 2007). They also find various industrial applications (Reis *et al.*, 2013) and exhibit a wide spectrum of biological activities (da Silva *et al.*, 2011). Arylsulfonylhydrazones have shown antitumour activity in addition to their role as a versatile source of diazo compounds in many metal-catalysed and metal-free reactions (Hashemi, 2012). In a continuation of our efforts to explore the effect of site and nature of substituents on the crystal structures of 4-chloro-arylsulfonohydrazide derivatives (Salian *et al.*, 2018), we report herein the synthesis, characterization, crystal structures



and Hirshfeld surface analysis of the title compounds, (I) and (II), and compare them with those of the recently reported structures of (*E*)-4-chloro-*N'*-(benzylidene) benzenesulfonylhydrazide (III), (*E*)-4-chloro-*N'*-(2-methylbenzylidene)benzenesulfonylhydrazide (IV) and (*E*)-4-chloro-*N'*-(4-methylbenzylidene)benzenesulfonylhydrazide (V) (Salian *et al.*, 2018).



- (I) $R = \text{Cl}$, $R' = \text{H}$
 (II) $R = \text{NO}_2$, $R' = \text{H}$
 (III) $R = \text{H}$, $R' = \text{H}$
 (IV) $R = \text{H}$, $R' = \text{CH}_3$
 (V) $R = \text{CH}_3$, $R' = \text{H}$

2. Structural commentary

Compound (I), crystallizes in the triclinic crystal system, space group $P\bar{1}$, with one molecule in the asymmetric unit (Fig. 1), while compound (II) crystallizes in the monoclinic crystal system, space group $P2_1/c$, with two independent molecules [(IIA) and (IIB)] in the asymmetric unit (Fig. 2). For both the compounds, the configuration about the C=N bond is *E* and the conformations of the N—H and C—H bonds in the hydrazone segments are *syn* to each other.

The C=N bond lengths of 1.269 (3), 1.269 (3) and 1.269 (3) Å in (I), (IIA) and (IIB), and the N—N bond lengths of 1.388 (2), 1.397 (3) and 1.390 (2) Å in (I), (IIA) and (IIB), respectively, indicate the delocalization of the π -electron density over the hydrazone part of the molecules. The other bond lengths are in close agreement with those of the parent compound (III), and the *ortho*-methyl (IV) and *para*-methyl

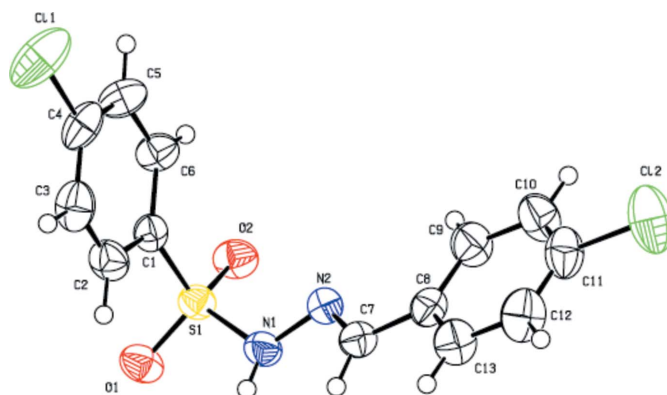


Figure 1
Molecular structure of (I), with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

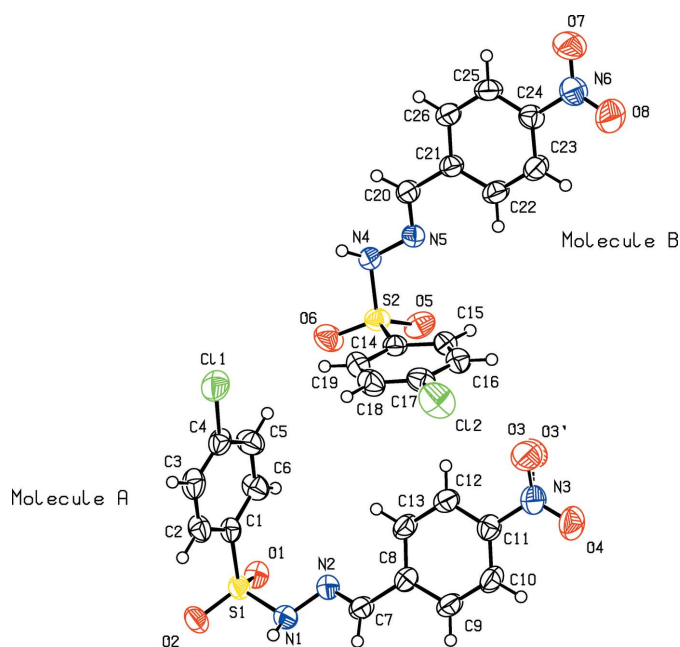


Figure 2
Molecular structure of (II), with the atom labelling and displacement ellipsoids drawn at the 50% probability level.

(V) derivatives (Salian *et al.*, 2018). Selected geometrical parameters of compounds (I)–(V) are compared in Table 1 (Salian *et al.*, 2018).

Table 1

Comparison of selected geometrical parameters (Å, °) of compounds (I)–(V).

The dihedral angle is that between the aromatic rings. The equivalent bond lengths and torsion angles are given for (IIB).

Bond length	(I)	(II) Molecule A	(II) Molecule B	(III)	(IV)	(V)
C1—S1	1.763 (2)	1.754 (2)	1.760 (2)	1.752 (4)	1.751 (5)	1.761 (2)
S1—N1	1.631 (2)	1.645 (2)	1.641 (2)	1.644 (4)	1.645 (4)	1.625 (2)
N1—N2	1.388 (2)	1.397 (3)	1.390 (2)	1.394 (5)	1.407 (5)	1.393 (2)
N2—C7	1.269 (3)	1.269 (3)	1.269 (3)	1.258 (5)	1.272 (5)	1.273 (3)
C7—C8	1.463 (3)	1.465 (3)	1.462 (3)	1.473 (6)	1.461 (6)	1.458 (3)
Torsion angle						
C1—S1—N1—N2	−62.4 (2)	−46.8 (2)	56.8 (2)	−66.0 (3)	−66.0 (3)	−58.4 (2)
S1—N1—N2—C7	158.9 (2)	171.4 (2)	−165.3 (2)	166.5 (3)	165.4 (3)	157.9 (2)
N1—N2—C7—C8	175.0 (2)	−175.9 (2)	178.2 (2)	177.8 (4)	175.8 (4)	175.8 (2)
Dihedral angle	81.0 (1)	75.9 (1)	73.4 (1)	78.4 (2)	74.8 (2)	76.9 (1)

In the title compounds the molecules are twisted at the S atom with C–S–N–N torsion angles of $-62.4(2)^\circ$ in (I), and $-46.8(2)$ and $56.8(2)^\circ$ in (IIA) and (IIB), respectively. The respective S–N–N=C torsion angles of $158.9(2)^\circ$ in (I), and $171.4(2)$ and $-165.3(2)^\circ$ in (IIA) and (IIB), denote the non-planarity of the sulfonylhydrazone parts of the molecules. However, the N–N–C–C torsion angles of $175.0(2)^\circ$ in (I), and $-175.9(2)$ and $178.2(2)^\circ$ in (IIA) and (IIB), indicate near coplanarity of the hydrazone units with the benzylidene rings. The dihedral angles between the 4-chloro-substituted phenylsulfonyl ring and 4-substituted benzylidene ring are $81.0(1)^\circ$ in (I), and $75.9(1)$ and $73.4(1)^\circ$ in molecules A and B of compound (II). In comparison, the corresponding values in compounds (III), (IV) and (V) are $78.4(2)$, $74.8(2)$ and $76.9(1)^\circ$, respectively (see Table 1). In (II) the A and B molecules are linked by a C–H \cdots Cl interaction (Table 3).

3. Supramolecular features

The pattern of the hydrogen-bonding interactions in the crystal structures of (I) and (II) are different. In the crystal of (I), molecules are linked by pairs of N–H \cdots O hydrogen bonds, forming inversion dimers enclosing $R_2^2(8)$ loops (Fig. 3, Table 2). The dimers are linked by C–Cl \cdots π interactions, forming a three-dimensional arrangement (Fig. 3). This is very similar to the situation observed in the crystal of compound (V) [(*E*)-4-chloro-*N'*-(4-methylbenzylidene)benzenesulfonylhydrazone; Salian *et al.*, 2018].

