Crystal structure and Hirshfeld surface analysis of (E)-N′-benzylidene-4-chlorobenzenesulfono-hydrazide and of its (E)-4-chloro-N′-(ortho- and para-methylbenzylidene)benzenesulfonohydrazide derivatives

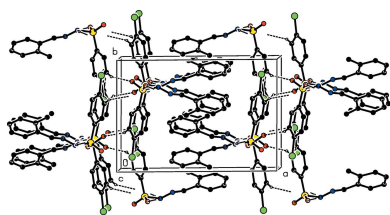**Akshatha R. Salian,[a] Sabine Foro[b] and B. Thimme Gowda[a,c]***

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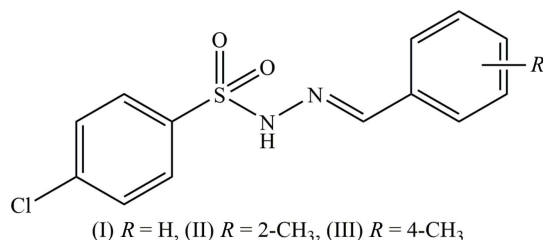
(E)-N′-Benzylidene-4-chlorobenzenesulfonohydrazide, $C_{13}H_{11}ClN_2O_2S$, (I), and its ortho- and para-methylsubstituted derivatives, $C_{14}H_{13}ClN_2O_2S$, namely (E)-4-chloro-N′-(2-methylbenzylidene)benzenesulfonohydrazide, (II), and (E)-4-chloro-N′-(4-methylbenzylidene)benzenesulfonohydrazide, (III), have been synthesized, characterized spectroscopically and their crystal structures determined to investigate the effect of the substitution site of the benzylidene group on the structural and supramolecular features in these compounds. Compounds (I) and (II) are isotypic while compound (III) is different. All three molecules are bent at the S atom with C—S—N—N torsion angles of −66.0 (3), −66.0 (3) and −58.4 (2)° for (I), (II) and (III), respectively. The hydrazone portions of the molecules, S—N—N=C, are slightly twisted from planarity, with a torsion angle of 166.5 (3)° in (I), 165.4 (3)° in (II) and 157.9 (2)° in (III). The two aromatic rings present in the compounds are inclined to each other by 78.4 (2), 74.8 (2) and 76.9 (1)° in (I), (II) and (III), respectively. In the crystal structure of the parent compound (I), and of the ortho-methyl derivative (II), an N—H···O hydrogen bond links the molecules into chains along [001], which are interconnected by weak intermolecular C—H···O interactions, generating layers lying parallel to the bc plane. In the crystal of the para derivative (III), however, the packing is significantly different. Here molecules are linked by pairs of N—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(8)$ ring motif. The dimers are then linked by C—Cl···π interactions, forming ribbons propagating along [1$\bar{1}$0]. Hirshfeld surface analyses show that the van der Waals interactions constitute the major contribution to the intermolecular interactions in the crystal structures of all three compounds. The fingerprint plots indicate that the H···H contacts make the largest contributions to the Hirshfeld surfaces.

1. Chemical context

Schiff bases are an important class of compounds in the field of coordination chemistry and catalysis (Mahfouz et al., 2015). The photochromic and thermochromic properties of Schiff bases make their study interesting (Girisha et al., 2018). They form second-order NLO organic materials, which are being used in computers, optical communication and medical imaging (Zarei et al., 2015). Hydrazones also play an important role in curing diseases effectively with less toxicity. Sulfonyl hydrazones are known for their good enzymatic modulation, analgesic, anti-Alzheimer's, antidepressant and antidiabetic activities (Cunha et al., 2016). To investigate the

impact of substitution, and also the variation of the site of substituent, on the structural parameters and the hydrogen-bonding interactions, we report herein on the synthesis and crystal structures of (*E*)-*N'*-(benzylidene)-4-chlorobenzene-sulfonohydrazide (I) and its *ortho*- and *para*-methyl-substituted benzylidene derivatives, (II) and (III), respectively.

(I) *R* = H, (II) *R* = 2-CH$_3$, (III) *R* = 4-CH$_3$

2. Structural commentary

The title hydrazide (I) and its derivatives, (II) and (III), crystallize in the monoclinic crystal system with space group $P2_1/c$ for (I) and (II) and $P2_1/n$ for (III). The molecular structures of compounds (I), (II) and (III) are illustrated in Figs. 1, 2 and 3, respectively. All three molecules adopt an *E* configuration about the C=N bond of the central imine group. In the *ortho*-methyl-substituted derivative (II), the N—H and C—H bonds in the hydrazide part are *anti* with respect to the methyl substituent. These parts of the molecules, S—N—N=C, show similar bond lengths of 1.258 (5), 1.272 (5) and 1.273 (3) Å for C7=N2 and 1.394 (5), 1.407 (5) and 1.393 (2) Å for N1—N2 in compounds (I), (II) and (III), respectively. These bond lengths are consistent with the C=N double-bond and N—N single-bond lengths, respectively. Furthermore, the S—N—N=C segments are slightly twisted from planarity, with torsion angles of 166.5 (3)° in (I), 165.4 (3)° in (II) and 157.9 (2)° in (III). All three compounds are bent at the S atom with C—S—N—N torsion angles of
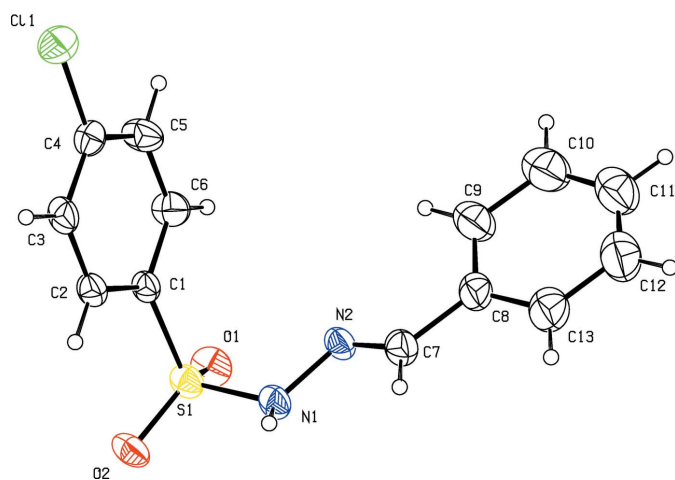
−66.0 (3), −66.0 (3) and −58.4 (2)° for (I), (II) and (III), respectively. The two aromatic rings present in these compounds are inclined to each other by 78.4 (2), 74.8 (2) and 76.9 (1)° in (I), (II) and (III), respectively. Hence the conformations of (I) and (II) are very similar while that of (III) is slightly different.

3. Supramolecular features

In the crystals of all three compounds, an O atom of the sulfonyl group acts as an acceptor and the amino H atom of the hydrazide segment as a donor in N—H⋯O hydrogen-bonding interactions with neighbouring molecules (Tables 1, 2 and 3). The patterns of the hydrogen-bonding interactions in the crystal structures of (I) and (II) are very similar, and will be illustrated for compound (II) only. The N—H⋯O hydrogen-bonding interactions result in a *C*(4) graph-set motif generating chains propagating along the *c*-axis direction (Fig. 4). These chains are linked by weak C—H⋯O interactions involving an aromatic H atom of the benzylidenephenyl ring and a sulfonyl O atom, resulting in the

Figure 2
Molecular structure of (II), showing the atom labelling and displacement ellipsoids drawn at the 30% probability level.

Figure 1
Molecular structure of (I), showing the atom labelling and displacement ellipsoids drawn at the 30% probability level.

