

Layer architecture in 4-nitrophenyl and 4-chlorophenyl 3-nitrobenzenesulfonate at 100 K

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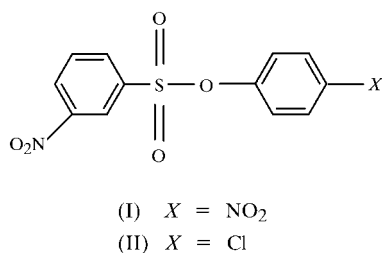
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The structures of the title compounds, C₁₂H₈N₂O₇S and C₁₂H₈ClNO₅S, contain weak C—H···O interactions creating layers of molecules which, taking the conformation of the molecules into account, are arranged in an *ABAB* sequence. Both structures can be designated, therefore, as ordered racemates of rotameric species.

Comment

Aromatic sulfonates are used in detecting specific organic anion-binding proteins in the liver plasma membrane (Yachi *et al.*, 1989) and in many other fields (Spungin *et al.*, 1992; Tharakan *et al.*, 1992; Alford *et al.*, 1991; Jiang *et al.*, 1990; Narayanan & Krakow, 1983). The present X-ray study of 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 molecules of (I) and (II) are shown in Figs. 1 and 2, respectively. Ignoring the difference in the nature of the *para*-substituent of the phenol ring, *viz.* NO₂ for (I) and Cl for (II), it is readily seen that the molecules of (I) and (II) are mirror images of one another. The mirror-image relationship is clearly brought about by rotational isomerism, *i.e.* the

relative positions of the two molecular fragments in terms of rotation about the C—S bond connecting them. Selected geometric parameters for both molecules are given in Table 1. The internal geometries of the molecules of (I) and (II) are clearly very similar and the torsion angles are entirely consistent with the mirror-image relationship between them noted above. The C—C distances within the 3-nitrophenyl and 4-nitrophenyl rings of (I) are in the ranges 1.370 (8)–1.394 (6) and 1.374 (6)–1.385 (6) Å, respectively, and for (II), the corresponding ranges are 1.375 (7)–1.393 (6) and 1.366 (8)–1.404 (7) Å. In (I), atoms N1, O1 and O2 deviate by 0.014 (7), 0.055 (7) and –0.028 (8) Å, respectively, from the C1–C6 mean plane, while atoms N2, O6 and O7 deviate by 0.085 (6), –0.164 (7) and –0.052 (7) Å, respectively, from the C7–C12 mean plane. In (II), atoms N1, O1 and O2 deviate by 0.018 (8), –0.246 (9) and 0.274 (10) Å, respectively, from the C1–C6 mean plane. The dihedral angles between the two aromatic planes are 57.7 (7) and 51.0 (2)^o in (I) and (II), respectively. This is similar to the situation reported for other aromatic sulfonates (Vembu *et al.*, 2004*a,b*), but is in contrast with the near coplanar orientation found in 2,4-dinitrophenyl 4-toluenesulfonate (Vembu, Nallu, Garrison & Youngs, 2003), 4-methoxyphenyl 4-toluenesulfonate (Vembu, Nallu, Garrison, Hindi & Youngs, 2003) and 8-quinolyl 3-nitrobenzenesulfonate (Vembu, Nallu, Spencer & Howard, 2003). This difference arises from the synclinal C1–S–O5–C7 torsion angles in (I) and (II) [–62.6 (3) and 68.9 (4)^o, respectively], as distinct from the antiperiplanar/anticlinal arrangement, *e.g.* 162.5 (2)^o for the corresponding angle in 4-methoxyphenyl 4-toluenesulfonate, which permits the strain-relieving near-coplanar orientation of the aromatic species.

Weak intermolecular C—H···O interactions (Tables 2 and 3) of the type described by Desiraju & Steiner (1999) are present in both structures. In the structure of (I), the contacts C6–H6···O3ⁱ, C8–H8···O6ⁱⁱ and C12–H12···O4ⁱⁱⁱ (the first three entries in Table 2) interconnect the molecules to form layers parallel to (001), as shown in Fig. 3. The molecules within any one layer are identical in conformation and

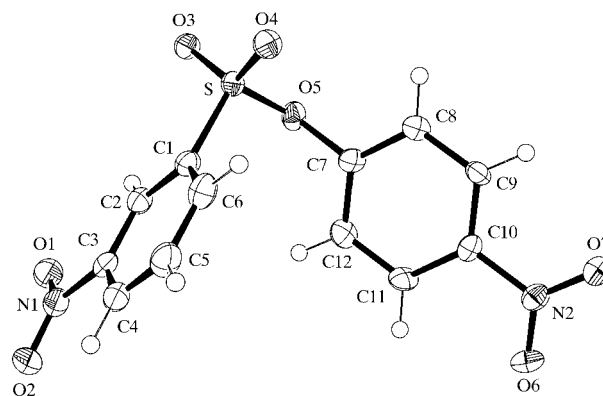


Figure 1

A view of a molecule of (I), showing the atom-numbering scheme. Non-H atoms are shown as 50% probability displacement ellipsoids.