Replacement of the 4-chloro group in (I) by the 4-nitro group to produce compound (II) introduces C–H \cdots O interactions, which stabilize the crystal packing (Table 3 and

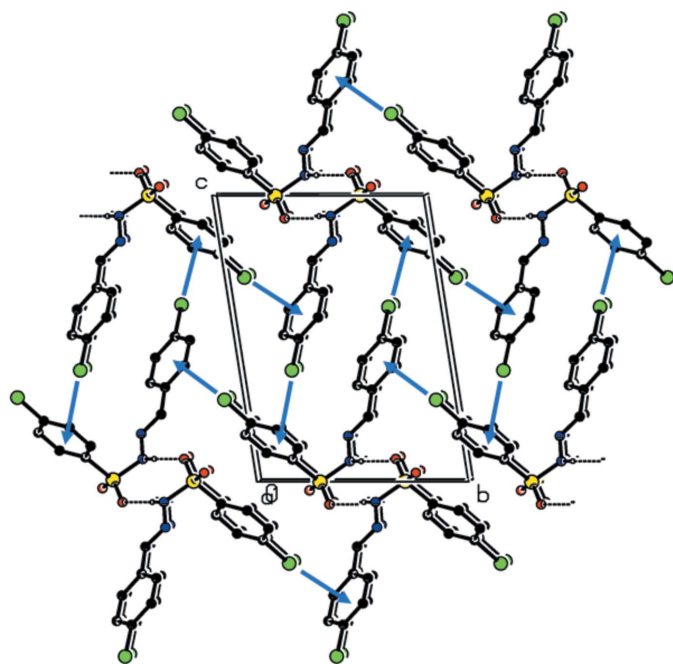


Figure 3
Crystal packing of (I), viewed along the *a* axis, with hydrogen bonds (Table 2) shown as dashed lines and C–Cl \cdots π interactions as blue arrows. C-bound H atoms have been omitted.

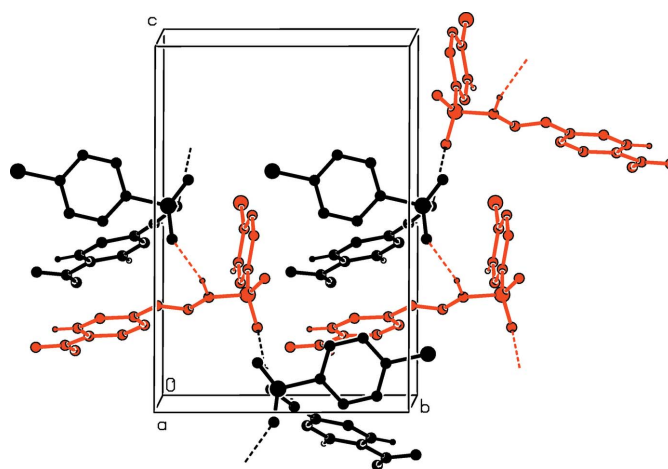


Figure 4
A partial view along the *a* axis of the crystal packing of (II), with hydrogen bonds (Table 3) shown as dashed lines. H atoms not involved in these interactions have been omitted. Colour code: black A molecules; red B molecules.

Figs. 4 and 5). The N–H \cdots O hydrogen bond involving the sulfonyl O atom and the amino H atom of the hydrazone segment between the A and B molecules results in the formation of $-A-B-A-B-$ chains propagating along the *c*-axis direction (Fig. 4). The chains are linked by C–H \cdots O interactions involving O atoms O4 in (IIA) and O5 in (IIB) and O7 of the nitro group and the aromatic hydrogen atoms *ortho* to the Cl or NO₂ group. The sulfonyl O atom of (IIB), *i.e.* O5,

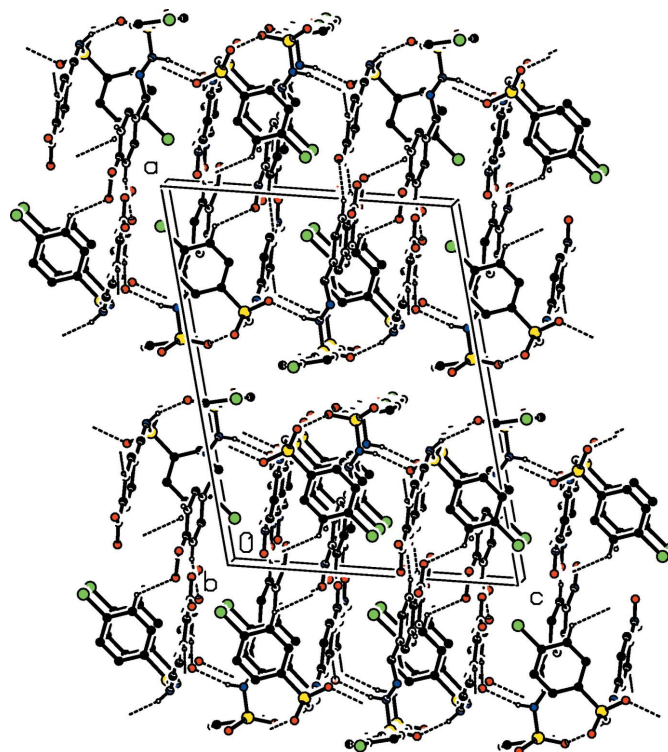


Figure 5
Crystal packing of (II), viewed along the *b* axis, with hydrogen bonds shown as dashed lines. H atoms not involved in these interactions have been omitted.

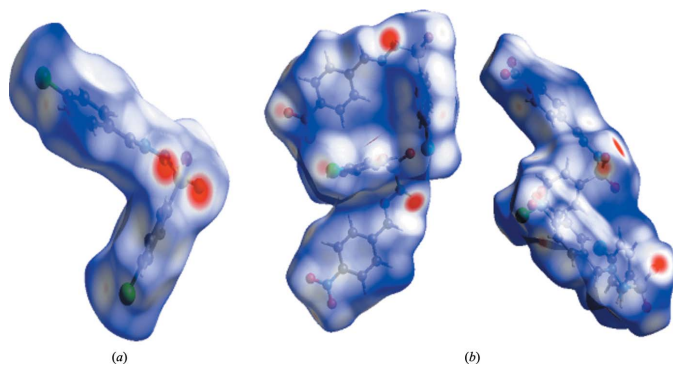


Figure 6
(a) View of the Hirshfeld surface mapped over d_{norm} for (I); (b) two views of the Hirshfeld surface mapped over d_{norm} for (II).

shows bifurcated hydrogen bonding, one with the amino H atom of the hydrazide segment and the other with one of the aromatic H atoms (H25), adjacent to the nitro group. These interactions link the chains, forming layers lying parallel to the bc plane (Table 3 and Fig. 5).

4. Hirshfeld surface analysis

Hirshfeld surfaces and two-dimensional fingerprint plots were generated for the two substituted compounds (I) and (II) using *CrystalExplorer* (Turner *et al.*, 2017) to visualize the intermolecular interactions, to investigate the impact of each kind of intermolecular contact on the crystal packing and to study the relative strengths of the different interactions in the two compounds. The molecular Hirshfeld surfaces were generated using a standard (high) surface resolution. d_i and d_e are the contact distances from the Hirshfeld surface to the nearest atom inside and outside, respectively [Fig. 6(a) for (I) and Fig. 6(b) for (II)]. The strong hydrogen bonds appear as dark-red spots and weak interactions as light-red spots on the

Table 2
Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$Cg1$ and $Cg2$ are the centroids of rings C1–C6 and C8–C13, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots O1^i$	0.83 (2)	2.07 (2)	2.903 (2)	178 (2)
$C4-C11\cdots Cg2^{ii}$	1.73 (1)	3.41 (1)	5.112 (2)	166 (1)
$C11-C12\cdots Cg1^{iii}$	1.74 (1)	3.65 (1)	5.372 (3)	171 (1)

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

Table 3
Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$Cg3$ is the centroid of the C14–C19 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1N\cdots O5^i$	0.85 (2)	2.06 (2)	2.887 (3)	163 (2)
$N4-H4N\cdots O1^{ii}$	0.84 (2)	2.13 (2)	2.918 (2)	157 (2)
$C10-H10\cdots O7^{iii}$	0.93	2.58	3.465 (3)	159
$C16-H16\cdots O4^{iv}$	0.93	2.58	3.259 (3)	131
$C25-H25\cdots O5^{ii}$	0.93	2.45	3.340 (3)	161
$C12-H12\cdots Cg3$	0.93	2.96	3.843 (2)	160

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

d_{norm} surface (McKinnon *et al.*, 2004; Spackman & Jayatilaka, 2009).