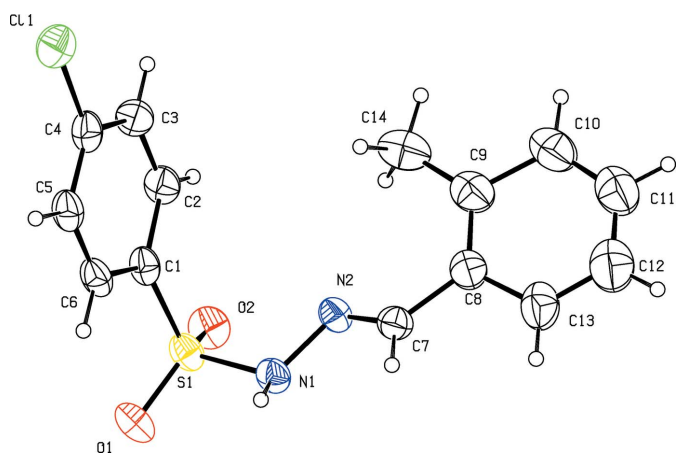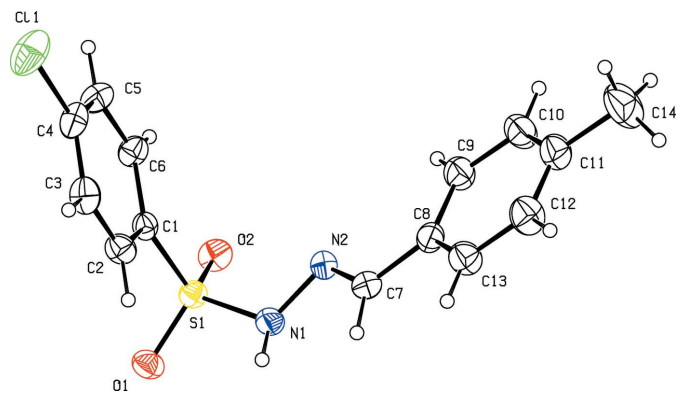**Figure 3**
Molecular structure of (III), showing the atom labelling and displacement ellipsoids drawn at the 30% probability level.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N1—H1$N\cdots$O1^{i}	0.83 (2)	2.14 (3)	2.897 (4)	152 (4)
C3—H3$\cdots$O2^{ii}	0.93	2.43	3.305 (5)	158

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N1—H1$N\cdots$O2^{i}	0.86 (2)	2.06 (2)	2.913 (4)	168 (4)
C5—H5$\cdots$O1^{ii}	0.93	2.44	3.303 (5)	155

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

Table 3
Hydrogen-bond geometry (Å, °) for (III).

$Cg1$ is the centroid of ring C8-C13.

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N1—H1$N\cdots$O1^{i}	0.85 (2)	2.09 (2)	2.935 (2)	177 (2)
C4—Cl1$\cdots Cg$1^{ii}	1.74 (1)	3.47 (1)	5.175 (3)	168 (1)

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

Figure 5
A view along the c axis of the crystal packing of (II), with hydrogen bonds shown as dashed lines. Only the H atoms involved in the intermolecular interactions have been included.

Figure 6
A view along the b axis of the crystal packing of (III), with hydrogen bonds shown as dashed lines. Only the H atoms involved in the intermolecular interactions have been included. The C—Cl$\cdots\pi$ interactions are indicated by blue arrows.

formation of layers lying parallel to the bc plane (Tables 2 and 3, and Fig. 5). On changing the position of the methyl substituent from *ortho-* to *para-* the crystal packing changes significantly. Molecules are now linked by pairs of N—H$\cdots$O hydrogen bonds, forming inversion dimers enclosing $R_2^2(8)$ loops (Fig. 6, Table 3). The dimers are linked by a C—Cl$\cdots\pi$ interaction, forming ribbons that propagate along the [1$\bar{1}$0] direction (Fig. 6, Table 3).

4. Hirshfeld Surface analysis

The nature of the intermolecular contacts and their quantitative contributions to the crystal packing in all the three title
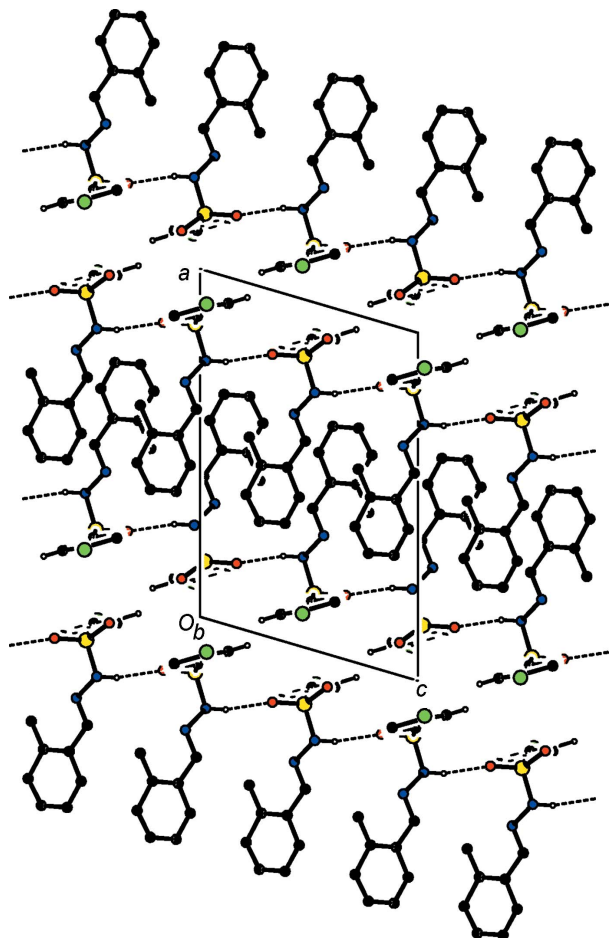

Figure 4
A partial view along the b axis of the crystal packing of (II), with hydrogen bonds shown as dashed lines. Only the H atoms involved in the intermolecular interactions have been included.
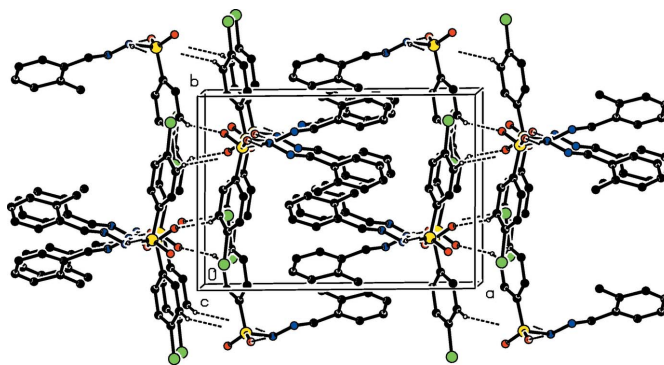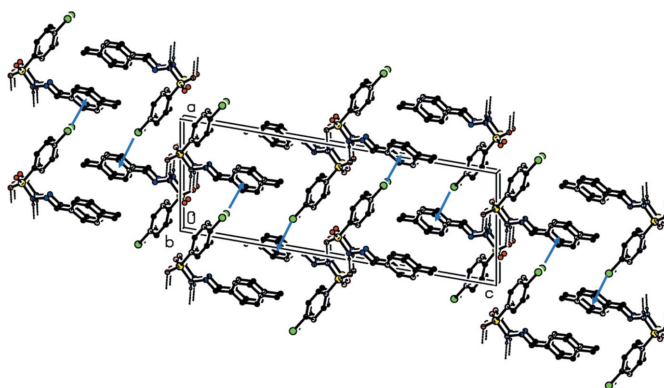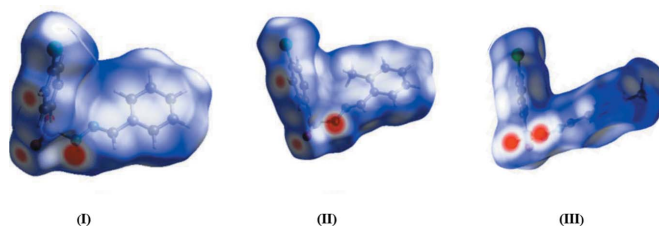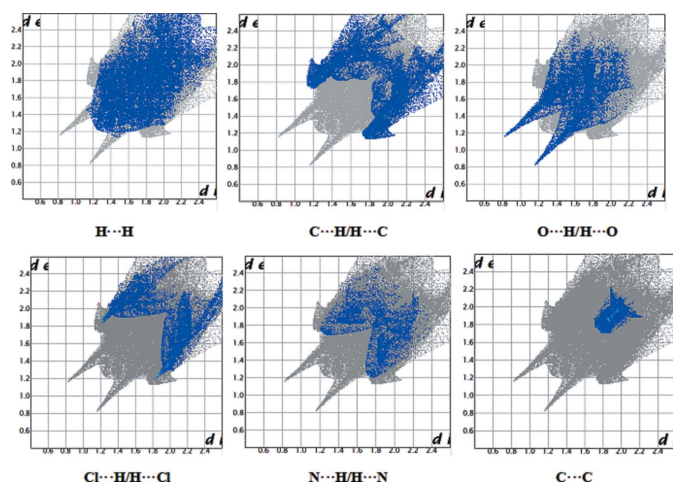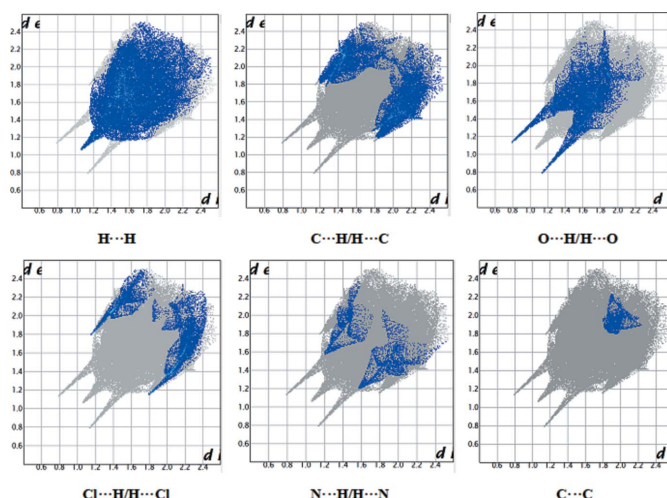

