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2-Chlorophenyl 3-nitrobenzenesulfonate and 2,4-dichlorophenyl 3-nitrobenzenesulfonate: supramolecular aggregation through C–H···O, π–π and van der Waals interactions

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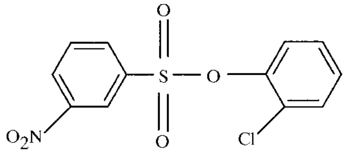
In 2-chlorophenyl 3-nitrobenzenesulfonate, $C_{12}H_8ClNO_5S$, and 2,4-dichlorophenyl 3-nitrobenzenesulfonate, $C_{12}H_7Cl_2NO_5S$, weak C—H···O interactions generate *S*(5), *S*(6) and $R_2^2(7)$ rings. The supramolecular aggregation is completed by the presence of π–π interactions and intermolecular van der Waals short contacts.

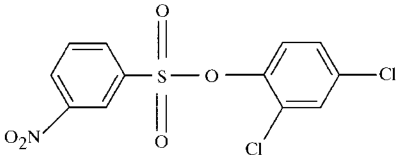
Comment

Aromatic sulfonates are used in monitoring the merging of lipids (Yachi *et al.*, 1989) and in many other fields (Narayanan & Krakow, 1983; Jiang *et al.*, 1990; Alford *et al.*, 1991; Spungin *et al.*, 1992; Tharakan *et al.*, 1992). The molecular and crystal structures of 3-nitrobenzenesulfonyl chloride (Vembu, Nallu, Spencer & Howard, 2003*c*) and a few of its derivatives (Vembu, Nallu, Spencer & Howard, 2003*d*,*e*,*f*,*g*,*h*) have been reported recently. An X-ray study of the title compounds, (I) and (II), was undertaken in order to determine their crystal and molecular structures. This study may serve as a forerunner both for an assessment of the biological significance of these compounds and for studies of the quantitative structure–activity relationships of aromatic sulfonates.

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. Atoms N, O1 and O2 deviate from the mean plane formed by atoms C1–C6 by 0.087 (2), 0.360 (3) and −0.125 (2) Å, respectively. The Cl atom deviates by 0.009 (2) Å from the C7–C12 plane. The molecular structure of (II) is shown in Fig. 2 and selected geometric parameters are given in Table 3. Atoms N1, O1 and O2 lie on the same side of the mean plane formed by atoms C1–C6, deviating by 0.075 (3), 0.043 (4) and 0.152 (4) Å, respectively. Atoms Cl1 and Cl2 deviate by 0.018 (3) and 0.043 (3) Å, respectively, from the mean plane formed by atoms C7–C12. The dihedral angle between the planes of the two aromatic rings is 53.03 (4)° in (I) and 50.0 (6)° in (II).



(I)



(II)

These rings thus have a non-coplanar orientation, similar to that reported for other aromatic sulfonates (Vembu, Nallu, Garrison & Youngs, 2003*b*,*c*,*d*,*e*; Vembu, Nallu, Spencer & Howard, 2003*a*,*b*,*d*,*e*,*g*,*h*) and in contrast to the near coplanar orientation found in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003*a*), 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003) and 8-quinolyl 3-nitrobenzenesulfonate (Vembu, Nallu, Spencer & Howard, 2003*f*). In these compounds, the anti-periplanar/anticlinal (Ar)C—S—O—C(O—Ar) conformation

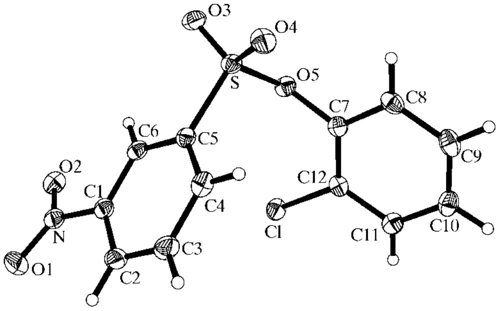


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

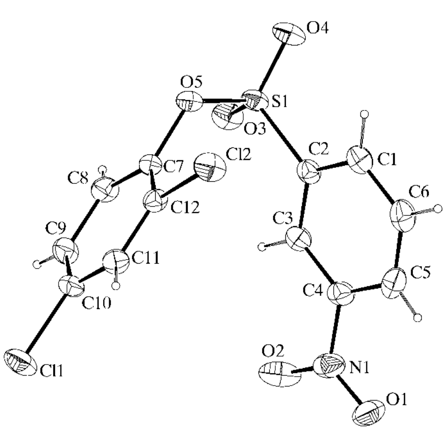


Figure 2
The molecular structure of (II), showing 50% probability displacement ellipsoids.