Comparison of fingerprint plots for various atom–atom interactions show that the percentage contributions of these interactions to the Hirshfeld surfaces vary significantly from (I) to (II). The major contribution to the Hirshfeld surface in (I) is from $H\cdots H$ contacts (26.6%), followed by $Cl\cdots H/H\cdots Cl$ (21.3%), $O\cdots H/H\cdots O$ (15.5%), $Cl\cdots C/C\cdots Cl$ (10.7%) and $C\cdots H/H\cdots C$ (9.1%) [Fig. 7(a)], while in (II), as a result of $C-H\cdots O$ interactions, $O\cdots H/H\cdots O$ contacts are dominant and serve as the major contributors (34.8%) in the crystal packing, followed by $H\cdots H$ contacts (15.2%), $C\cdots H/H\cdots C$ (14.0%) and $Cl\cdots H/H\cdots Cl$ (10.0%) [Fig. 7(b)]. The $Cl\cdots C/C\cdots Cl$ contribution to the d_{norm} surface is almost

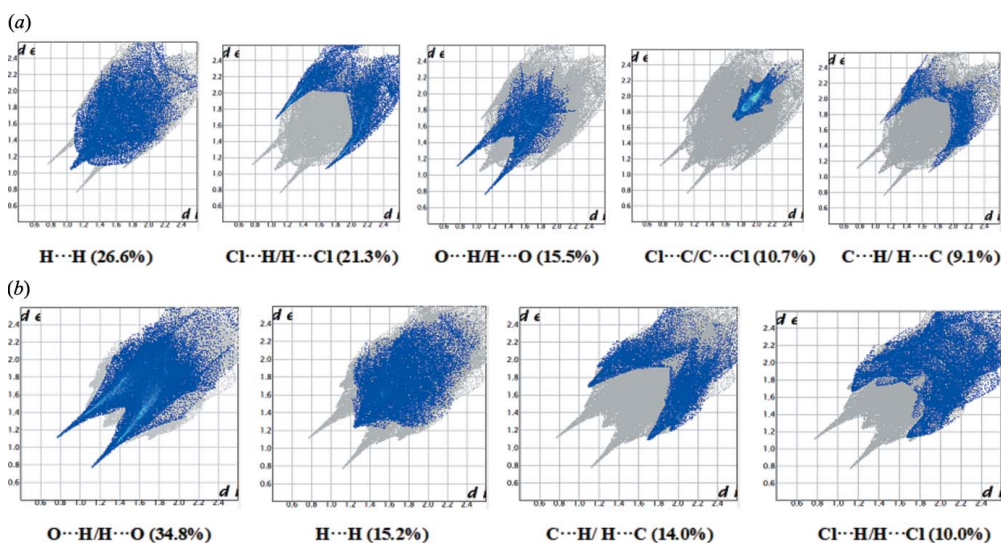


Figure 7
Two-dimensional fingerprint plots for (a) (I) and (b) (II). d_i is the closest internal distance from a given point on the Hirshfeld surface and d_e is the closest external contact.

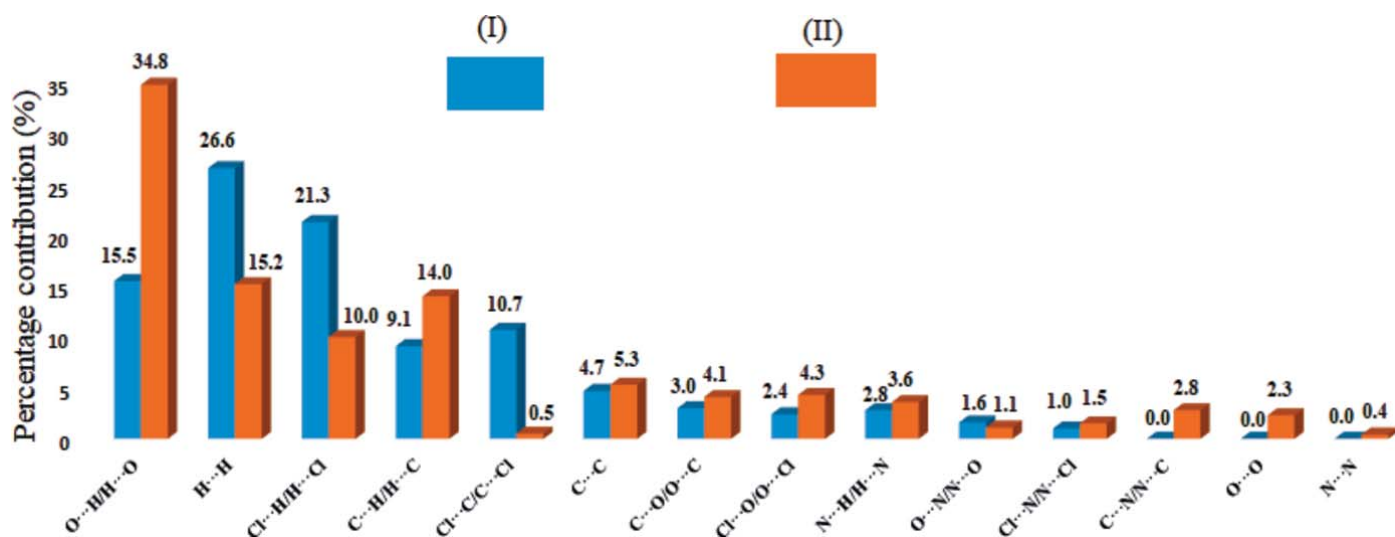


Figure 8
Quantitative results of different intermolecular interactions contributing to the Hirshfeld surfaces of (I) and (II).

negligible (0.5%) in (II). However, C...C, H...N/N...H and C...O/O...C contacts make very similar contributions in the two compounds, their respective contributions being 4.7, 2.8, 3.0%, in (I) and 5.3, 3.6 and 4.1% in (II). Two pairs of symmetrical, long narrow spikes are present at $d_i + d_e \sim 2.2$ Å for the O...H/H...O contacts in the fingerprint plots of (I) and (II) and these values are very close to the H...A distances for the N—H...O hydrogen bonds observed in the crystal structures (Tables 2 and 3). The contributions of the other weak intermolecular contacts to the Hirshfeld surfaces are: Cl...N/N...Cl (1.0 and 1.5%), C...N/N...C (0.0 and 2.8%), O...O (0, 2.3%), N...N (0, 0.4%) in (I) and (II), respectively. The result of the quantitative analysis of all types of intermolecular contacts present in (I) and (II) is summarized in Fig. 8.

5. Database survey

The structures reported in the literature similar to the title compounds include (*E*)-*N'*-(4-chlorobenzylidene)-*p*-toluenesulfonohydrazide 0.15-hydrate (Kia *et al.*, 2009a), (*E*)-*N'*-(4-chlorobenzylidene)-*p*-toluenesulfonohydrazide (Balaji *et al.*, 2014), (*E*)-*N'*-(4-bromobenzylidene)-*p*-toluenesulfonohydrazide (Kia *et al.*, 2009b), (*E*)-*N'*-(4-nitrobenzylidene)benzenesulfonohydrazide (Hussain *et al.*, 2017a) and (*E*)-4-methyl-*N'*-(4-nitrobenzylidene)benzenesulfonohydrazide (Hussain *et al.*, 2017b). In all of these structures, intermolecular N—H...O hydrogen bonds link neighbouring molecules to form chains, which are linked by C—H...O hydrogen bonds. There are also intermolecular π - π interactions present, which further stabilize the crystal structures.

6. Synthesis and crystallization

Synthesis of 4-chlorobenzenesulfonohydrazide

4-Chlorobenzenesulfonohydrazide was synthesized by a recently reported procedure (Salian *et al.*, 2018).

Synthesis of compounds (I) and (II)

A mixture of 4-chlorobenzenesulfonohydrazide (0.01 mol) and 4-chlorobenzaldehyde (0.01 mol) for (I), and 4-nitrobenzaldehyde (0.01 mol) for (II), in ethanol (30 ml) and two drops of glacial acetic acid were stirred for 4 h. The reaction mixtures were cooled to room temperature and concentrated by evaporating off the excess of solvent. The solid products obtained were washed with cold water, dried and recrystallized to constant melting points from ethanol to obtain the pure compounds. The purity of the compounds was checked by TLC.

Crystals of compounds (I) and (II), suitable for X-ray diffraction analysis, were obtained by slow evaporation of their DMF solutions at room temperature.

Both compounds were characterized by measuring their IR, ^1H and ^{13}C NMR spectra.