(I)   **(II)**   **(III)**

Figure 7
Hirshfeld surface mapped over d_{norm} for (I), (II) and (III).

Table 4
Hirshfeld contact interactions (%).

Contact type	(I)	(II)	(III)
H···H	30.1	34.0	38.0
C···H/H···C	22.7	20.2	18.0
O···H/H···O	16.1	16.1	15.7
Cl···H/H···Cl	12.1	12.3	9.4
N···H/H···N	6.3	5.2	3.9
C···C	5.2	5.0	2.1
Cl···C/C···Cl	0	0	5.3
Cl···O/O···Cl	5.0	4.8	2.3
C···O/O···C	1.0	1.0	2.6
Cl···Cl	0.5	0.5	0
C···S/S···C	0	0.1	0.1

Figure 9
Two-dimensional fingerprint plots for (III), showing the contributions of different types of interactions.

compounds were analysed by Hirshfeld surface analysis and two-dimensional fingerprint plots, generated using *Crystal-Explorer3.1* (McKinnon *et al.*, 2004; Spackman & Jayatilaka, 2009; Wolff *et al.*, 2012). The Hirshfeld surfaces of the three compounds mapped over d_{norm} are shown in Fig. 7. The N—H···O interactions between the corresponding donor and acceptor atoms are visualized as bright-red spots and represent the short interatomic interactions in the crystal structures. The presence of two other light-red spots in (I) and (II) correspond to the C—H···O interactions, which are considered to be weak interactions.

The two-dimensional fingerprint plots for the contacts H···H, C···H/H···C, O···H/H···O, Cl···H/H···Cl, C···C and N···H/H···N are illustrated in Figs. 8 and 9, for (I) and (III), respectively. The fingerprint plots of various contacts and their percentage contribution to the Hirshfeld surfaces are similar in (I) and (II) but, as expected, different from those for (III) (see Table 4). H···H contacts are the major contributors to the Hirshfeld surface: 30.1% in (I), 34.0% (II) and 38.0% in (III). The C···H/H···C contacts make the second largest contribution, *i.e.* 22.7, 20.2 and 18.0% for (I), (II) and (III), respectively. This is followed by O···H/H···O contacts arising from N—H···O and C—H···O interactions, contributing

16.1% in (I) and (II), and 15.7% in (III). N···H/H···N contacts arising from O—H···N hydrogen bonds contribute 6.3, 5.2 and 3.9%, respectively, in (I), (II) and (III). Cl···H/H···Cl interactions make a relatively significant contribution to the total Hirshfeld surfaces, comprising 12.1% in (I), 12.3% in (II) and 9.4% in (III). The C···C contacts representing π–π interactions contribute 5.2, 5.0 and 2.1% in (I), (II) and (III), respectively. Cl···O/O···Cl contacts comprise 5.0% in (I), 4.8% in (II) and 2.3% in (III). Weak Cl···Cl, C···O/O···C and C···S/S···C interactions are also observed; however, they exhibit minimal respect contributions of 0.5, 1.0 and 0% in (I), 0.5, 1.0, 0.1% in (II) and 0, 2.6 and 0.1% in (III), reflecting negligible or no effect on the molecular packing.

The most significant difference for compounds (I) and (II) compared to compound (III) is the presence of a relatively strong Cl···C/C···Cl interaction in (III), in accordance with the C—Cl···π interaction in the crystal (Table 3), which makes a contribution of 5.3%, while for (I) and (II) this interaction is not present.

5. Database survey

The crystal structures of (E)-N′-(4-chlorobenzylidene)-4-methylbenzenesulfonohydrazide (IV) (Balaji *et al.*, 2014) and N′-[(E)-4-methylbenzylidene]4-methylbenzenesulfonohydrazide (V) (Tabatabaee *et al.*, 2007) have been reported. They exhibit an *E* configuration with respect to the C=N bond and an almost perpendicular orientation of the two aromatic rings with dihedral angles of 81.9 (3)° in (IV) and 82.4 (1)° in (V), very similar to the values of 78.4 (2), 74.8 (2) and 76.9 (1)° in (I), (II) and (III), respectively. In the structures of these related compounds (I)–(V) and also those of benzylidene, 3,3-diphenylallylidene (Mehrabi & Kia, 2009; Mehrabi *et al.*, 2008), 4-bromo/5-bromo-2-hydroxy/5-chloro-2-hydroxy (Kia *et al.*, 2008*a*,*b*) and 2-hydroxy-5-iodo (Ghorbanloo & Notash, 2012) derivatives of *p*-toluenesulfonohydrazide, the aryl-

Figure 8
Two-dimensional fingerprint plots for (I), showing the contributions of different types of interactions.

1616 Salian *et al.* · C$_{13}$H$_{11}$ClN$_2$O$_2$S, C$_{14}$H$_{13}$ClN$_2$O$_2$S and C$_{14}$H$_{13}$ClN$_2$O$_2$S

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Table 5
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_{13}H_{11}ClN_2O_2S$	$C_{14}H_{13}ClN_2O_2S$	$C_{14}H_{13}ClN_2O_2S$
M_r	294.75	308.77	308.77
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	293	293	293
a, b, c (Å)	14.949 (2), 10.020 (1), 9.641 (1)	15.034 (2), 10.180 (1), 9.8119 (9)	9.406 (1), 5.8353 (6), 26.930 (2)
β (°)	104.27 (1)	106.34 (1)	99.621 (9)
V (Å^3)	1399.6 (3)	1441.0 (3)	1457.3 (2)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.42	0.41	0.41
Crystal size (mm)	$0.20 \times 0.16 \times 0.08$	$0.22 \times 0.16 \times 0.08$	$0.48 \times 0.16 \times 0.14$
Data collection			
Diffractometer	Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
Absorption correction	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.921, 0.967	0.915, 0.968	0.829, 0.945
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4831, 2547, 1034	5157, 2636, 1713	9653, 2652, 2106
R_{int}	0.075	0.038	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.602	0.602	0.602
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.113, 0.91	0.067, 0.195, 1.07	0.040, 0.095, 1.05
No. of reflections	2547	2636	2652
No. of parameters	175	185	185
No. of restraints	30	32	1
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	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.21	0.66, −0.32	0.21, −0.31

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

sulfonohydrazide molecules are directly connected to one another *via* significant N—H···O hydrogen-bonding interactions involving a sulfonyl oxygen atom and the amino hydrogen atom.

