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2-[*N*-(*X*-Chlorophenyl)carbamoyl]-benzenesulfonamide (with *X* = 2 and 4)

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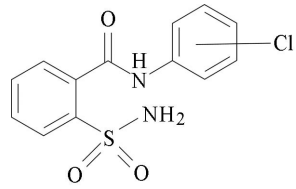
The structures of 2-[*N*-(2-chlorophenyl)carbamoyl]benzenesulfonamide and 2-[*N*-(4-chlorophenyl)carbamoyl]benzenesulfonamide, both $C_{13}H_{11}ClN_2O_3S$, are stabilized by extensive intra- and intermolecular hydrogen bonds. In both structures, sulfonamide groups are hydrogen bonded *via* the N and O atoms and form chains of molecules. The carbamoyl groups are also hydrogen bonded, involving the O and N atoms, further strengthening the polymeric chains running along the *c* and *a* axes in the 2- and 4-chloro derivatives, respectively. Carbamoylsulfonamide derivatives are novel compounds with a great potential for medicinal applications.

Comment

Benzenesulfonamide derivatives are well known in the biological sciences for their antibacterial, anticancer and anti-HIV activities (Brzozowski, 1996; Stawinski, 1997; Alovero *et al.*, 2001). In the field of catalysis, their chloro derivatives are particularly important for carrying out a large number of oxidation reactions wherein the reaction kinetics are very important (Shashikala & Rangappa, 2002; Puttaswamy, 2001). The crystal structures of a number of interesting derivatives of benzenesulfonamide have been reported recently (Clark *et al.*, 2003; Vyas *et al.*, 2003; Singh *et al.*, 2004; Bocelli *et al.*, 1995; Sutton & Cody, 1989; Furuya *et al.*, 1989). While continuing our research on the synthesis of biologically important 1,2-benzothiazine derivatives (Siddiqui *et al.*, 2007, 2008), we have devised a simple and straightforward route for the synthesis of 2-[(chlorophenyl)carbamoyl]benzenesulfonamide derivatives directly from saccharin as starting material. The syntheses of only two unsubstituted 2-cyclohexyl and 2-phenylcarbamoyl-benzenesulfonamide derivatives have been reported to date, utilizing *N*-vinylsulfobenzimide as starting material (Kiyoshi, 1959). We report here the syntheses and crystal structures of two new benzenesulfonamides, namely 2-[*N*-(2-chlorophenyl)-carbamoyl]benzenesulfonamide, (I), and 2-[*N*-(4-chloro-phenyl)carbamoyl]benzenesulfonamide, (II).



(I) = 2-Cl
(II) = 4-Cl

The molecular structure of (I) is presented in Fig. 1. The mean planes of the C1–C6 and C8–C13 benzene rings are inclined at 48.83 (8)° with respect to each other, while the carbamoyl group (O1/N2/C7) is inclined at 70.51 (13) and 29.6 (2)°, respectively, with respect to these benzene rings. The structure contains two distinct patterns of hydrogen bonds involving intermolecular N—H···O interactions (Fig. 2). The sulfonamide groups are hydrogen bonded *via* atoms N1 and O3, forming chains of molecules. The carbamoyl groups are also hydrogen bonded, *via* atoms O1 and N2, resulting in two parallel hydrogen-bonding patterns and affording stability to the polymeric chains running parallel to the *c* axis. There are two nonclassical intermolecular C—H···O hydrogen bonds and the structure is further stabilized by four additional intramolecular interactions, *viz.* N1—H1N*A*···O1, C13—H13···O1, C2—H2···O3 and N2—H2N···Cl1, resulting in seven-, six-, five- and five-membered rings with *S*(7), *S*(6), *S*(5) and *S*(5) motifs, respectively (Bernstein *et al.*, 1994); details of the hydrogen-bonding geometry are given in Table 1.