(*E*)-4-Chloro-*N'*-(4-chlorobenzylidene)benzenesulfonohydrazide (I)

Colourless rod-shaped crystals; m.p. 432–433 K; IR (cm^{-1}): 3180.6 (N—H asym. stretch), 1573.9 (C=N), 1327.0 (S=O asym. stretch) and 1166.9 (S=O sym. stretch).

^1H NMR (400 MHz, DMSO- d_6): δ 7.32 (*d*, 1H, $J = 8.4$ Hz, Ar-H), 7.51–7.56 (*m*, 4H, Ar-H), 7.87–7.89 (*m*, 2H, Ar-H), 7.92 (*s*, 1H), 11.50 (*s*, 1H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 128.38, 129.42, 130.73, 132.06, 134.96, 137.47, 138.39, 139.32, 145.66.

(*E*)-4-Chloro-*N'*-(4-nitrobenzylidene)benzenesulfonohydrazide (II)

Yellow rod-shaped crystals; m.p. 414–415 K; IR (cm^{-1}): 3093.8 (N—H asym. stretch), 1653.0 (C=N), 1392.6 (S=O asym. stretch) and 1153.4 (S=O sym. stretch).

^1H NMR (400 MHz, DMSO- d_6): δ 7.0 (*d*, 1H, $J = 8.80$, Ar-H), 7.38 (*d*, 1H, $J = 8.52$, Ar-H), 7.63 (*d*, 1H, $J = 8.36$, Ar-H), 7.64 (*s*, 1H), 7.79 (*d*, 1H, $J = 8.56$, Ar-H), 7.80 (*d*, 2H, $J = 8.28$, Ar-H), 7.90 (*s*, 1H), 11.60 (*s*, 1H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 115.49, 124.47, 128.45, 129.63, 136.85, 137.87, 138.28, 147.97, 159.43.

Table 4
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	C ₁₃ H ₁₀ Cl ₂ N ₂ O ₂ S	C ₁₃ H ₁₀ ClN ₃ O ₄ S
M_r	329.19	339.75
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Temperature (K)	293	293
a, b, c (Å)	5.9306 (6), 9.477 (1), 13.040 (2)	19.903 (1), 10.2517 (7), 15.064 (1)
α, β, γ (°)	98.822 (9), 96.046 (9), 92.416 (9)	90, 103.929 (7), 90
V (Å ³)	718.94 (15)	2983.3 (3)
Z	2	8
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.60	0.42
Crystal size (mm)	0.48 × 0.40 × 0.36	0.48 × 0.40 × 0.36
Data collection		
Diffractometer	Oxford Diffraction Xcalibur diffractometer with Sapphire CCD	Oxford Diffraction Xcalibur diffractometer with Sapphire CCD
Absorption correction	Multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2009)	Multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2009)
T_{\min}, T_{\max}	0.762, 0.814	0.825, 0.864
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4153, 2626, 2321	19194, 5455, 4247
R_{int}	0.016	0.025
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.602	0.602
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.102, 1.08	0.038, 0.101, 1.02
No. of reflections	2626	5455
No. of parameters	185	414
No. of restraints	1	15
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.37, -0.35	0.43, -0.38

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. C-bound H atoms were positioned with idealized geometry and refined using a riding model: C—H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The amino H atoms were located in difference-Fourier maps and refined with an N—H distance restraint of 0.86 (2) Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. In (I), reflection 011 was masked by the beam stop and omitted from the refinement. In (II), atom O3 is disordered and was refined using a split model. The corresponding site-occupation factors were fixed at 0.55:0.45 and the corresponding N—O bond lengths in the disordered group were restrained to be equal. The U^{ij} components of O3 and O3' were restrained to be approximately isotropic.

Acknowledgements

The authors thank SAIF Panjab University for extending the services of their NMR facility and Mangalore University for providing all the facilities required.

Funding information

ARS thanks the Department of Science and Technology, Government of India, New Delhi, for a research fellowship under its DST-PURSE Program and BTG thanks the University Grants Commission, Government of India, New

Delhi, for a special grant under a UGC–BSR one-time grant to faculty.

References

- Balaji, J., John Francis Xavier, J., Prabu, S. & Srinivasan, P. (2014). *Acta Cryst. E* **70**, o1250–o1251.
- Hashemi, S. A. (2012). *Tetrahedron Lett.* **53**, 5141–5143.
- Hussain, M. M., Rahman, M. M., Arshad, M. N. & Asiri, A. M. (2017a). *ACS Omega*, **2**, 420–431.
- Hussain, M. M., Rahman, M. M., Arshad, M. N. & Asiri, A. M. (2017b). *Sci. Rep.* **7**, 5832.
- Kia, R., Etemadi, B., Fun, H.-K. & Kargar, H. (2009b). *Acta Cryst. E* **65**, o821–o822.
- Kia, R., Fun, H.-K. & Kargar, H. (2009a). *Acta Cryst. E* **65**, o1119–o1120.
- McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Cryst. B* **60**, 627–668.
- Ogawa, C., Konishi, H., Sugiura, M. & Kobayashi, S. (2004). *Org. Biomol. Chem.* **2**, 446–448.
- Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd., Abingdon, England.
- Reis, D. C., Despaigne, A. A. R., Da Silva, J. G., Silva, N. F., Vilela, C. F., Mendes, I. C., Takahashi, J. A. & Beraldo, H. (2013). *Molecules*, **18**, 12645–12662.
- Rollas, S. & Küçükgüzel, S. G. (2007). *Molecules*, **12**, 1910–1939.
- Salian, A. R., Foro, S. & Gowda, B. T. (2018). *Acta Cryst. E* **74**, 1613–1618.
- Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.

- Silva, C. M. da, da Silva, D. L., Modolo, L. V., Alves, R. B., de Resende, M. A., Martins, C. V. B. & de Fátima, A. (2011). *J. Adv. Res.* **2**, 1–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Turner, M. J., McKinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). *Crystal Explorer*. The University of Western Australia.
- Weber, B., Tandon, R. & Himsl, D. (2007). *Z. Anorg. Allg. Chem.* **633**, 1159–1162.

supporting information

Acta Cryst. (2018). E74, 1808-1814 [https://doi.org/10.1107/S205698901801592X]

Crystal structure and Hirshfeld surface analysis of two (*E*)-*N'*-(*para*-substituted benzylidene) 4-chlorobenzenesulfonohydrazides

Akshatha R. Salian, Sabine Foro and B. Thimme Gowda

Computing details

For both structures, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

(*E*)-4-Chloro-*N'*-(4-chlorobenzylidene)benzenesulfonohydrazide (I)

Crystal data

$C_{13}H_{10}Cl_2N_2O_2S$

$M_r = 329.19$

Triclinic, $P\bar{1}$

$a = 5.9306$ (6) Å

$b = 9.477$ (1) Å

$c = 13.040$ (2) Å

$\alpha = 98.822$ (9)°

$\beta = 96.046$ (9)°

$\gamma = 92.416$ (9)°

$V = 718.94$ (15) Å³

$Z = 2$

$F(000) = 336$

$D_x = 1.521$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2722 reflections

$\theta = 2.9$ – 27.8 °

$\mu = 0.60$ mm⁻¹

$T = 293$ K

Rod, colourless

$0.48 \times 0.40 \times 0.36$ mm

Data collection

Oxford Diffraction Xcalibur

diffractometer with Sapphire CCD

Radiation source: Enhance (Mo) X-ray Source

Rotation method data acquisition using ω scans.