6. Synthesis and crystallization

Synthesis of 4-chlorobenzenesulfonohydrazide

To 4-chlrobenzenesulfonyl chloride (0.01 mol) dissolved in propanol (30 ml), 99% hydrazine hydrate (5 ml) was added at 273 K under constant stirring. The stirring continued for 15 min at 273 K and then at 303 K for 3 h. After completion of the reaction (monitored by TLC), the reaction mixture was concentrated by evaporating the excess propanol. The solid product, 4-chlorobenzenesulfonohydrazide was washed with cold water and dried.

Synthesis of compounds (I), (II) and (III)

The parent, *ortho*- and *para*- substituted (*E*)-*N*′-(benzylidene)-4-chlorobenzenesulfonohydrazides (I), (II) and (III), were synthesized by refluxing mixtures of 4-chlorobenzenesulfonohydrazide (0.01 mol) and benzaldehyde, 2-methylbenzaldehyde or 4-methylbenzaldehyde (0.01 mol), respectively, in ethanol (30 ml) and two drops of glacial acetic acid for 4 h. The reaction mixtures were cooled to room temperature

and concentrated by evaporating the excess of solvent. The solid products (I), (II) and (III) 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. Single crystals of the hydrazides suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation of their DMF solutions at room temperature. All three compounds were characterized by measuring their IR, ^{1}H and ^{13}C NMR spectra.

(*E*)-*N*-(benzylidene) 4-chlorobenzenesulfonohydrazide (I):
Plate-like colourless single crystals; m.p. 381–382 K; IR (cm^{-1}): 3174.8 (N—H asym stretch), 1577.8 (C=N), 1323.2 (S=O asym stretch) and 1159.2 (S=O sym stretch); ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 7.29–7.33 (*m*, 3H, Ar-H), 7.52 (*t*, 2H, Ar-H, *J* = 7.44), 7.53–7.56 (*m*, 3H, Ar-H), 7.94 (*d*, 1H, Ar-H, *J* = 8.4Hz), 7.93 (*s*, 1H), 11.54 (*s*, 1H) and ^{13}C NMR (400 MHz, CDCl$_3$, δ ppm): 125.46, 127.21, 127.72, 127.86, 128.63, 132.23, 136.52, 136.99, 146.11.

(*E*)-*N*-(2-methylbenzylidene) 4-chlorobenzenesulfonohydrazide (II):
Rod-shaped colourless single crystals; m.p. 399–400 K; IR (cm^{-1}): 3155.5 (N—H asym stretch), 1585.6 (C=N), 1325.1 (S=O asym stretch) and 1153.4 (S=O sym stretch); ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 2.33 (*s*, 3H), 7.09–7.17 (*m*, 1H, Ar-

H), 7.21–7.26 (*m*, 1H, Ar-H), 7.43–7.48 (*m*, 1H, Ar-H), 7.63 (*d*, 1H, Ar-H, *J* = 7.7 Hz), 7.86 (*d*, 2H, Ar-H, *J* = 8.6 Hz), 7.93 (*d*, 2H, Ar-H, *J* = 8.5 Hz), 8.08 (*s*, 1H), 11.67 (*s*, 1H) and ^{13}C NMR (400 MHz, CDCl$_3$, δ ppm): 19.77, 126.17, 127.27, 129.13, 129.31, 129.81, 130.23, 131.14, 136.88, 139.72, 140.26, 147.62.

(*E*)-*N*-(4-methylbenzylidene) 4-chlorobenzenesulfono-hydrazide (III):

Rod-shaped colourless single crystals; m.p. 425–426K; IR (cm^{-1}): 3184.5 (N—H asym stretch), 1580.7 (C=N), 1326.5 (S=O asym stretch) and 1163.3 (S=O sym stretch); ^{1}H NMR (400 MHz, CDCl$_3$, δ ppm): 2.27 (*s*, 3H), 7.12 (*d*, 2H, Ar-H, *J* = 8.0 Hz), 7.41 (*d*, 2H, Ar-H, *J* = 8.0Hz), 7.52–7.57 (*m*, 2H, Ar-H), 7.86–7.90 (*m*, 2H, Ar-H), 7.92 (*s*, 1H), 11.40 (*s*, 1H) and ^{13}C NMR (400 MHz, CDCl$_3$, δ ppm): 20.96, 126.64, 128.95, 129.61, 130.75, 137.75, 139.41, 139.78, 145.66.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. For all three compounds, the H atom of the NH group was located in difference-Fourier maps and later restrained to N—H = 0.86 (2) Å. C-bound H atoms were positioned with idealized geometry and refined using a riding model: C—H = 0.93–0.96 Å with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C-methyl) and 1.2$U_{\rm eq}$(C-aromatic, N) for other H atoms. The U^{ij} components of C9, C10, C11 and C12 in (I) and C10, C11, C12 and C13 in (II) and (III) were restrained to approximate isotropic behaviour.

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supporting information

Crystal structure and Hirshfeld surface analysis of (*E*)-*N*′-benzylidene-4-chloro-benzenesulfonohydrazide and of its (*E*)-4-chloro-*N*′-(*ortho*- and *para*-methyl-benzylidene)benzenesulfonohydrazide derivatives

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

Computing details

For all structures, data collection: *CrysAlis CCD* (Oxford Diffraction, 2009). Cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2009) for (I); *CrysAlis RED* (Oxford Diffraction, 2009) for (II), (III). For all structures, 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) and *PLATON* (Spek, 2009).

(*E*)-*N*′-Benzylidene-4-chlorobenzenesulfonohydrazide (I)

Crystal data

$C_{13}H_{11}ClN_2O_2S$	$F(000) = 608$
$M_r = 294.75$	$D_x = 1.399$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.949$ (2) Å	Cell parameters from 692 reflections
$b = 10.020$ (1) Å	$\theta = 2.8$–28.0°
$c = 9.641$ (1) Å	$\mu = 0.42$ mm^{-1}
$\beta = 104.27$ (1)°	$T = 293$ K
$V = 1399.6$ (3) Å^3	Plate, colourless
$Z = 4$	$0.20 \times 0.16 \times 0.08$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	2547 independent reflections
	1034 reflections with $I > 2\sigma(I)$
Radiation source: Enhance (Mo) X-ray Source	$R_{int} = 0.075$
Rotation method data acquisition using ω scans.	$\theta_{max} = 25.4°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan	$h = -16 \rightarrow 18$
(CrysAlis RED; Oxford Diffraction, 2009)	$k = -12 \rightarrow 8$
$T_{min} = 0.921$, $T_{max} = 0.967$	$l = -8 \rightarrow 11$
4831 measured reflections	

Refinement

Refinement on F^2	175 parameters
Least-squares matrix: full	30 restraints
$R[F^2 > 2\sigma(F^2)] = 0.062$	Hydrogen site location: mixed
$wR(F^2) = 0.113$	H atoms treated by a mixture of independent
$S = 0.91$	and constrained refinement
2547 reflections	

$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-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 (Å^2)