The molecular structure of (II) is presented in Fig. 3. The mean planes of the C1–C6 and C8–C13 benzene rings are inclined at 42.92 (6)° with respect to each other, while the carbamoyl group (O1/N2/C7) is inclined at 57.10 (11) and 17.96 (18)°, respectively, with respect to these benzene rings. The structure of (II) also contains two patterns of hydrogen bonds (Fig. 4), similar to those observed in (I). The sulfonamide groups in (II) are hydrogen bonded *via* atoms N1 and O3, forming chains of molecules. The carbamoyl groups are also hydrogen bonded, *via* atoms O1 and N2, resulting in two parallel hydrogen-bonding patterns and affording stability to the polymeric chains running parallel to the *a* axis. There are two nonclassical C—H···O hydrogen bonds and the structure is further stabilized by three additional intramolecular interactions, *viz.* N1—H1N*A*···O1, C13—H13···O1 and C2—H2···O3, resulting in seven-, six- and five-membered rings with *S*(7), *S*(6) and *S*(5) motifs, respectively; details of the hydrogen-bonding geometry are given in Table 2.

In both molecules, the conformation about the S—N bond is in agreement with the conformation of a handful of structures containing an 2-C-substituted benzenesulfonamide fragment; there were 14 hits in the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002). The N1 atoms in both structures are tetrahedral, with angles at N1 in the ranges 105 (3)–120 (3) (sum 338°) and 112 (2)–116 (3)° (sum 342°)

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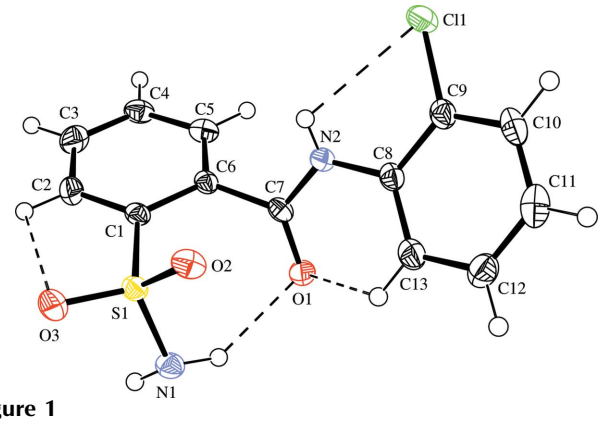

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds and short contacts are represented by dashed lines.

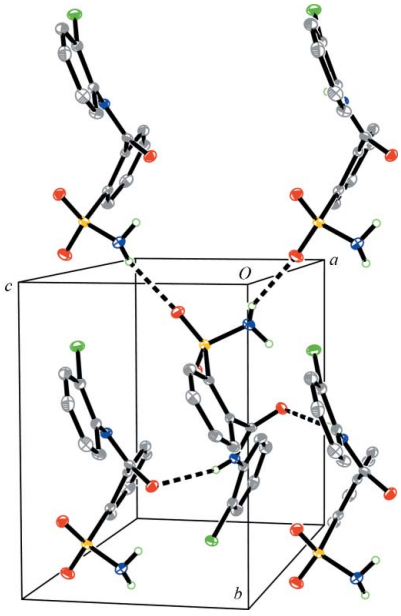

Figure 2
Intramolecular interactions (dashed lines) in the unit cell of (I) involving sulfonamide and carbamoyl groups, resulting in two parallel hydrogen-bonding patterns which form polymeric chains running parallel to the *c* axis.

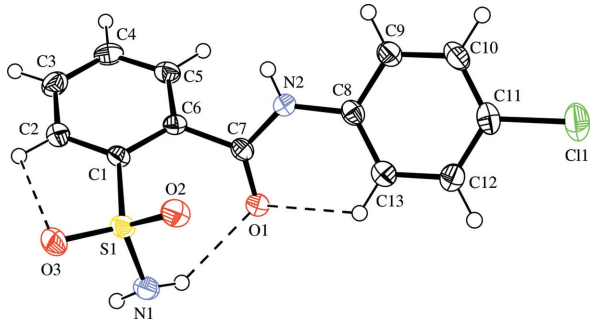

Figure 3
A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds and short contacts are represented by dashed lines.