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2009)

$T_{\min} = 0.762$, $T_{\max} = 0.814$

4153 measured reflections

2626 independent reflections

2321 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 25.4$ °, $\theta_{\min} = 3.2$ °

$h = -4 \rightarrow 7$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.102$

$S = 1.08$

2626 reflections

185 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.3082P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.35$ e Å⁻³

Extinction correction: SHELXL,
 $F_c^* = kF_c [1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.025 (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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3867 (3)	0.1943 (2)	0.08046 (14)	0.0366 (4)
C2	0.6099 (3)	0.2317 (2)	0.12163 (17)	0.0481 (5)
H2	0.6853	0.3119	0.1052	0.058*
C3	0.7193 (4)	0.1486 (3)	0.18737 (19)	0.0556 (6)
H3	0.8683	0.1731	0.2166	0.067*
C4	0.6054 (4)	0.0289 (2)	0.20921 (17)	0.0526 (6)
C5	0.3850 (4)	-0.0103 (2)	0.16683 (18)	0.0549 (6)
H5	0.3118	-0.0925	0.1813	0.066*
C6	0.2746 (4)	0.0736 (2)	0.10286 (16)	0.0450 (5)
H6	0.1248	0.0493	0.0747	0.054*
C7	0.1757 (3)	0.5784 (2)	0.22864 (16)	0.0423 (4)
H7	0.2965	0.6386	0.2185	0.051*
C8	0.0609 (3)	0.6140 (2)	0.32242 (16)	0.0427 (5)
C9	-0.1405 (4)	0.5433 (3)	0.33612 (18)	0.0542 (5)
H9	-0.2037	0.4681	0.2855	0.065*
C10	-0.2480 (4)	0.5832 (3)	0.4236 (2)	0.0618 (6)
H10	-0.3837	0.5356	0.4319	0.074*
C11	-0.1539 (4)	0.6935 (3)	0.49867 (18)	0.0575 (6)
C12	0.0449 (4)	0.7658 (3)	0.48740 (19)	0.0630 (6)
H12	0.1068	0.8410	0.5383	0.076*
C13	0.1518 (4)	0.7252 (3)	0.39922 (18)	0.0548 (6)
H13	0.2872	0.7734	0.3913	0.066*
N1	0.2346 (3)	0.45985 (18)	0.07324 (14)	0.0426 (4)
H1N	0.345 (3)	0.517 (2)	0.0743 (19)	0.051*
N2	0.1173 (3)	0.46871 (18)	0.16049 (13)	0.0414 (4)
O1	0.3856 (3)	0.33553 (16)	-0.07638 (11)	0.0487 (4)
O2	0.0199 (2)	0.24297 (16)	-0.03067 (12)	0.0492 (4)
Cl1	0.74291 (16)	-0.07477 (8)	0.29214 (6)	0.0886 (3)
Cl2	-0.29271 (14)	0.74500 (11)	0.60842 (6)	0.0909 (3)
S1	0.24404 (8)	0.30435 (5)	0.00069 (4)	0.03746 (17)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0347 (9)	0.0351 (9)	0.0370 (9)	-0.0002 (7)	0.0035 (7)	-0.0024 (8)
C2	0.0372 (10)	0.0498 (12)	0.0547 (12)	-0.0056 (9)	0.0048 (9)	0.0032 (10)
C3	0.0394 (11)	0.0632 (15)	0.0580 (13)	0.0069 (10)	-0.0054 (10)	-0.0029 (11)

C4	0.0661 (14)	0.0415 (11)	0.0443 (11)	0.0170 (10)	-0.0079 (10)	-0.0060 (9)
C5	0.0682 (15)	0.0346 (11)	0.0581 (13)	-0.0040 (10)	-0.0038 (11)	0.0044 (9)
C6	0.0433 (11)	0.0377 (10)	0.0499 (11)	-0.0066 (8)	-0.0053 (9)	0.0033 (9)
C7	0.0429 (11)	0.0383 (10)	0.0459 (11)	0.0015 (8)	0.0056 (9)	0.0078 (9)
C8	0.0460 (11)	0.0406 (10)	0.0420 (11)	0.0083 (8)	0.0036 (9)	0.0068 (8)
C9	0.0571 (13)	0.0519 (13)	0.0501 (12)	-0.0022 (10)	0.0100 (10)	-0.0040 (10)
C10	0.0570 (14)	0.0708 (16)	0.0574 (14)	0.0003 (12)	0.0175 (11)	0.0030 (12)
C11	0.0581 (14)	0.0723 (16)	0.0416 (11)	0.0186 (12)	0.0071 (10)	0.0023 (11)
C12	0.0666 (16)	0.0666 (16)	0.0473 (13)	0.0053 (12)	-0.0027 (11)	-0.0117 (11)
C13	0.0522 (13)	0.0573 (13)	0.0512 (12)	0.0001 (10)	0.0031 (10)	-0.0004 (10)
N1	0.0459 (9)	0.0357 (9)	0.0461 (9)	-0.0045 (7)	0.0133 (8)	0.0032 (7)
N2	0.0426 (9)	0.0396 (9)	0.0438 (9)	0.0039 (7)	0.0110 (7)	0.0074 (7)
O1	0.0569 (9)	0.0475 (8)	0.0396 (7)	-0.0107 (7)	0.0117 (6)	0.0005 (6)
O2	0.0413 (8)	0.0474 (8)	0.0559 (9)	-0.0080 (6)	-0.0055 (6)	0.0093 (7)
Cl1	0.1200 (7)	0.0595 (4)	0.0754 (5)	0.0290 (4)	-0.0372 (4)	0.0025 (3)
Cl2	0.0868 (5)	0.1270 (7)	0.0546 (4)	0.0193 (5)	0.0230 (4)	-0.0133 (4)
S1	0.0382 (3)	0.0352 (3)	0.0372 (3)	-0.00503 (18)	0.00356 (19)	0.00245 (19)

Geometric parameters (Å, °)

C1—C6	1.384 (3)	C8—C9	1.386 (3)
C1—C2	1.385 (3)	C9—C10	1.376 (3)
C1—S1	1.763 (2)	C9—H9	0.9300
C2—C3	1.382 (3)	C10—C11	1.373 (4)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.377 (4)	C11—C12	1.371 (4)
C3—H3	0.9300	C11—Cl2	1.741 (2)
C4—C5	1.377 (3)	C12—C13	1.382 (3)
C4—Cl1	1.734 (2)	C12—H12	0.9300
C5—C6	1.374 (3)	C13—H13	0.9300
C5—H5	0.9300	N1—N2	1.388 (2)
C6—H6	0.9300	N1—S1	1.6311 (17)
C7—N2	1.269 (3)	N1—H1N	0.830 (16)
C7—C8	1.463 (3)	O1—S1	1.4316 (14)
C7—H7	0.9300	O2—S1	1.4212 (15)
C8—C13	1.385 (3)		
C6—C1—C2	120.77 (19)	C10—C9—H9	119.6
C6—C1—S1	120.05 (15)	C8—C9—H9	119.6
C2—C1—S1	119.18 (15)	C11—C10—C9	119.6 (2)
C3—C2—C1	119.3 (2)	C11—C10—H10	120.2
C3—C2—H2	120.4	C9—C10—H10	120.2
C1—C2—H2	120.4	C12—C11—C10	121.0 (2)
C4—C3—C2	119.3 (2)	C12—C11—Cl2	119.5 (2)
C4—C3—H3	120.3	C10—C11—Cl2	119.4 (2)
C2—C3—H3	120.3	C11—C12—C13	119.0 (2)
C5—C4—C3	121.6 (2)	C11—C12—H12	120.5
C5—C4—Cl1	119.19 (19)	C13—C12—H12	120.5

C3—C4—C11	119.22 (18)	C12—C13—C8	121.2 (2)
C6—C5—C4	119.2 (2)	C12—C13—H13	119.4
C6—C5—H5	120.4	C8—C13—H13	119.4
C4—C5—H5	120.4	N2—N1—S1	118.76 (13)
C5—C6—C1	119.84 (19)	N2—N1—H1N	118.8 (17)
C5—C6—H6	120.1	S1—N1—H1N	115.6 (17)
C1—C6—H6	120.1	C7—N2—N1	114.02 (16)
N2—C7—C8	122.74 (19)	O2—S1—O1	119.93 (9)
N2—C7—H7	118.6	O2—S1—N1	109.69 (9)
C8—C7—H7	118.6	O1—S1—N1	102.85 (9)
C13—C8—C9	118.4 (2)	O2—S1—C1	107.94 (9)
C13—C8—C7	119.19 (19)	O1—S1—C1	109.14 (9)
C9—C8—C7	122.40 (19)	N1—S1—C1	106.52 (9)
C10—C9—C8	120.8 (2)		
C6—C1—C2—C3	-1.2 (3)	C10—C11—C12—C13	-0.6 (4)
S1—C1—C2—C3	177.57 (16)	C12—C11—C12—C13	-179.08 (19)
C1—C2—C3—C4	1.1 (3)	C11—C12—C13—C8	0.4 (4)
C2—C3—C4—C5	0.2 (3)	C9—C8—C13—C12	-0.3 (4)
C2—C3—C4—C11	-179.75 (17)	C7—C8—C13—C12	177.7 (2)
C3—C4—C5—C6	-1.3 (4)	C8—C7—N2—N1	175.01 (17)
C11—C4—C5—C6	178.64 (17)	S1—N1—N2—C7	158.96 (15)
C4—C5—C6—C1	1.1 (3)	N2—N1—S1—O2	54.13 (17)
C2—C1—C6—C5	0.1 (3)	N2—N1—S1—O1	-177.17 (15)
S1—C1—C6—C5	-178.67 (17)	N2—N1—S1—C1	-62.44 (17)
N2—C7—C8—C13	172.1 (2)	C6—C1—S1—O2	-0.97 (19)
N2—C7—C8—C9	-10.0 (3)	C2—C1—S1—O2	-179.78 (15)
C13—C8—C9—C10	0.3 (4)	C6—C1—S1—O1	-132.84 (16)
C7—C8—C9—C10	-177.6 (2)	C2—C1—S1—O1	48.35 (18)
C8—C9—C10—C11	-0.5 (4)	C6—C1—S1—N1	116.77 (17)
C9—C10—C11—C12	0.7 (4)	C2—C1—S1—N1	-62.04 (18)
C9—C10—C11—C12	179.13 (19)		

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of rings C1—C6 and C8—C13, respectively.