	x	*y*	*z*	$U_{iso}*/U_{eq}$
C1	−0.1391 (3)	−0.4315 (4)	−0.0093 (5)	0.0399 (11)
C2	−0.0889 (3)	−0.4861 (5)	0.1175 (5)	0.0475 (12)
H2	−0.0645	−0.4313	0.1955	0.057*
C3	−0.0749 (3)	−0.6222 (5)	0.1283 (5)	0.0506 (13)
H3	−0.0400	−0.6591	0.2129	0.061*
C4	−0.1128 (3)	−0.7031 (4)	0.0134 (5)	0.0494 (13)
C5	−0.1615 (3)	−0.6477 (5)	−0.1149 (5)	0.0612 (15)
H5	−0.1848	−0.7023	−0.1936	0.073*
C6	−0.1751 (3)	−0.5130 (5)	−0.1255 (4)	0.0572 (14)
H6	−0.2087	−0.4759	−0.2110	0.069*
C7	−0.4066 (4)	−0.3017 (4)	−0.0120 (5)	0.0566 (14)
H7	−0.4032	−0.2745	0.0814	0.068*
C8	−0.4945 (4)	−0.3538 (5)	−0.1000 (6)	0.0631 (15)
C9	−0.4990 (4)	−0.4207 (5)	−0.2256 (6)	0.0806 (18)
H9	−0.4455	−0.4349	−0.2562	0.097*
C10	−0.5837 (5)	−0.4678 (5)	−0.3082 (7)	0.0977 (18)
H10	−0.5875	−0.5122	−0.3942	0.117*
C11	−0.6607 (5)	−0.4463 (6)	−0.2579 (7)	0.0966 (18)
H11	−0.7171	−0.4770	−0.3127	0.116*
C12	−0.6596 (5)	−0.3852 (6)	−0.1370 (7)	0.0965 (18)
H12	−0.7135	−0.3750	−0.1062	0.116*
C13	−0.5748 (4)	−0.3354 (5)	−0.0552 (6)	0.0836 (17)
H13	−0.5728	−0.2898	0.0295	0.100*
N1	−0.2581 (3)	−0.2379 (4)	0.0314 (3)	0.0489 (10)
H1N	−0.254 (3)	−0.240 (4)	0.119 (2)	0.059*
N2	−0.3361 (3)	−0.2933 (3)	−0.0607 (4)	0.0484 (10)
O1	−0.1806 (2)	−0.2192 (3)	−0.1656 (3)	0.0587 (9)
O2	−0.0928 (2)	−0.1919 (3)	0.0868 (3)	0.0574 (9)
Cl1	−0.09997 (10)	−0.87458 (12)	0.02899 (14)	0.0712 (5)
S1	−0.16184 (9)	−0.25981 (12)	−0.01912 (12)	0.0476 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.035 (3)	0.046 (3)	0.034 (3)	0.000 (2)	0.002 (2)	−0.001 (2)
C2	0.040 (3)	0.051 (4)	0.045 (3)	−0.001 (3)	−0.001 (2)	−0.001 (3)

C3	0.042 (3)	0.058 (4)	0.044 (3)	0.002 (3)	−0.006 (2)	0.007 (3)
C4	0.044 (3)	0.053 (3)	0.053 (3)	0.004 (3)	0.017 (3)	0.001 (3)
C5	0.074 (4)	0.058 (4)	0.044 (3)	−0.007 (3)	0.000 (3)	−0.010 (3)
C6	0.068 (4)	0.051 (4)	0.041 (3)	0.006 (3)	−0.008 (3)	0.004 (3)
C7	0.048 (4)	0.054 (3)	0.062 (3)	0.001 (3)	0.003 (3)	0.003 (3)
C8	0.049 (4)	0.046 (3)	0.087 (4)	0.002 (3)	0.004 (3)	0.013 (3)
C9	0.074 (4)	0.065 (3)	0.091 (3)	−0.013 (3)	−0.003 (3)	0.001 (3)
C10	0.099 (4)	0.083 (3)	0.101 (3)	−0.016 (3)	0.007 (3)	−0.002 (3)
C11	0.082 (3)	0.081 (4)	0.113 (3)	−0.014 (3)	−0.002 (3)	0.017 (3)
C12	0.070 (3)	0.093 (4)	0.121 (4)	−0.004 (3)	0.013 (3)	0.016 (3)
C13	0.073 (4)	0.068 (4)	0.103 (4)	0.004 (3)	0.010 (3)	0.015 (3)
N1	0.044 (2)	0.060 (3)	0.037 (2)	−0.001 (2)	−0.001 (2)	−0.006 (2)
N2	0.041 (3)	0.046 (3)	0.049 (2)	−0.003 (2)	−0.005 (2)	−0.0005 (19)
O1	0.073 (2)	0.066 (2)	0.0337 (17)	−0.0022 (18)	0.0068 (15)	0.0120 (16)
O2	0.057 (2)	0.055 (2)	0.0502 (19)	−0.0147 (17)	−0.0068 (17)	−0.0039 (15)
Cl1	0.0744 (11)	0.0529 (9)	0.0819 (10)	0.0069 (8)	0.0112 (8)	0.0037 (7)
S1	0.0490 (8)	0.0505 (8)	0.0378 (7)	−0.0037 (7)	0.0001 (6)	0.0014 (7)

Geometric parameters (Å, º)

C1—C2	1.380 (5)	C8—C13	1.385 (7)
C1—C6	1.383 (5)	C9—C10	1.400 (7)
C1—S1	1.752 (4)	C9—H9	0.9300
C2—C3	1.379 (5)	C10—C11	1.372 (7)
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.377 (5)	C11—C12	1.313 (7)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.387 (6)	C12—C13	1.409 (7)
C4—Cl1	1.732 (5)	C12—H12	0.9300
C5—C6	1.365 (6)	C13—H13	0.9300
C5—H5	0.9300	N1—N2	1.394 (5)
C6—H6	0.9300	N1—S1	1.644 (4)
C7—N2	1.258 (5)	N1—H1N	0.831 (18)
C7—C8	1.473 (6)	O1—S1	1.429 (3)
C7—H7	0.9300	O2—S1	1.432 (3)
C8—C9	1.371 (6)		
C2—C1—C6	120.1 (4)	C8—C9—H9	119.7
C2—C1—S1	119.5 (4)	C10—C9—H9	119.7
C6—C1—S1	120.3 (4)	C11—C10—C9	117.7 (6)
C3—C2—C1	119.8 (4)	C11—C10—H10	121.1
C3—C2—H2	120.1	C9—C10—H10	121.1
C1—C2—H2	120.1	C12—C11—C10	124.0 (7)
C4—C3—C2	119.8 (4)	C12—C11—H11	118.0
C4—C3—H3	120.1	C10—C11—H11	118.0
C2—C3—H3	120.1	C11—C12—C13	118.3 (7)
C3—C4—C5	120.3 (4)	C11—C12—H12	120.9
C3—C4—Cl1	120.0 (4)	C13—C12—H12	120.9

C5—C4—Cl1	119.8 (4)	C8—C13—C12	120.5 (6)
C6—C5—C4	119.8 (4)	C8—C13—H13	119.7
C6—C5—H5	120.1	C12—C13—H13	119.7
C4—C5—H5	120.1	N2—N1—S1	114.5 (3)
C5—C6—C1	120.1 (4)	N2—N1—H1N	118 (3)
C5—C6—H6	119.9	S1—N1—H1N	117 (3)
C1—C6—H6	119.9	C7—N2—N1	115.8 (4)
N2—C7—C8	121.3 (5)	O1—S1—O2	120.03 (19)
N2—C7—H7	119.4	O1—S1—N1	106.33 (18)
C8—C7—H7	119.4	O2—S1—N1	104.79 (18)
C9—C8—C13	118.9 (6)	O1—S1—C1	108.75 (19)
C9—C8—C7	121.7 (5)	O2—S1—C1	109.4 (2)
C13—C8—C7	119.5 (6)	N1—S1—C1	106.7 (2)
C8—C9—C10	120.5 (6)		
C6—C1—C2—C3	−0.3 (7)	C10—C11—C12—C13	1.6 (9)
S1—C1—C2—C3	176.6 (3)	C9—C8—C13—C12	0.4 (8)
C1—C2—C3—C4	−1.4 (6)	C7—C8—C13—C12	−179.5 (5)
C2—C3—C4—C5	2.8 (7)	C11—C12—C13—C8	−1.6 (9)
C2—C3—C4—Cl1	−177.1 (3)	C8—C7—N2—N1	177.8 (4)
C3—C4—C5—C6	−2.7 (7)	S1—N1—N2—C7	166.5 (3)
Cl1—C4—C5—C6	177.2 (4)	N2—N1—S1—O1	49.9 (3)
C4—C5—C6—C1	1.1 (7)	N2—N1—S1—O2	178.0 (3)
C2—C1—C6—C5	0.4 (7)	N2—N1—S1—C1	−66.0 (3)
S1—C1—C6—C5	−176.4 (4)	C2—C1—S1—O1	157.4 (3)
N2—C7—C8—C9	13.9 (7)	C6—C1—S1—O1	−25.7 (4)
N2—C7—C8—C13	−166.2 (5)	C2—C1—S1—O2	24.6 (4)
C13—C8—C9—C10	0.9 (8)	C6—C1—S1—O2	−158.6 (3)
C7—C8—C9—C10	−179.2 (5)	C2—C1—S1—N1	−88.2 (4)
C8—C9—C10—C11	−0.9 (8)	C6—C1—S1—N1	88.6 (4)
C9—C10—C11—C12	−0.4 (9)		