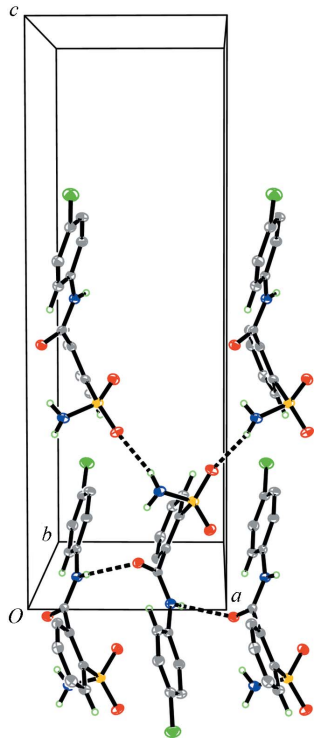

Figure 4
Intramolecular interactions (dashed lines) in the unit cell of (II) involving sulfonamide and carbamoyl groups, resulting in two parallel hydrogen-bonding patterns which form polymeric chains running parallel to the *a* axis.

for (I) and (II), respectively. The H atoms bonded to atom N1 and atoms O2 and O3 bonded to atom S1 are staggered, as observed in the compound with CSD refcode COYVER (Foresti *et al.*, 1985). Several structures have been reported wherein the H and O atoms of the sulfonamide group are eclipsed, *e.g.* CSD refcodes ENIROI (Vyas *et al.*, 2003), GUFQED01 (Clark *et al.*, 2003) and ZZZULS01 (Tremayne *et al.*, 2002). In a toluenesulfonamide (Helliwell *et al.*, 1997), the C-substituents on the N atom and the O atoms of the sulfonamide group are also eclipsed. The N1—S1—C1—C6 torsion angles in (I) and (II) are −71.6 (3) and −76.1 (2)°, respectively. The corresponding angles in the structures quoted above vary between −18.95 (ZZZULS01) and −87.85° (ENIROI), depending on the substituents present on the benzene ring, as well as on the inter- and intramolecular interactions between the substituents.

The molecular dimensions in the two structures are in agreement with the corresponding dimensions reported for similar structures quoted above (Clark *et al.*, 2003; Vyas *et al.*, 2003; Singh *et al.*, 2004; Bocelli *et al.*, 1995; Sutton & Cody, 1989; Furuya *et al.*, 1989), with an average S═O distance of 1.435 (5) Å and S—N, S—C and Cl—C distances of 1.613 (3), 1.774 (3) and 1.734 (3) Å, respectively, in (I), and an average S═O distance of 1.433 (4) Å and S—N, S—C and Cl—C distances of 1.609 (2), 1.778 (2) and 1.739 (3) Å, respectively, in (II). The only minor difference in the bond lengths is observed for the N2—C7 bond [1.357 (4) and 1.340 (3) Å in (I) and (II), respectively]. The bond angles at atoms N2 and C8 also reflect a slight influence of atom Cl1, which is bonded to atoms C9 and C11 in (I) and (II), respectively. Thus, the

C7—N2—C8 bond angles are 126.0 (3) and 128.8 (2)° in (I) and (II), respectively, while the N2—C8—C9 and N2—C8—C13 angles have values of 119.1 (3) and 122.6 (3)° in (I), and 116.4 (2) and 123.8 (2)° in (II), respectively.