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leads to the two aromatic rings adopting a free coplanar orientation; the C—S—O—C torsion angle is 162.5 (2)° in 4-methoxyphenyl 4-toluenesulfonate, for example. The antiperiplanar/anticlinal orientation relieves the molecule from steric strain, thereby facilitating the adoption of a coplanar orientation. In (I) and (II), the C—S—O—C torsion angles (Tables 1 and 3) are synclinal and therefore the two aromatic rings are non-coplanar.

The crystal structures of (I) and (II) are stabilized by weak C—H···O interactions (Tables 2 and 4). The H···O distances found in (I) and (II) agree with those found for weak C—H···O bonds (Desiraju & Steiner, 1999). In (I), each of the C2—H2···O1, C4—H4···O4, C6—H6···O2 and C6—H6···O3 interactions generates an *S*(5) graph-set motif (Etter, 1990; Bernstein *et al.*, 1995). The C6—H6···O2 and C6—H6···O3 interactions constitute a pair of bifurcated donor bonds. The *S*(5) rings generated by the C2—H2···O1, C4—H4···O4, C6—H6···O2 and C6—H6···O3 interactions in (I) are non-planar, with atoms O1, O4, O2 and O3 deviating by 0.27 (1), 0.548 (8), 0.22 (1) and 0.49 (2) Å, respectively, from the corresponding mean planes formed by the other four atoms in the ring. The non-planar orientation of these rings can best be described as an envelope conformation, similar to that observed in cyclopentane derivatives. The C8—H8···O4 interaction generates an *S*(6) motif. The C4—H4···O2^{ii} and C3—H3···O1^{ii} interactions [symmetry code: (ii) $x-1, y, z$] generate a nitro-fork $R_2^2(7)$ motif. Several other weak C—H···O interactions contribute to the supramolecular aggregation of (I). In the crystal structure of (I) (Fig. 3), the molecules are stacked in layers held together by a π–π interaction, with a centroid–centroid separation of 3.746 Å between the inversion-related chlorophenyl rings (symmetry code: $2-x, -y, -z$) (*PLATON*; Spek, 2003). There is an intermolecular short contact, C1···O3($1-x, 2-y, 1-z$), of 3.212 (2) Å.

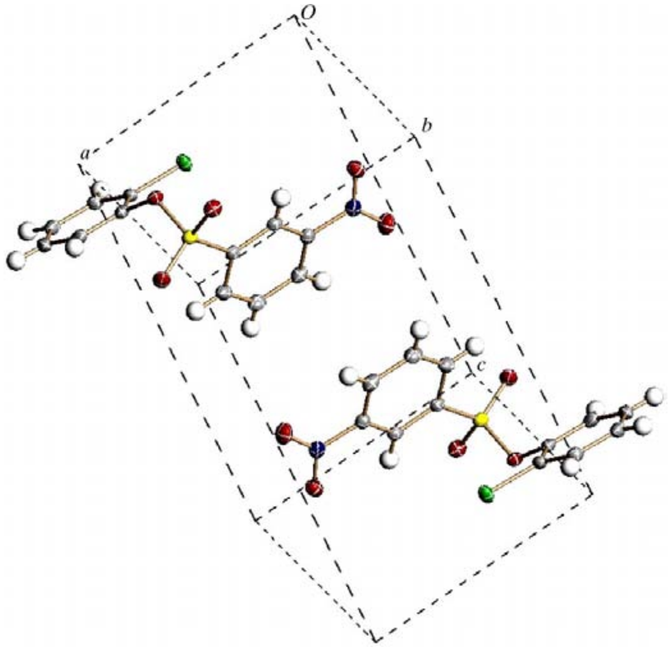

Figure 3
The packing of (I) in the unit cell, viewed along the *b* axis.

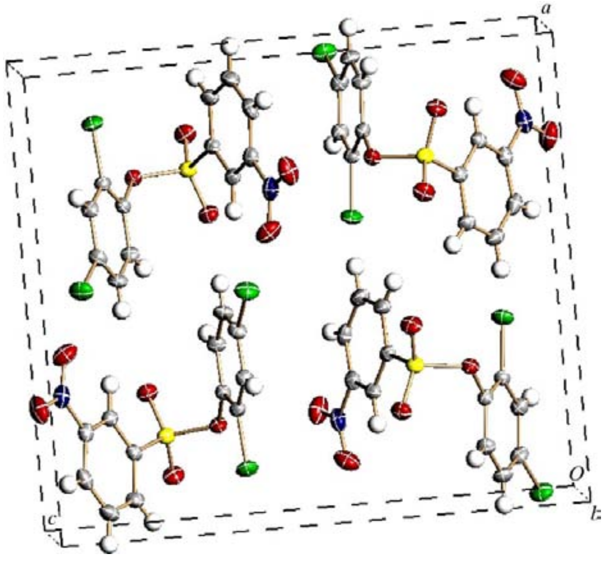

Figure 4
The packing of (II) in the unit cell, viewed along the *b* axis.