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯O1[i]	0.83 (2)	2.14 (3)	2.897 (4)	152 (4)
C3—H3⋯O2[ii]	0.93	2.43	3.305 (5)	158

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

(*E*)-4-Chloro-*N′*-(2-methylbenzylidene)benzenesulfonohydrazide (II)

Crystal data

$C_{14}H_{13}ClN_2O_2S$	$V = 1441.0$ (3) Å^3
$M_r = 308.77$	$Z = 4$
Monoclinic, $P2_1/c$	$F(000) = 640$
$a = 15.034$ (2) Å	$D_x = 1.423$ Mg m^{-3}
$b = 10.180$ (1) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$c = 9.8119$ (9) Å	Cell parameters from 1546 reflections
$\beta = 106.34$ (1)°	$\theta = 2.8$–27.7°

$\mu = 0.41$ mm^{-1}

$T = 293$ K

Rod, colourless

$0.22 \times 0.16 \times 0.08$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	2636 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1713 reflections with $I > 2\sigma(I)$
Rotation method data acquisition using ω scans.	$R_{int} = 0.038$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)	$\theta_{max} = 25.4°$, $\theta_{min} = 2.8°$
	$h = -13 \rightarrow 18$
	$k = -9 \rightarrow 12$
$T_{min} = 0.915$, $T_{max} = 0.968$	$l = -11 \rightarrow 11$
5157 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.067$	
$wR(F^2) = 0.195$	$w = 1/[\sigma^2(F_o^2) + (0.0912P)^2 + 1.1282P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
2636 reflections	$(\Delta/\sigma)_{max} < 0.001$
185 parameters	$\Delta\rho_{max} = 0.66$ e Å^{-3}
32 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.1380 (3)	0.5693 (5)	0.0113 (4)	0.0511 (11)
C2	0.1696 (3)	0.4872 (5)	0.1299 (4)	0.0603 (12)
H2	0.2001	0.5234	0.2176	0.072*
C3	0.1560 (3)	0.3542 (5)	0.1178 (5)	0.0637 (13)
H3	0.1783	0.2995	0.1959	0.076*
C4	0.1083 (3)	0.3027 (5)	−0.0130 (5)	0.0592 (12)
C5	0.0748 (3)	0.3818 (5)	−0.1302 (5)	0.0604 (12)
H5	0.0424	0.3454	−0.2168	0.072*
C6	0.0896 (3)	0.5142 (5)	−0.1179 (4)	0.0586 (12)
H6	0.0671	0.5679	−0.1967	0.070*
C7	0.4065 (3)	0.6873 (4)	0.0171 (5)	0.0568 (11)
H7	0.3990	0.7111	−0.0770	0.068*
C8	0.4969 (3)	0.6382 (5)	0.0999 (6)	0.0679 (11)
C9	0.5125 (4)	0.5615 (5)	0.2183 (6)	0.0810 (12)
C10	0.6096 (4)	0.5259 (6)	0.2885 (7)	0.0973 (16)
H10	0.6255	0.4756	0.3710	0.117*
C11	0.6757 (4)	0.5696 (7)	0.2276 (8)	0.1023 (18)
H11	0.7370	0.5475	0.2724	0.123*
C12	0.6595 (5)	0.6409 (7)	0.1098 (9)	0.109 (2)

H12	0.7078	0.6654	0.0733	0.130*
C13	0.5728 (4)	0.6766 (6)	0.0452 (7)	0.0871 (15)
H13	0.5608	0.7274	−0.0368	0.104*
C14	0.4420 (5)	0.5137 (7)	0.2741 (6)	0.0985 (19)
H14A	0.4687	0.4582	0.3543	0.148*
H14B	0.3981	0.4642	0.2025	0.148*
H14C	0.4110	0.5863	0.3036	0.148*
N1	0.2586 (2)	0.7565 (4)	−0.0264 (3)	0.0539 (9)
H1N	0.245 (3)	0.748 (4)	−0.118 (2)	0.065*
N2	0.3375 (2)	0.6990 (4)	0.0672 (3)	0.0539 (9)
O1	0.0942 (2)	0.8064 (3)	−0.0839 (3)	0.0690 (9)
O2	0.1843 (2)	0.7771 (3)	0.1677 (3)	0.0685 (9)
Cl1	0.09551 (9)	0.13260 (14)	−0.02983 (15)	0.0787 (5)
S1	0.16318 (7)	0.73763 (12)	0.02214 (10)	0.0551 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.041 (2)	0.075 (3)	0.037 (2)	0.000 (2)	0.0101 (16)	−0.004 (2)
C2	0.060 (3)	0.077 (4)	0.041 (2)	−0.005 (2)	0.0085 (19)	0.000 (2)
C3	0.066 (3)	0.072 (4)	0.051 (3)	−0.002 (2)	0.013 (2)	0.006 (2)
C4	0.043 (2)	0.081 (3)	0.056 (3)	−0.004 (2)	0.0170 (19)	−0.005 (2)
C5	0.046 (2)	0.082 (4)	0.047 (2)	−0.005 (2)	0.0034 (19)	−0.007 (2)
C6	0.044 (2)	0.085 (4)	0.041 (2)	0.006 (2)	0.0023 (17)	0.005 (2)
C7	0.058 (3)	0.052 (3)	0.058 (3)	0.003 (2)	0.013 (2)	0.003 (2)
C8	0.062 (2)	0.049 (3)	0.087 (3)	0.001 (2)	0.012 (2)	−0.0128 (18)
C9	0.088 (2)	0.062 (3)	0.082 (3)	0.006 (3)	0.006 (2)	−0.011 (2)
C10	0.096 (3)	0.084 (3)	0.099 (3)	0.020 (3)	0.006 (2)	0.001 (3)
C11	0.085 (2)	0.095 (4)	0.112 (4)	0.007 (3)	0.004 (3)	−0.012 (3)
C12	0.089 (4)	0.104 (4)	0.131 (4)	−0.001 (3)	0.027 (3)	−0.018 (3)
C13	0.066 (3)	0.083 (3)	0.112 (3)	0.000 (2)	0.025 (2)	−0.016 (3)
C14	0.123 (5)	0.087 (4)	0.079 (4)	0.020 (4)	0.019 (4)	0.012 (3)
N1	0.053 (2)	0.066 (2)	0.0376 (17)	0.0006 (17)	0.0055 (15)	0.0026 (18)
N2	0.049 (2)	0.061 (2)	0.0474 (19)	0.0036 (17)	0.0057 (16)	0.0021 (17)
O1	0.0607 (19)	0.081 (2)	0.0580 (18)	0.0250 (17)	0.0050 (15)	0.0039 (17)
O2	0.080 (2)	0.083 (2)	0.0421 (16)	0.0000 (17)	0.0162 (15)	−0.0115 (15)
Cl1	0.0758 (9)	0.0776 (9)	0.0815 (9)	−0.0119 (7)	0.0200 (7)	−0.0071 (7)
S1	0.0512 (6)	0.0729 (8)	0.0384 (6)	0.0101 (5)	0.0081 (4)	−0.0012 (5)

Geometric parameters (Å, °)

C1—C6	1.390 (6)	C9—C14	1.409 (8)
C1—C2	1.403 (6)	C9—C10	1.474 (8)
C1—S1	1.751 (5)	C10—C11	1.369 (9)
C2—C3	1.369 (7)	C10—H10	0.9300
C2—H2	0.9300	C11—C12	1.328 (9)
C3—C4	1.385 (6)	C11—H11	0.9300
C3—H3	0.9300	C12—C13	1.329 (8)