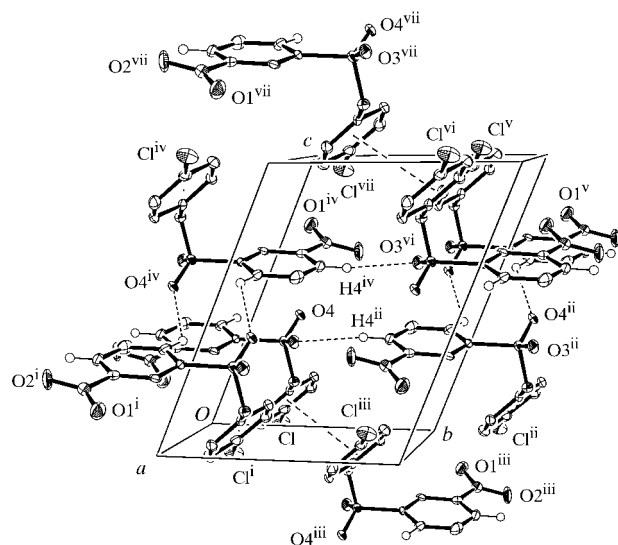


Figure 6

The unit cell of (II) viewed along *a*. Intermolecular interactions, one within the layers and the others at the layer interfaces, are represented by dashed lines. Non-H atoms are shown as 50% probability displacement ellipsoids and H atoms involved in the C—H...O contacts are drawn as small spheres of arbitrary radii. Selected atoms are labelled. [Symmetry codes: (i) $1+x, y, z$; (ii) $x, 1+y, z$; (iii) $-x, 1-y, -z$; (iv) $1-x, -y, 1-z$; (v) $-x, 1-y, 1-z$; (vi) $1-x, 1-y, 1-z$; (vii) $1+x, y, 1+z$.]

contacts within these layers are typified by the contacts C4—H4...O3^v, C8—H8...O2^{vi} and C9—H9...O3^{vii} (the first three entries in Table 3). The molecules within the layer are identical in conformation and orientation, because they are related to one another purely by cell translation. In this case, while one surface of the layer is populated by the 3-nitrophenyl group, it is now the 4-chlorophenyl group which protrudes from the other surface (Fig. 6), the converse of the situation in the layers of (I) described above. The stacking of the layers in the *c* direction once again induces an *ABAB* pattern when the conformation of the molecules within the layers is taken into account, but the inversion in conformation from one layer to the next is now brought about by the operation of crystallographic centres of symmetry. The stacking of the layers (Fig. 6) now creates two distinct forms of interface between them. In the first, at or near $z = \frac{1}{2}$, the interface is between the 3-nitrophenyl surfaces of a pair of layers. This permits the further interaction C6—H6...O4^{viii} (Table 3). At this interface, there is no significant overlap or π — π interaction between the phenyl rings. It is only at the other interface between the layers, at $z = 0$ and 1, that π — π interaction occurs, where it involves centrosymmetrically related pairs of 4-chlorophenyl rings, with a centroid—centroid separation and perpendicular distance between the ring planes of 3.725 and 3.415 Å, respectively. This is the only significant intermolecular interaction at this interface. This layer sequence can also be thought of in terms of double layers centred on the face-to-face interface at $z = \frac{1}{2}$, which then interact with the creation of the π — π interactions at $z = 0$ and 1.

Rotational isomerism is present in both structures but the structures are completely ordered and may be designated as fully ordered racemates of rotameric species.

Experimental

The title compounds were prepared by the addition of a solution of 3-nitrobenzenesulfonyl chloride (1.1 g, 5 mmol) dissolved in acetone (5 ml) to a solution of the appropriate phenol (5 mmol) dissolved in NaOH (4 ml, 5%, 5 g/100 ml) and thorough shaking of the mixture. The precipitated solid products [1.2 g, 3.7 mmol, yield 74% for (I); 1.0 g, 3.2 mmol, yield 64% for (II)] were recrystallized from ethanol.

Compound (I)

Crystal data

C₁₂H₈N₂O₇S
M_r = 324.26
 Monoclinic, *C*₂
a = 7.891 (2) Å
b = 8.798 (3) Å
c = 18.829 (6) Å
 β = 94.597 (5)°
V = 1303.1 (7) Å³
Z = 4
D_x = 1.653 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 1812 reflections
 θ = 3.5–26.2°
 μ = 0.29 mm⁻¹
T = 100 (2) K
 Block, colourless
 0.30 × 0.10 × 0.10 mm

Table 1

Selected geometric parameters (Å, °) for (I) and (II).