In (II), each of the C1—H1···O4, C3—H3···O2, C3—H3···O3 and C5—H5···O1 interactions generates an *S*(5) graph-set motif. The C3—H3···O2 and C3—H3···O3 interactions constitute a pair of bifurcated donor bonds. The *S*(5) rings generated by the C3—H3···O2 and C5—H5···O1 interactions in (II) are planar, whereas the *S*(5) rings formed by the C1—H1···O4 and C3—H3···O3 interactions are non-planar, with atoms O4 and O3 deviating by 0.53 (2) and 0.52 (2) Å from the corresponding mean planes formed by the other four atoms in the ring. The non-planar orientation of these rings can best be described as an envelope conformation. The C8—H8···O3 interaction generates an *S*(6) motif. The C3—H3···O3 and C8—H8···O3 interactions together constitute a pair of bifurcated acceptor bonds. The C6—H6···O5^{vi} and C1—H1···O4^{vi} interactions [symmetry code: (vi) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$] generate a fork $R_2^2(7)$ motif. Several other weak C—H···O interactions contribute to the supramolecular aggregation of (II). In the crystal structure of (II) (Fig. 4), the molecules are stacked in layers held together by a pair of π–π interactions, with a centroid–centroid separation of 3.873 Å between the symmetry-related aromatic rings [$Cg1\cdots Cg2(\frac{1}{2}-x, -y, \frac{1}{2}+z)$ and $Cg2\cdots Cg1(\frac{1}{2}-x, -y, z-\frac{1}{2})$, where *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C7–C12 rings, respectively] (*PLATON*; Spek, 2003). Other short intermolecular contacts are Cl1···O2($x-\frac{1}{2}, \frac{3}{2}-y, 2-z$) of 3.143 (2) Å, N1···O3($x-1, y, z$) of 3.022 (3) Å, O1···O3($x-1, y, z$) of 3.016 (3) Å, O1···O5($\frac{3}{2}-x, 1-y, z-\frac{1}{2}$) of 2.930 (3) Å and C5···O4($x-1, y, z$) of 3.119 (3) Å.

Experimental

For the preparation of (I), 3-nitrobenzenesulfonyl chloride (5 mmol) dissolved in acetone (5 ml) was added to 2-chlorophenol (5 mmol) dissolved in NaOH (4 ml, 5%) and the mixture was shaken well. The precipitated solid product, (I) (2 mmol, yield 40%), was recrystallized from a 1:1 mixture of petroleum ether and acetone. For the preparation of (II), 3-nitrobenzenesulfonyl chloride (5 mmol) dissolved in acetone (5 ml) was added to 2,4-dichlorophenol (5.5 mmol) dissolved in NaOH (4 ml, 5%) and the mixture was shaken well. The precipitated solid product, (II) (2.9 mmol, yield 58%), was recrystallized from a 1:1 mixture of petroleum ether and acetone.

Compound (I)

Crystal data

$C_{12}H_8ClNO_5S$
$M_r = 313.70$
Triclinic, $P\overline{1}$
$a = 7.4315\ (18)$ Å
$b = 8.474\ (2)$ Å
$c = 10.991\ (3)$ Å
$\alpha = 67.889\ (4)^\circ$
$\beta = 85.220\ (4)^\circ$
$\gamma = 81.617\ (4)^\circ$
$V = 634.1\ (3)$ Å^3
$Z = 2$
$D_x = 1.643$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3667 reflections
$\theta = 2.6$–28.3°
$\mu = 0.48$ mm^{-1}
$T = 100\ (2)$ K
Block, colorless
$0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.830$, $T_{\max} = 0.953$
5585 measured reflections
2918 independent reflections
2723 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 28.3^\circ$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.083$
$S = 1.06$
2918 reflections
213 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.2748P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cl—C12	1.7334 (15)	O1—N	1.2279 (17)
S—O3	1.4259 (12)	O2—N	1.2285 (17)
S—O4	1.4263 (11)	O5—C7	1.4099 (17)
S—O5	1.5972 (11)	N—C1	1.471 (2)
S—C5	1.7560 (15)		
O3—S—O4	120.68 (7)	O5—S—C5	103.13 (6)
O3—S—O5	102.60 (6)	C7—O5—S	121.60 (9)
O4—S—O5	109.87 (6)	O1—N—O2	124.34 (14)
O3—S—C5	109.71 (7)	O1—N—C1	118.10 (13)
O4—S—C5	109.31 (7)	O2—N—C1	117.55 (13)
C5—S—O5—C7	−71.82 (11)		

Compound (II)