<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—H1N...O1 ⁱ	0.83 (2)	2.07 (2)	2.903 (2)	178 (2)
C4—C11...Cg2 ⁱⁱ	1.73 (1)	3.41 (1)	5.112 (2)	166 (1)
C11—C12...Cg1 ⁱⁱⁱ	1.74 (1)	3.65 (1)	5.372 (3)	171 (1)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y-1, z$; (iii) $-x, -y+1, -z+1$.**(*E*)-4-chloro-*N'*-(4-Nitrobenzylidene)benzenesulfonohydrazide (II)***Crystal data*

C₁₃H₁₀ClN₃O₄S
M_r = 339.75
 Monoclinic, *P*2₁/*c*

a = 19.903 (1) Å
b = 10.2517 (7) Å
c = 15.064 (1) Å

$\beta = 103.929 (7)^\circ$
 $V = 2983.3 (3) \text{ \AA}^3$
 $Z = 8$
 $F(000) = 1392$
 $D_x = 1.513 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7054 reflections
 $\theta = 2.8\text{--}27.8^\circ$
 $\mu = 0.42 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Rod, yellow
 $0.48 \times 0.40 \times 0.36 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur
 diffractometer with Sapphire CCD
 Radiation source: Enhance (Mo) X-ray Source
 Rotation method data acquisition using ω scans.
 Absorption correction: multi-scan
 (CrysAlis RED; Oxford Diffraction, 2009)
 $T_{\min} = 0.825$, $T_{\max} = 0.864$
 19194 measured reflections

5455 independent reflections
 4247 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 2.8^\circ$
 $h = -23 \rightarrow 23$
 $k = -12 \rightarrow 12$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.101$
 $S = 1.02$
 5455 reflections
 414 parameters
 15 restraints
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 1.8451P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL,
 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0034 (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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.44715 (4)	0.44299 (7)	0.63321 (5)	0.0692 (2)	
S1	0.41281 (3)	1.03308 (5)	0.53686 (4)	0.03843 (15)	
O1	0.42255 (8)	1.04883 (15)	0.44626 (10)	0.0447 (4)	
O2	0.44990 (8)	1.11288 (16)	0.60973 (11)	0.0529 (4)	
O3	0.0285 (6)	0.5036 (8)	0.3381 (6)	0.081 (3)	0.55
O3'	0.0324 (8)	0.5149 (10)	0.3044 (7)	0.075 (3)	0.45
O4	-0.04648 (9)	0.6576 (2)	0.30599 (13)	0.0681 (5)	
N1	0.33087 (10)	1.06413 (19)	0.53180 (14)	0.0449 (5)	
H1N	0.3271 (13)	1.086 (2)	0.5849 (12)	0.054*	
N2	0.28443 (9)	0.97344 (18)	0.48183 (12)	0.0426 (4)	
N3	0.01310 (11)	0.6206 (2)	0.32944 (15)	0.0562 (5)	
C1	0.42530 (10)	0.8671 (2)	0.56436 (14)	0.0367 (5)	
C2	0.44115 (12)	0.8290 (2)	0.65534 (15)	0.0465 (6)	
H2	0.4461	0.8912	0.7014	0.056*	

C3	0.44953 (12)	0.6982 (3)	0.67705 (16)	0.0519 (6)
H3	0.4610	0.6714	0.7378	0.062*
C4	0.44062 (11)	0.6085 (2)	0.60760 (17)	0.0457 (6)
C5	0.42596 (13)	0.6447 (2)	0.51720 (17)	0.0534 (6)
H5	0.4209	0.5821	0.4714	0.064*
C6	0.41891 (13)	0.7760 (2)	0.49545 (15)	0.0484 (6)
H6	0.4099	0.8027	0.4347	0.058*
C7	0.22211 (11)	0.9867 (2)	0.48701 (16)	0.0438 (5)
H7	0.2100	1.0569	0.5192	0.053*
C8	0.16896 (11)	0.8929 (2)	0.44293 (15)	0.0406 (5)
C9	0.09969 (12)	0.9292 (2)	0.42131 (17)	0.0499 (6)
H9	0.0877	1.0142	0.4327	0.060*
C10	0.04837 (12)	0.8412 (2)	0.38318 (17)	0.0497 (6)
H10	0.0021	0.8661	0.3679	0.060*
C11	0.06736 (11)	0.7159 (2)	0.36837 (16)	0.0443 (5)
C12	0.13570 (12)	0.6763 (2)	0.38937 (18)	0.0508 (6)
H12	0.1472	0.5907	0.3787	0.061*
C13	0.18635 (12)	0.7649 (2)	0.42624 (17)	0.0476 (6)
H13	0.2326	0.7395	0.4402	0.057*
Cl2	0.11071 (4)	0.30845 (9)	0.53034 (6)	0.0814 (3)
S2	0.32436 (3)	0.34333 (5)	0.28991 (4)	0.04203 (16)
O5	0.28924 (9)	0.38026 (17)	0.19868 (11)	0.0542 (4)
O6	0.38459 (9)	0.41231 (17)	0.33703 (13)	0.0610 (5)
O7	0.10708 (11)	-0.49600 (19)	0.13632 (16)	0.0778 (6)
O8	0.03109 (10)	-0.3435 (2)	0.12357 (18)	0.0896 (7)
N4	0.34961 (10)	0.19182 (18)	0.28409 (13)	0.0413 (4)
H4N	0.3793 (11)	0.167 (2)	0.3306 (13)	0.050*
N5	0.29454 (9)	0.10878 (17)	0.24828 (12)	0.0386 (4)
N6	0.09076 (11)	-0.3814 (2)	0.14089 (16)	0.0582 (6)
C14	0.26262 (11)	0.3420 (2)	0.35620 (15)	0.0388 (5)
C15	0.19424 (12)	0.3099 (2)	0.31583 (15)	0.0432 (5)
H15	0.1803	0.2948	0.2532	0.052*
C16	0.14730 (12)	0.3006 (2)	0.36964 (17)	0.0479 (6)
H16	0.1014	0.2790	0.3437	0.058*
C17	0.16929 (13)	0.3237 (2)	0.46229 (17)	0.0483 (6)
C18	0.23655 (13)	0.3573 (3)	0.50252 (16)	0.0534 (6)
H18	0.2500	0.3742	0.5650	0.064*
C19	0.28388 (12)	0.3655 (2)	0.44925 (16)	0.0489 (6)
H19	0.3298	0.3868	0.4757	0.059*
C20	0.30626 (12)	-0.0126 (2)	0.25909 (15)	0.0413 (5)
H20	0.3503	-0.0419	0.2881	0.050*
C21	0.25043 (11)	-0.1061 (2)	0.22580 (15)	0.0395 (5)
C22	0.18148 (12)	-0.0665 (2)	0.20002 (18)	0.0496 (6)
H22	0.1707	0.0215	0.2026	0.060*
C23	0.12929 (12)	-0.1552 (2)	0.17098 (18)	0.0511 (6)
H23	0.0834	-0.1283	0.1534	0.061*
C24	0.14638 (12)	-0.2851 (2)	0.16848 (16)	0.0436 (5)
C25	0.21363 (12)	-0.3280 (2)	0.19346 (17)	0.0498 (6)