	(I), <i>X</i> = NO ₂	(II), <i>X</i> = Cl
S—O3	1.422 (3)	1.430 (4)
S—O4	1.429 (3)	1.424 (4)
S—O5	1.579 (3)	1.589 (4)
S—C1	1.743 (5)	1.756 (6)
C3—N1	1.479 (6)	1.474 (7)
N1—O1	1.215 (6)	1.230 (5)
N1—O2	1.221 (5)	1.224 (6)
O5—C7	1.419 (5)	1.430 (6)
C10— <i>X</i>	1.473 (5)	1.763 (6)
<i>X</i> —O6	1.218 (5)	
<i>X</i> —O7	1.227 (5)	
O3—S—O4	120.86 (18)	119.7 (3)
O3—S—O5	103.33 (17)	103.8 (2)
O4—S—O5	109.07 (17)	109.9 (2)
O3—S—C1	110.76 (19)	109.6 (2)
O4—S—C1	107.8 (2)	108.8 (2)
O5—S—C1	103.60 (18)	103.9 (2)
C7—O5—S	122.3 (3)	120.3 (3)
O1—N1—O2	124.8 (4)	124.1 (5)
O1—N1—C3	116.8 (4)	117.8 (5)
O2—N1—C3	118.4 (5)	118.1 (4)
O6— <i>X</i> —O7	123.2 (4)	
O6— <i>X</i> —C10	118.5 (4)	
O7— <i>X</i> —C10	118.3 (3)	
O3—S—C1—C2	33.1 (4)	−23.0 (5)
O4—S—C1—C2	167.4 (3)	−155.5 (4)
O5—S—C1—C2	−77.1 (4)	87.5 (4)
O3—S—C1—C6	−148.4 (3)	157.2 (4)
O4—S—C1—C6	−14.1 (4)	24.7 (5)
O5—S—C1—C6	101.4 (4)	−92.3 (4)
S—O5—C7—C12	99.3 (4)	−110.6 (5)
S—O5—C7—C8	−86.6 (4)	74.0 (5)
C1—S—O5—C7	−62.6 (3)	68.9 (4)
O3—S—O5—C7	−178.2 (3)	−176.5 (4)
O4—S—O5—C7	52.1 (3)	−47.3 (4)

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 5467 measured reflections
 2971 independent reflections
 2534 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -10 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.139$
 $S = 1.06$
 2971 reflections
 200 parameters
 Only H-atom U values refined
 $w = 1/[\sigma^2(F_o^2) + (0.0665P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983);
 1406 Friedel pairs
 Flack parameter = 0.08 (12)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.183$
 $S = 1.00$
 1713 reflections
 182 parameters
 Only H-atom U values refined

$w = 1/[\sigma^2(F_o^2) + (0.1188P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.48 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$

All H atoms were included in calculated positions, with C—H distances of 0.95 Å, and refined with a riding model. Their displacement parameters were tied to a common free variable, which was refined.

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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Table 2

Hydrogen-bonding geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C6-H6 \cdots O3^i$	0.95	2.45	3.100 (5)	126
$C12-H12 \cdots O4^{ii}$	0.95	2.30	3.197 (5)	158
$C8-H8 \cdots O6^{iii}$	0.95	2.45	3.350 (5)	158
$C5-H5 \cdots O7^{iv}$	0.95	2.43	3.184 (6)	136

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

Compound (II)

Crystal data

$C_{12}H_8ClNO_5S$
 $M_r = 313.70$
 Triclinic, $P\bar{1}$
 $a = 7.556$ (9) Å
 $b = 8.562$ (8) Å
 $c = 10.851$ (13) Å
 $\alpha = 67.86$ (6)°
 $\beta = 89.93$ (11)°
 $\gamma = 87.01$ (8)°
 $V = 649.2$ (13) Å³

$Z = 2$
 $D_x = 1.605 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3154 reflections
 $\theta = 2.6\text{--}28.2^\circ$
 $\mu = 0.47 \text{ mm}^{-1}$
 $T = 100$ (2) K
 Block, colourless
 $0.46 \times 0.13 \times 0.12 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.812, T_{\text{max}} = 0.945$
 5715 measured reflections

1713 independent reflections
 1261 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.068$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -3 \rightarrow 9$
 $k = -10 \rightarrow 9$
 $l = -14 \rightarrow 8$

Table 3

Hydrogen-bonding geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C4-H4 \cdots O3^v$	0.95	2.50	3.441 (8)	170
$C8-H8 \cdots O2^{vi}$	0.95	2.48	3.307 (8)	145
$C9-H9 \cdots O3^{vii}$	0.95	2.57	3.293 (8)	133
$C6-H6 \cdots O4^{viii}$	0.95	2.62	3.311 (7)	129

Symmetry codes: (v) $x, y - 1, z$; (vi) $x - 1, 1 + y, z$; (vii) $x - 1, y, z$; (viii) $-x, -y, 1 - z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1553). Services for accessing these data are described at the back of the journal.

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