Crystal data

$C_{12}H_7Cl_2NO_5S$
$M_r = 348.15$
Orthorhombic, $P2_12_12_1$
$a = 6.878\ (5)$ Å
$b = 13.330\ (10)$ Å
$c = 14.990\ (11)$ Å
$V = 1374.3\ (17)$ Å^3
$Z = 4$
$D_x = 1.683$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7544 reflections
$\theta = 2.7$–28.3°
$\mu = 0.64$ mm^{-1}
$T = 100\ (2)$ K
Block, colorless
$0.50 \times 0.30 \times 0.30$ mm

Table 2
Hydrogen-bonding and short-contact geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O1	0.931 (19)	2.472 (18)	2.740 (2)	96.6 (13)
C4—H4···O4	0.93 (2)	2.626 (19)	2.973 (2)	102.8 (13)
C6—H6···O2	0.909 (19)	2.404 (18)	2.6968 (19)	98.8 (13)
C6—H6···O3	0.909 (19)	2.615 (18)	2.9396 (19)	101.9 (13)
C8—H8···O4	0.95 (2)	2.67 (2)	3.0772 (19)	106.4 (14)
C2—H2···O3$^{\rm i}$	0.931 (19)	2.531 (19)	3.324 (2)	143.2 (15)
C4—H4···O2$^{\rm ii}$	0.93 (2)	2.511 (19)	3.033 (2)	115.7 (14)
C3—H3···O1$^{\rm ii}$	0.90 (2)	2.99 (2)	3.733 (2)	141.9 (16)
C9—H9···O3$^{\rm ii}$	0.90 (2)	2.86 (2)	3.539 (2)	132.8 (15)
C4—H4···O4$^{\rm iii}$	0.93 (2)	2.59 (2)	3.335 (2)	137.6 (15)
C8—H8···O1$^{\rm iv}$	0.95 (2)	2.40 (2)	3.316 (2)	162.5 (16)
C11—H11···O2$^{\rm v}$	0.910 (19)	2.532 (19)	3.3726 (19)	153.8 (15)

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

Table 3
Selected geometric parameters (Å, °) for (II).

Cl1—C10	1.739 (2)	S1—C2	1.757 (2)
Cl2—C12	1.722 (2)	N1—O1	1.219 (3)
S1—O3	1.4229 (17)	N1—O2	1.232 (3)
S1—O4	1.4240 (16)	N1—C4	1.467 (3)
S1—O5	1.6006 (18)	O5—C7	1.406 (2)
O3—S1—O4	120.90 (10)	O5—S1—C2	103.41 (9)
O3—S1—O5	108.26 (9)	O1—N1—O2	124.1 (2)
O4—S1—O5	103.06 (9)	O1—N1—C4	117.7 (2)
O3—S1—C2	109.18 (10)	O2—N1—C4	118.16 (19)
O4—S1—C2	110.45 (10)	C7—O5—S1	118.30 (12)
C2—S1—O5—C7	−55.15 (16)		

Table 4
Hydrogen-bonding and short-contact geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O4	0.94 (3)	2.63 (3)	2.982 (3)	102.8 (17)
C3—H3···O2	0.98 (2)	2.41 (2)	2.708 (3)	96.7 (17)
C3—H3···O3	0.98 (2)	2.60 (3)	2.935 (3)	100.2 (17)
C5—H5···O1	0.81 (3)	2.37 (3)	2.716 (3)	106 (2)
C8—H8···O3	0.84 (3)	2.65 (2)	3.055 (3)	111.3 (18)
C6—H6···O5$^{\rm vi}$	0.93 (3)	2.95 (3)	3.805 (3)	153 (2)
C1—H1···O4$^{\rm vi}$	0.94 (3)	2.83 (2)	3.349 (3)	116.1 (19)
C9—H9···O2$^{\rm vii}$	0.85 (2)	2.72 (2)	3.294 (3)	126 (2)
C9—H9···O3$^{\rm viii}$	0.85 (2)	2.56 (3)	3.362 (3)	158 (2)
C11—H11···O1$^{\rm ix}$	0.85 (3)	2.48 (3)	3.301 (3)	163 (2)

Symmetry codes: (vi) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$; (vii) $\frac{1}{2}+x, \frac{3}{2}-y, 2-z$; (viii) $x-\frac{1}{2}, \frac{3}{2}-y, 2-z$; (ix) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.739$, $T_{\max} = 0.830$
11 316 measured reflections
3268 independent reflections
3158 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 28.4^\circ$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.081$
$S = 1.08$
3268 reflections
218 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.1269P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Absolute structure: Flack (1983), 1283 Friedel pairs
Flack parameter = 0.02 (6)

All H atoms were located from difference Fourier maps and their positional coordinates and isotropic displacement parameters were refined. The C—H bond lengths in (I) and (II) are in the ranges 0.90 (2)–0.95 (2) and 0.81 (3)–0.98 (2) Å, respectively.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1154). Services for accessing these data are described at the back of the journal.

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