H25	0.2238	-0.4163	0.1907	0.060*
C26	0.26565 (12)	-0.2384 (2)	0.22262 (17)	0.0482 (6)
H26	0.3114	-0.2663	0.2404	0.058*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0651 (4)	0.0455 (4)	0.0853 (5)	-0.0022 (3)	-0.0048 (4)	0.0214 (3)
S1	0.0359 (3)	0.0367 (3)	0.0404 (3)	-0.0048 (2)	0.0046 (2)	-0.0003 (2)
O1	0.0414 (8)	0.0469 (9)	0.0454 (9)	-0.0022 (7)	0.0096 (7)	0.0086 (7)
O2	0.0544 (10)	0.0450 (10)	0.0524 (10)	-0.0110 (8)	-0.0006 (8)	-0.0087 (8)
O3	0.058 (3)	0.050 (3)	0.129 (7)	-0.007 (2)	0.010 (5)	-0.002 (4)
O3'	0.069 (4)	0.062 (4)	0.087 (5)	-0.005 (4)	0.005 (4)	-0.018 (4)
O4	0.0382 (10)	0.0845 (15)	0.0791 (13)	-0.0053 (9)	0.0093 (9)	-0.0026 (11)
N1	0.0406 (10)	0.0446 (11)	0.0488 (11)	-0.0001 (9)	0.0094 (9)	-0.0083 (9)
N2	0.0380 (10)	0.0443 (11)	0.0438 (10)	-0.0011 (9)	0.0065 (8)	-0.0028 (9)
N3	0.0421 (12)	0.0600 (15)	0.0649 (14)	-0.0050 (11)	0.0102 (10)	-0.0023 (12)
C1	0.0310 (10)	0.0404 (12)	0.0371 (11)	-0.0048 (9)	0.0051 (8)	0.0017 (9)
C2	0.0483 (13)	0.0506 (14)	0.0360 (12)	-0.0052 (11)	0.0014 (10)	-0.0009 (10)
C3	0.0507 (14)	0.0594 (16)	0.0393 (13)	-0.0033 (12)	-0.0015 (11)	0.0136 (12)
C4	0.0367 (12)	0.0401 (13)	0.0557 (14)	-0.0023 (10)	0.0021 (10)	0.0126 (11)
C5	0.0664 (16)	0.0405 (13)	0.0511 (14)	-0.0042 (12)	0.0097 (12)	-0.0031 (11)
C6	0.0650 (15)	0.0447 (14)	0.0337 (12)	-0.0035 (12)	0.0085 (11)	0.0028 (10)
C7	0.0400 (12)	0.0392 (12)	0.0527 (14)	0.0061 (10)	0.0119 (10)	0.0010 (10)
C8	0.0355 (11)	0.0437 (13)	0.0434 (12)	0.0033 (10)	0.0113 (9)	0.0039 (10)
C9	0.0397 (12)	0.0435 (13)	0.0667 (16)	0.0103 (11)	0.0131 (11)	-0.0002 (12)
C10	0.0324 (11)	0.0535 (15)	0.0614 (15)	0.0076 (11)	0.0081 (11)	0.0050 (12)
C11	0.0383 (12)	0.0475 (14)	0.0472 (13)	-0.0010 (10)	0.0105 (10)	0.0034 (11)
C12	0.0419 (13)	0.0418 (13)	0.0677 (16)	0.0059 (11)	0.0113 (11)	-0.0033 (12)
C13	0.0327 (11)	0.0481 (14)	0.0616 (15)	0.0079 (10)	0.0106 (10)	0.0033 (12)
Cl2	0.0824 (5)	0.0998 (6)	0.0759 (5)	-0.0171 (5)	0.0459 (4)	-0.0163 (4)
S2	0.0445 (3)	0.0341 (3)	0.0487 (3)	-0.0011 (2)	0.0137 (2)	0.0007 (2)
O5	0.0642 (11)	0.0510 (10)	0.0514 (10)	0.0132 (9)	0.0218 (8)	0.0169 (8)
O6	0.0524 (10)	0.0512 (10)	0.0824 (13)	-0.0141 (8)	0.0219 (9)	-0.0147 (9)
O7	0.0715 (13)	0.0450 (11)	0.1165 (18)	-0.0122 (10)	0.0217 (12)	-0.0072 (11)
O8	0.0452 (11)	0.0735 (15)	0.143 (2)	-0.0107 (10)	0.0096 (12)	-0.0044 (14)
N4	0.0401 (10)	0.0353 (10)	0.0446 (11)	0.0022 (8)	0.0027 (8)	-0.0006 (8)
N5	0.0395 (10)	0.0349 (10)	0.0397 (10)	-0.0002 (8)	0.0064 (8)	0.0001 (8)
N6	0.0521 (13)	0.0532 (14)	0.0700 (15)	-0.0095 (11)	0.0160 (11)	-0.0011 (11)
C14	0.0439 (12)	0.0315 (11)	0.0407 (12)	0.0031 (9)	0.0094 (9)	-0.0009 (9)
C15	0.0451 (13)	0.0432 (13)	0.0388 (12)	0.0024 (10)	0.0050 (10)	-0.0056 (10)
C16	0.0425 (13)	0.0468 (14)	0.0533 (14)	-0.0016 (11)	0.0093 (11)	-0.0062 (11)
C17	0.0542 (14)	0.0443 (13)	0.0511 (14)	-0.0032 (11)	0.0216 (11)	-0.0061 (11)
C18	0.0642 (16)	0.0565 (16)	0.0388 (13)	-0.0021 (13)	0.0110 (11)	-0.0084 (11)
C19	0.0462 (13)	0.0501 (14)	0.0474 (14)	-0.0060 (11)	0.0051 (11)	-0.0078 (11)
C20	0.0411 (12)	0.0405 (13)	0.0419 (12)	0.0052 (10)	0.0092 (10)	0.0001 (10)
C21	0.0423 (12)	0.0346 (12)	0.0413 (12)	0.0043 (10)	0.0094 (10)	0.0013 (10)
C22	0.0452 (13)	0.0356 (12)	0.0669 (16)	0.0070 (10)	0.0112 (12)	0.0032 (11)

C23	0.0389 (12)	0.0443 (14)	0.0683 (16)	0.0054 (11)	0.0089 (11)	0.0055 (12)
C24	0.0441 (13)	0.0399 (13)	0.0486 (13)	-0.0041 (10)	0.0149 (10)	-0.0008 (10)
C25	0.0517 (14)	0.0334 (12)	0.0660 (16)	0.0041 (11)	0.0173 (12)	-0.0051 (11)
C26	0.0404 (12)	0.0403 (13)	0.0631 (15)	0.0058 (10)	0.0107 (11)	-0.0031 (11)

Geometric parameters (Å, °)

C11—C4	1.738 (2)	C12—C17	1.735 (2)
S1—O2	1.4245 (16)	S2—O6	1.4252 (17)
S1—O1	1.4331 (16)	S2—O5	1.4346 (17)
S1—N1	1.6452 (19)	S2—N4	1.6414 (19)
S1—C1	1.754 (2)	S2—C14	1.760 (2)
O3—N3	1.237 (8)	O7—N6	1.226 (3)
O3'—N3	1.239 (10)	O8—N6	1.217 (3)
O4—N3	1.213 (3)	N4—N5	1.390 (2)
N1—N2	1.397 (3)	N4—H4N	0.839 (16)
N1—H1N	0.849 (16)	N5—C20	1.269 (3)
N2—C7	1.269 (3)	N6—C24	1.467 (3)
N3—C11	1.469 (3)	C14—C19	1.384 (3)
C1—C6	1.379 (3)	C14—C15	1.390 (3)
C1—C2	1.386 (3)	C15—C16	1.380 (3)
C2—C3	1.381 (3)	C15—H15	0.9300
C2—H2	0.9300	C16—C17	1.379 (3)
C3—C4	1.372 (4)	C16—H16	0.9300
C3—H3	0.9300	C17—C18	1.374 (3)
C4—C5	1.373 (3)	C18—C19	1.379 (3)
C5—C6	1.385 (3)	C18—H18	0.9300
C5—H5	0.9300	C19—H19	0.9300
C6—H6	0.9300	C20—C21	1.462 (3)
C7—C8	1.465 (3)	C20—H20	0.9300
C7—H7	0.9300	C21—C26	1.393 (3)
C8—C9	1.389 (3)	C21—C22	1.394 (3)
C8—C13	1.396 (3)	C22—C23	1.370 (3)
C9—C10	1.380 (3)	C22—H22	0.9300
C9—H9	0.9300	C23—C24	1.377 (3)
C10—C11	1.372 (3)	C23—H23	0.9300
C10—H10	0.9300	C24—C25	1.373 (3)
C11—C12	1.381 (3)	C25—C26	1.375 (3)
C12—C13	1.371 (3)	C25—H25	0.9300
C12—H12	0.9300	C26—H26	0.9300
C13—H13	0.9300		
O2—S1—O1	120.35 (10)	C8—C13—H13	119.8
O2—S1—N1	104.40 (10)	O6—S2—O5	120.24 (11)
O1—S1—N1	107.10 (10)	O6—S2—N4	105.33 (10)
O2—S1—C1	110.93 (10)	O5—S2—N4	106.46 (10)
O1—S1—C1	106.87 (10)	O6—S2—C14	109.87 (10)
N1—S1—C1	106.33 (10)	O5—S2—C14	107.46 (10)