Experimental

A suspension of saccharin (1.0 g, 5.46 mmol) and 2- or 4-chloroaniline (5 ml, in excess) was stirred first at room temperature (1.5 h) and then at high temperature (373 K, 2–4 h). The resulting light-brown solution was cooled to room temperature, diluted in chloroform, and washed with dilute hydrochloric acid (2*M*, 2 × 20 ml) and water. The organic layer was dried over magnesium sulfate and then evaporated at reduced pressure (11 Torr; 1 Torr = 133.322 Pa) to obtain light-pink [for (I)] and colourless [for (II)] solid products. The products were crystallized from MeOH–$CHCl_3$ (1:4 *v*/*v*) solutions by slow evaporation at 313 K. Analysis for (I), IR (neat, ν_{max}, cm^{-1}): NH and NH_2 3306 (*br*), CO 1662 (*m*), SO_2 1342 and 1165 (*s*); ^{1}H NMR (300 MHz, acetone-d_6): δ 6.62 (*s*, 2H, NH_2), 7.30 (*ddd*, 1H, J = 1.46, 7.68 and 9.14 Hz, H4′), 7.34 (*m*, 1H, H5′), 7.46 (*dd*, 1H, J = 1.47 and 8.05 Hz, H3′), 7.73–7.83 (*m*, 2H, H6′ and H4), 7.93 (*d*, 1H, J = 7.1 Hz, H5), 8.09 (*dd*, 2H, J = 1.46 and 7.32 Hz, H3 and H6), 9.51 (*s*, 1H, NH); ^{13}C NMR (750 MHz, acetone-d_6): δ 206.2, 133.2, 131.6, 131.5, 130.4, 129.7, 128.5, 128.3, 127.8, 127.1; yield: 1.16 g, 3.77 mmol, 69%; m.p. 382–383 K. Analysis for (II), IR (neat, ν_{max}, cm^{-1}): NH 3355 (*m*), NH_2 3265, 3235 (*m*), CO 1636 (*s*), SO_2 1349, 1157 (*s*); ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.91–7.10 (4H, *m*, C_6H_4), 7.32–7.53 (4H, *m*, C_6H_4), 10.55 (1H, *s*, NH); ^{13}C NMR (750 MHz, acetone-d_6): δ 165.7, 140.1, 138.1, 133.8, 131.4, 129.9, 129.9, 129.2, 129.0, 128.6, 124.2, 121.0, 120.3; yield: 1.32 g, 4.26 mmol, 78%; m.p. 475–476 K.

Compound (I)

Crystal data

$C_{13}H_{11}ClN_2O_3S$
M_r = 310.75
Orthorhombic, $Pna2_1$
a = 15.734 (9) Å
b = 10.614 (6) Å
c = 7.717 (3) Å
V = 1288.7 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.47 mm^{-1}
T = 173 (2) K
0.18 × 0.12 × 0.07 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.921, T_{max} = 0.968
2709 measured reflections
1571 independent reflections
1353 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.083
S = 1.01
1571 reflections
191 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Compound (II)

Crystal data

$C_{13}H_{11}ClN_2O_3S$
M_r = 310.75
Orthorhombic, $Pbca$
a = 7.435 (2) Å
b = 16.006 (6) Å
c = 22.061 (7) Å
V = 2625.4 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 173 (2) K
0.12 × 0.07 × 0.06 mm

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···Cl1	0.77 (4)	2.64 (4)	2.981 (3)	109 (3)
N1—H1NA···O1	0.93 (4)	2.16 (4)	2.955 (4)	144 (3)
N1—H1NB···O3^{i}	0.85 (4)	2.28 (4)	3.009 (4)	144 (3)
N2—H2N···O1^{ii}	0.77 (4)	2.40 (4)	3.152 (4)	163 (3)
C2—H2···O3	0.95	2.49	2.890 (4)	106
C13—H13···O1	0.95	2.32	2.881 (4)	117
C3—H3···O2^{iii}	0.95	2.44	3.380 (4)	173
C5—H5···O2^{iv}	0.95	2.45	3.382 (4)	167

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O1^{i}	0.81 (3)	2.32 (3)	3.028 (3)	146 (3)
N1—H1NA···O1	0.80 (3)	2.28 (3)	2.941 (3)	141 (3)
N1—H1NB···O3^{ii}	0.84 (3)	2.20 (3)	3.021 (3)	168 (3)
C12—H12···O1^{iii}	0.95	2.58	3.512 (3)	167
C2—H2···O3	0.95	2.47	2.874 (3)	106
C13—H13···O1	0.95	2.33	2.914 (3)	120

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

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.947, T_{max} = 0.973
9119 measured reflections
3005 independent reflections
2019 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.122
S = 1.03
3005 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

For both structures, H atoms bonded to C atoms were included in the refinements at geometrically idealized positions, with C—H distances of 0.95 Å and U_{iso}(H) values of 1.2U_{eq}(C). H atoms bonded to N atoms were allowed to refine, with U_{iso}(H) values of 1.2U_{eq}(N). The final difference maps were free of chemically significant features. An absolute structure could not be established by the Flack method (Flack, 1983), as a twin refinement gave a 0.55 (8):0.45 (8) mixture. Friedel pairs were, therefore, merged.

For both compounds, data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3069). Services for accessing these data are described at the back of the journal.

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