C4—C5	1.378 (6)	C12—H12	0.9300
C4—Cl1	1.745 (5)	C13—H13	0.9300
C5—C6	1.365 (7)	C14—H14A	0.9600
C5—H5	0.9300	C14—H14B	0.9600
C6—H6	0.9300	C14—H14C	0.9600
C7—N2	1.272 (5)	N1—N2	1.407 (5)
C7—C8	1.461 (6)	N1—S1	1.645 (4)
C7—H7	0.9300	N1—H1N	0.864 (19)
C8—C9	1.365 (7)	O1—S1	1.428 (3)
C8—C13	1.446 (8)	O2—S1	1.431 (3)
C6—C1—C2	118.9 (5)	C11—C10—H10	121.3
C6—C1—S1	119.9 (3)	C9—C10—H10	121.3
C2—C1—S1	121.1 (3)	C12—C11—C10	125.4 (7)
C3—C2—C1	120.7 (4)	C12—C11—H11	117.3
C3—C2—H2	119.7	C10—C11—H11	117.3
C1—C2—H2	119.7	C13—C12—C11	118.7 (7)
C2—C3—C4	118.7 (5)	C13—C12—H12	120.7
C2—C3—H3	120.6	C11—C12—H12	120.7
C4—C3—H3	120.6	C12—C13—C8	121.3 (7)
C5—C4—C3	121.6 (5)	C12—C13—H13	119.3
C5—C4—Cl1	119.8 (4)	C8—C13—H13	119.3
C3—C4—Cl1	118.6 (4)	C9—C14—H14A	109.5
C6—C5—C4	119.4 (4)	C9—C14—H14B	109.5
C6—C5—H5	120.3	H14A—C14—H14B	109.5
C4—C5—H5	120.3	C9—C14—H14C	109.5
C5—C6—C1	120.6 (4)	H14A—C14—H14C	109.5
C5—C6—H6	119.7	H14B—C14—H14C	109.5
C1—C6—H6	119.7	N2—N1—S1	114.0 (3)
N2—C7—C8	123.3 (4)	N2—N1—H1N	123 (3)
N2—C7—H7	118.3	S1—N1—H1N	108 (3)
C8—C7—H7	118.3	C7—N2—N1	114.6 (4)
C9—C8—C13	120.4 (5)	O1—S1—O2	120.1 (2)
C9—C8—C7	125.4 (5)	O1—S1—N1	104.20 (19)
C13—C8—C7	114.2 (5)	O2—S1—N1	106.83 (19)
C8—C9—C14	124.1 (5)	O1—S1—C1	109.6 (2)
C8—C9—C10	116.7 (6)	O2—S1—C1	108.58 (19)
C14—C9—C10	119.2 (6)	N1—S1—C1	106.73 (19)
C11—C10—C9	117.5 (6)		
C6—C1—C2—C3	2.3 (6)	C14—C9—C10—C11	177.3 (6)
S1—C1—C2—C3	−174.8 (4)	C9—C10—C11—C12	−0.4 (10)
C1—C2—C3—C4	−1.6 (7)	C10—C11—C12—C13	1.5 (11)
C2—C3—C4—C5	0.1 (7)	C11—C12—C13—C8	−0.6 (10)
C2—C3—C4—Cl1	177.3 (4)	C9—C8—C13—C12	−1.4 (8)
C3—C4—C5—C6	0.7 (7)	C7—C8—C13—C12	179.2 (5)
Cl1—C4—C5—C6	−176.4 (3)	C8—C7—N2—N1	175.8 (4)
C4—C5—C6—C1	0.0 (7)	S1—N1—N2—C7	165.4 (3)

C2—C1—C6—C5	−1.5 (6)	N2—N1—S1—O1	178.1 (3)
S1—C1—C6—C5	175.6 (3)	N2—N1—S1—O2	50.0 (3)
N2—C7—C8—C9	22.4 (7)	N2—N1—S1—C1	−66.0 (3)
N2—C7—C8—C13	−158.3 (5)	C6—C1—S1—O1	28.2 (4)
C13—C8—C9—C14	−176.4 (5)	C2—C1—S1—O1	−154.8 (3)
C7—C8—C9—C14	2.9 (8)	C6—C1—S1—O2	161.1 (3)
C13—C8—C9—C10	2.4 (7)	C2—C1—S1—O2	−21.9 (4)
C7—C8—C9—C10	−178.3 (5)	C6—C1—S1—N1	−84.1 (3)
C8—C9—C10—C11	−1.6 (8)	C2—C1—S1—N1	92.9 (4)

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1N⋯O2^i	0.86 (2)	2.06 (2)	2.913 (4)	168 (4)
C5—H5⋯O1^{ii}	0.93	2.44	3.303 (5)	155

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

(*E*)-4-Chloro-*N′*-(4-methylbenzylidene)benzenesulfonohydrazide (III)

Crystal data

$C_{14}H_{13}ClN_2O_2S$	$F(000) = 640$
$M_r = 308.77$	$D_x = 1.407$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.406$ (1) Å	Cell parameters from 3029 reflections
$b = 5.8353$ (6) Å	$\theta = 2.9$–27.8°
$c = 26.930$ (2) Å	$\mu = 0.41$ mm^{-1}
$\beta = 99.621$ (9)°	$T = 293$ K
$V = 1457.3$ (2) Å^3	Rod, colourless
$Z = 4$	$0.48 \times 0.16 \times 0.14$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	2652 independent reflections
	2106 reflections with $I > 2\sigma(I)$
Radiation source: Enhance (Mo) X-ray Source	$R_{int} = 0.027$
Rotation method data acquisition using ω scans.	$\theta_{max} = 25.4°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2009)	$h = -11 \rightarrow 11$
	$k = -7 \rightarrow 7$
$T_{min} = 0.829$, $T_{max} = 0.945$	$l = -31 \rightarrow 32$
9653 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.7905P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2652 reflections	$(\Delta/\sigma)_{max} = 0.001$
185 parameters	$\Delta\rho_{max} = 0.21$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.30$ e Å^{-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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.21023 (8)	0.70656 (16)	0.14097 (3)	0.0843 (3)
S1	0.69509 (6)	0.24496 (9)	0.00160 (2)	0.03860 (16)
O1	0.62933 (17)	0.4035 (3)	−0.03599 (5)	0.0493 (4)
O2	0.74225 (17)	0.0275 (3)	−0.01324 (6)	0.0501 (4)
N1	0.5723 (2)	0.2120 (3)	0.03686 (7)	0.0445 (5)
H1N	0.517 (2)	0.326 (3)	0.0367 (9)	0.053*
N2	0.60598 (19)	0.0841 (3)	0.08093 (7)	0.0434 (4)
C1	0.8426 (2)	0.3768 (4)	0.03983 (7)	0.0361 (5)
C2	0.8228 (3)	0.5883 (4)	0.06121 (8)	0.0464 (6)
H2	0.7336	0.6608	0.0546	0.056*
C3	0.9362 (3)	0.6891 (4)	0.09212 (9)	0.0537 (6)
H3	0.9244	0.8305	0.1069	0.064*
C4	1.0678 (3)	0.5796 (4)	0.10118 (8)	0.0511 (6)
C5	1.0885 (2)	0.3719 (4)	0.07935 (9)	0.0523 (6)
H5	1.1783	0.3014	0.0853	0.063*
C6	0.9746 (2)	0.2696 (4)	0.04858 (8)	0.0441 (5)
H6	0.9869	0.1286	0.0338	0.053*
C7	0.5267 (2)	0.1280 (4)	0.11369 (8)	0.0457 (6)
H7	0.4591	0.2450	0.1070	0.055*
C8	0.5363 (2)	0.0042 (4)	0.16116 (8)	0.0447 (5)
C9	0.6130 (3)	−0.1985 (4)	0.17103 (10)	0.0557 (7)
H9	0.6628	−0.2591	0.1470	0.067*
C10	0.6159 (3)	−0.3103 (5)	0.21616 (10)	0.0654 (7)
H10	0.6690	−0.4448	0.2223	0.078*
C11	0.5422 (3)	−0.2279 (5)	0.25255 (10)	0.0614 (7)
C12	0.4659 (3)	−0.0281 (5)	0.24265 (10)	0.0653 (8)
H12	0.4155	0.0308	0.2667	0.078*
C13	0.4623 (3)	0.0876 (5)	0.19761 (9)	0.0572 (7)
H13	0.4096	0.2226	0.1918	0.069*
C14	0.5452 (4)	−0.3541 (7)	0.30183 (11)	0.0970 (11)
H14A	0.4539	−0.3369	0.3129	0.146*
H14B	0.6201	−0.2918	0.3268	0.146*
H14C	0.5636	−0.5138	0.2971	0.146*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0677 (5)	0.1156 (7)	0.0697 (5)	−0.0376 (5)	0.0119 (4)	−0.0303 (5)
S1	0.0379 (3)	0.0396 (3)	0.0393 (3)	0.0037 (3)	0.0093 (2)	−0.0012 (3)