N2—N1—S1	114.59 (15)	N4—S2—C14	106.70 (10)
N2—N1—H1N	118.9 (18)	N5—N4—S2	112.16 (14)
S1—N1—H1N	108.5 (17)	N5—N4—H4N	118.0 (17)
C7—N2—N1	115.17 (19)	S2—N4—H4N	113.8 (17)
O4—N3—O3	122.2 (6)	C20—N5—N4	116.56 (18)
O4—N3—O3'	122.5 (8)	O8—N6—O7	123.5 (2)
O4—N3—C11	118.8 (2)	O8—N6—C24	118.5 (2)
O3—N3—C11	117.5 (6)	O7—N6—C24	118.0 (2)
O3'—N3—C11	116.8 (8)	C19—C14—C15	120.8 (2)
C6—C1—C2	120.7 (2)	C19—C14—S2	119.21 (17)
C6—C1—S1	119.78 (17)	C15—C14—S2	119.83 (17)
C2—C1—S1	119.49 (17)	C16—C15—C14	119.3 (2)
C3—C2—C1	119.6 (2)	C16—C15—H15	120.3
C3—C2—H2	120.2	C14—C15—H15	120.3
C1—C2—H2	120.2	C17—C16—C15	119.2 (2)
C4—C3—C2	119.0 (2)	C17—C16—H16	120.4
C4—C3—H3	120.5	C15—C16—H16	120.4
C2—C3—H3	120.5	C18—C17—C16	121.9 (2)
C3—C4—C5	122.2 (2)	C18—C17—C12	118.95 (19)
C3—C4—C11	119.75 (19)	C16—C17—C12	119.19 (19)
C5—C4—C11	118.1 (2)	C17—C18—C19	119.2 (2)
C4—C5—C6	118.8 (2)	C17—C18—H18	120.4
C4—C5—H5	120.6	C19—C18—H18	120.4
C6—C5—H5	120.6	C18—C19—C14	119.6 (2)
C1—C6—C5	119.6 (2)	C18—C19—H19	120.2
C1—C6—H6	120.2	C14—C19—H19	120.2
C5—C6—H6	120.2	N5—C20—C21	119.9 (2)
N2—C7—C8	120.8 (2)	N5—C20—H20	120.1
N2—C7—H7	119.6	C21—C20—H20	120.1
C8—C7—H7	119.6	C26—C21—C22	118.8 (2)
C9—C8—C13	119.0 (2)	C26—C21—C20	119.8 (2)
C9—C8—C7	119.9 (2)	C22—C21—C20	121.3 (2)
C13—C8—C7	121.0 (2)	C23—C22—C21	121.0 (2)
C10—C9—C8	121.0 (2)	C23—C22—H22	119.5
C10—C9—H9	119.5	C21—C22—H22	119.5
C8—C9—H9	119.5	C22—C23—C24	118.5 (2)
C11—C10—C9	118.3 (2)	C22—C23—H23	120.8
C11—C10—H10	120.8	C24—C23—H23	120.8
C9—C10—H10	120.8	C25—C24—C23	122.3 (2)
C10—C11—C12	122.2 (2)	C25—C24—N6	118.8 (2)
C10—C11—N3	118.8 (2)	C23—C24—N6	118.9 (2)
C12—C11—N3	119.0 (2)	C24—C25—C26	118.9 (2)
C13—C12—C11	119.0 (2)	C24—C25—H25	120.6
C13—C12—H12	120.5	C26—C25—H25	120.6
C11—C12—H12	120.5	C25—C26—C21	120.6 (2)
C12—C13—C8	120.4 (2)	C25—C26—H26	119.7
C12—C13—H13	119.8	C21—C26—H26	119.7

O2—S1—N1—N2	-164.14 (15)	C7—C8—C13—C12	176.5 (2)
O1—S1—N1—N2	67.20 (18)	O6—S2—N4—N5	173.52 (15)
C1—S1—N1—N2	-46.79 (18)	O5—S2—N4—N5	-57.76 (17)
S1—N1—N2—C7	171.43 (17)	C14—S2—N4—N5	56.77 (17)
O2—S1—C1—C6	-153.93 (18)	S2—N4—N5—C20	-165.33 (16)
O1—S1—C1—C6	-21.0 (2)	O6—S2—C14—C19	-19.8 (2)
N1—S1—C1—C6	93.2 (2)	O5—S2—C14—C19	-152.28 (18)
O2—S1—C1—C2	26.4 (2)	N4—S2—C14—C19	93.9 (2)
O1—S1—C1—C2	159.36 (17)	O6—S2—C14—C15	163.92 (18)
N1—S1—C1—C2	-86.50 (19)	O5—S2—C14—C15	31.5 (2)
C6—C1—C2—C3	-1.0 (3)	N4—S2—C14—C15	-82.38 (19)
S1—C1—C2—C3	178.61 (18)	C19—C14—C15—C16	-0.5 (3)
C1—C2—C3—C4	-1.2 (4)	S2—C14—C15—C16	175.69 (17)
C2—C3—C4—C5	2.3 (4)	C14—C15—C16—C17	0.2 (3)
C2—C3—C4—C11	-177.17 (18)	C15—C16—C17—C18	0.8 (4)
C3—C4—C5—C6	-1.0 (4)	C15—C16—C17—C12	-178.57 (18)
C11—C4—C5—C6	178.45 (19)	C16—C17—C18—C19	-1.3 (4)
C2—C1—C6—C5	2.3 (4)	C12—C17—C18—C19	178.0 (2)
S1—C1—C6—C5	-177.32 (19)	C17—C18—C19—C14	1.0 (4)
C4—C5—C6—C1	-1.3 (4)	C15—C14—C19—C18	-0.1 (4)
N1—N2—C7—C8	-175.87 (19)	S2—C14—C19—C18	-176.29 (19)
N2—C7—C8—C9	-157.7 (2)	N4—N5—C20—C21	178.17 (18)
N2—C7—C8—C13	25.5 (3)	N5—C20—C21—C26	168.5 (2)
C13—C8—C9—C10	-0.5 (4)	N5—C20—C21—C22	-13.9 (3)
C7—C8—C9—C10	-177.3 (2)	C26—C21—C22—C23	-0.7 (4)
C8—C9—C10—C11	1.0 (4)	C20—C21—C22—C23	-178.4 (2)
C9—C10—C11—C12	-0.7 (4)	C21—C22—C23—C24	0.5 (4)
C9—C10—C11—N3	178.8 (2)	C22—C23—C24—C25	-0.4 (4)
O4—N3—C11—C10	4.8 (3)	C22—C23—C24—N6	177.7 (2)
O3—N3—C11—C10	-161.9 (5)	O8—N6—C24—C25	176.1 (2)
O3'—N3—C11—C10	169.5 (6)	O7—N6—C24—C25	-4.1 (4)
O4—N3—C11—C12	-175.6 (2)	O8—N6—C24—C23	-2.1 (4)
O3—N3—C11—C12	17.7 (6)	O7—N6—C24—C23	177.8 (2)
O3'—N3—C11—C12	-10.9 (6)	C23—C24—C25—C26	0.5 (4)
C10—C11—C12—C13	0.0 (4)	N6—C24—C25—C26	-177.6 (2)
N3—C11—C12—C13	-179.6 (2)	C24—C25—C26—C21	-0.7 (4)
C11—C12—C13—C8	0.5 (4)	C22—C21—C26—C25	0.8 (4)
C9—C8—C13—C12	-0.2 (4)	C20—C21—C26—C25	178.5 (2)

Hydrogen-bond geometry (Å, °)

Cg3 is the centroid of the C14—C19 ring.

<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—H1 <i>N</i> ...O5 ⁱ	0.85 (2)	2.06 (2)	2.887 (3)	163 (2)
N4—H4 <i>N</i> ...O1 ⁱⁱ	0.84 (2)	2.13 (2)	2.918 (2)	157 (2)
C10—H10...O7 ⁱⁱⁱ	0.93	2.58	3.465 (3)	159
C16—H16...O4 ^{iv}	0.93	2.58	3.259 (3)	131

C25—H25···O5 ⁱⁱ	0.93	2.45	3.340 (3)	161
C12—H12···Cg3	0.93	2.96	3.843 (2)	160

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