O1	0.0511 (9)	0.0574 (10)	0.0403 (8)	0.0112 (8)	0.0099 (7)	0.0085 (8)
O2	0.0505 (9)	0.0428 (9)	0.0572 (10)	0.0034 (7)	0.0097 (7)	−0.0130 (8)
N1	0.0398 (10)	0.0472 (12)	0.0483 (10)	0.0086 (9)	0.0129 (8)	0.0081 (10)
N2	0.0406 (10)	0.0415 (10)	0.0485 (10)	−0.0008 (8)	0.0086 (9)	0.0067 (9)
C1	0.0388 (12)	0.0348 (11)	0.0370 (11)	0.0014 (9)	0.0129 (9)	0.0011 (9)
C2	0.0519 (14)	0.0378 (12)	0.0504 (13)	0.0075 (11)	0.0109 (11)	−0.0011 (11)
C3	0.0678 (17)	0.0410 (13)	0.0547 (14)	−0.0065 (12)	0.0173 (13)	−0.0093 (12)
C4	0.0499 (14)	0.0629 (16)	0.0423 (12)	−0.0185 (12)	0.0131 (11)	−0.0075 (12)
C5	0.0368 (13)	0.0638 (16)	0.0569 (14)	0.0016 (12)	0.0099 (11)	−0.0040 (13)
C6	0.0410 (12)	0.0433 (13)	0.0504 (13)	0.0021 (11)	0.0146 (10)	−0.0066 (11)
C7	0.0381 (12)	0.0483 (14)	0.0507 (13)	0.0032 (11)	0.0071 (10)	0.0029 (11)
C8	0.0408 (12)	0.0482 (13)	0.0455 (13)	−0.0054 (11)	0.0089 (10)	0.0015 (11)
C9	0.0562 (15)	0.0554 (16)	0.0595 (15)	0.0073 (12)	0.0210 (12)	0.0073 (13)
C10	0.0693 (18)	0.0591 (17)	0.0704 (17)	0.0118 (14)	0.0197 (14)	0.0191 (14)
C11	0.0667 (17)	0.0654 (17)	0.0535 (15)	−0.0035 (14)	0.0138 (13)	0.0098 (14)
C12	0.079 (2)	0.0709 (19)	0.0507 (15)	0.0037 (16)	0.0239 (14)	−0.0005 (14)
C13	0.0621 (16)	0.0549 (15)	0.0565 (15)	0.0074 (13)	0.0156 (12)	0.0029 (13)
C14	0.126 (3)	0.105 (3)	0.0663 (19)	0.014 (2)	0.0326 (19)	0.032 (2)

Geometric parameters (Å, º)

Cl1—C4	1.735 (2)	C6—H6	0.9300
S1—O2	1.4232 (16)	C7—C8	1.458 (3)
S1—O1	1.4330 (15)	C7—H7	0.9300
S1—N1	1.6248 (18)	C8—C13	1.383 (3)
S1—C1	1.761 (2)	C8—C9	1.388 (3)
N1—N2	1.393 (2)	C9—C10	1.376 (3)
N1—H1N	0.845 (16)	C9—H9	0.9300
N2—C7	1.273 (3)	C10—C11	1.378 (4)
C1—C6	1.375 (3)	C10—H10	0.9300
C1—C2	1.387 (3)	C11—C12	1.372 (4)
C2—C3	1.371 (3)	C11—C14	1.514 (4)
C2—H2	0.9300	C12—C13	1.383 (3)
C3—C4	1.378 (3)	C12—H12	0.9300
C3—H3	0.9300	C13—H13	0.9300
C4—C5	1.375 (3)	C14—H14A	0.9600
C5—C6	1.376 (3)	C14—H14B	0.9600
C5—H5	0.9300	C14—H14C	0.9600
O2—S1—O1	119.69 (9)	N2—C7—C8	123.4 (2)
O2—S1—N1	110.11 (10)	N2—C7—H7	118.3
O1—S1—N1	102.95 (9)	C8—C7—H7	118.3
O2—S1—C1	107.55 (10)	C13—C8—C9	118.1 (2)
O1—S1—C1	109.63 (10)	C13—C8—C7	118.9 (2)
N1—S1—C1	106.13 (10)	C9—C8—C7	123.0 (2)
N2—N1—S1	118.59 (14)	C10—C9—C8	120.4 (2)
N2—N1—H1N	118.5 (16)	C10—C9—H9	119.8
S1—N1—H1N	113.8 (17)	C8—C9—H9	119.8

C7—N2—N1	113.99 (18)	C9—C10—C11	121.6 (3)
C6—C1—C2	120.9 (2)	C9—C10—H10	119.2
C6—C1—S1	120.14 (16)	C11—C10—H10	119.2
C2—C1—S1	118.94 (17)	C12—C11—C10	117.9 (2)
C3—C2—C1	119.3 (2)	C12—C11—C14	121.1 (3)
C3—C2—H2	120.4	C10—C11—C14	121.0 (3)
C1—C2—H2	120.4	C11—C12—C13	121.4 (3)
C2—C3—C4	119.5 (2)	C11—C12—H12	119.3
C2—C3—H3	120.2	C13—C12—H12	119.3
C4—C3—H3	120.2	C12—C13—C8	120.6 (3)
C5—C4—C3	121.3 (2)	C12—C13—H13	119.7
C5—C4—Cl1	119.4 (2)	C8—C13—H13	119.7
C3—C4—Cl1	119.3 (2)	C11—C14—H14A	109.5
C4—C5—C6	119.3 (2)	C11—C14—H14B	109.5
C4—C5—H5	120.4	H14A—C14—H14B	109.5
C6—C5—H5	120.4	C11—C14—H14C	109.5
C1—C6—C5	119.7 (2)	H14A—C14—H14C	109.5
C1—C6—H6	120.2	H14B—C14—H14C	109.5
C5—C6—H6	120.2		
O2—S1—N1—N2	57.73 (19)	C2—C1—C6—C5	0.6 (3)
O1—S1—N1—N2	−173.56 (16)	S1—C1—C6—C5	−178.67 (17)
C1—S1—N1—N2	−58.39 (18)	C4—C5—C6—C1	0.5 (3)
S1—N1—N2—C7	157.85 (17)	N1—N2—C7—C8	175.80 (19)
O2—S1—C1—C6	2.2 (2)	N2—C7—C8—C13	169.8 (2)
O1—S1—C1—C6	−129.39 (17)	N2—C7—C8—C9	−12.3 (4)
N1—S1—C1—C6	120.07 (18)	C13—C8—C9—C10	−0.8 (4)
O2—S1—C1—C2	−177.10 (16)	C7—C8—C9—C10	−178.7 (2)
O1—S1—C1—C2	51.28 (18)	C8—C9—C10—C11	0.9 (4)
N1—S1—C1—C2	−59.26 (18)	C9—C10—C11—C12	−0.6 (4)
C6—C1—C2—C3	−1.1 (3)	C9—C10—C11—C14	179.4 (3)
S1—C1—C2—C3	178.25 (17)	C10—C11—C12—C13	0.2 (4)
C1—C2—C3—C4	0.4 (3)	C14—C11—C12—C13	−179.8 (3)
C2—C3—C4—C5	0.8 (4)	C11—C12—C13—C8	−0.1 (4)
C2—C3—C4—Cl1	−179.19 (17)	C9—C8—C13—C12	0.4 (4)
C3—C4—C5—C6	−1.2 (4)	C7—C8—C13—C12	178.4 (2)
Cl1—C4—C5—C6	178.76 (18)		

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of ring C8–C13.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1[i]	0.85 (2)	2.09 (2)	2.935 (2)	177 (2)
C4—Cl1···Cg1[ii]	1.74 (1)	3.47 (1)	5.175 (3)	168 (1)

Symmetry codes: (i) −x+1, −y+1, −z; (ii) x+1, y+1, z.