

Soft C—H···O hydrogen bonds in methyl 2,4-dinitrobenzenesulfenate: sheets built from $R_2^2(10)$ and $R_6^6(42)$ rings

Debbie Cannon,^a John N. Low,^{b†} Susan A. McWilliam,^b Janet M. S. Skakle,^b James L. Wardell^b and Christopher Glidewell^{c*}

^aDepartment of Electronic Engineering and Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland, ^bDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^cSchool of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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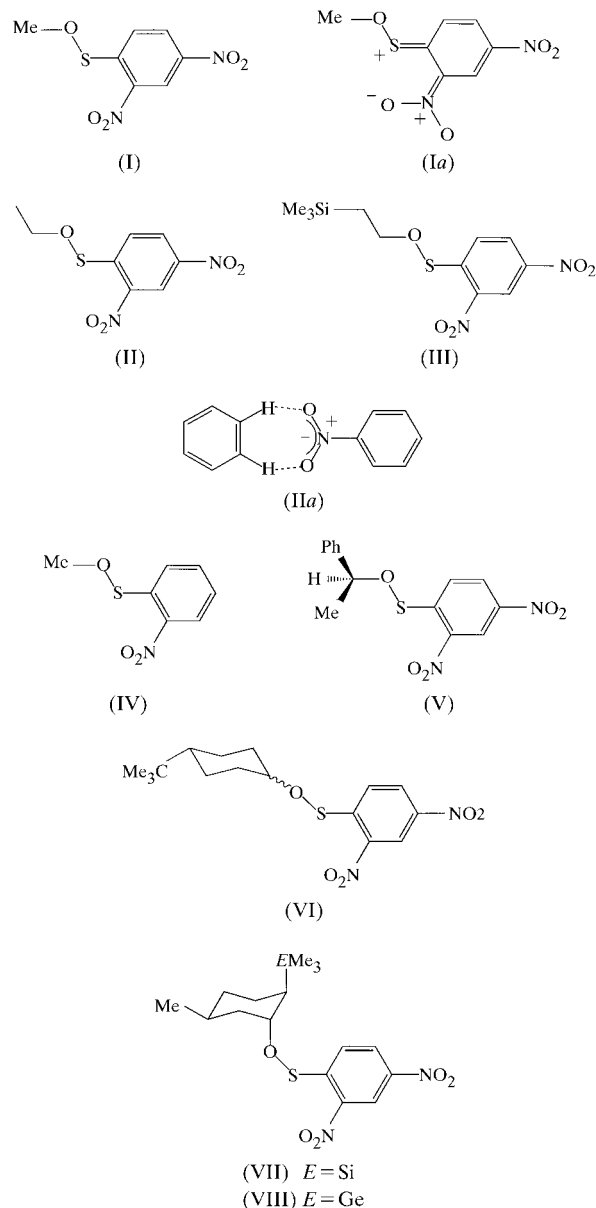
Molecules of the title compound, $C_7H_6N_2O_5S$, are linked into sheets containing $R_2^2(10)$ and $R_6^6(42)$ rings by C—H···O hydrogen bonds [C···O 3.405 (3) and 3.511 (2) Å; C—H···O 159 and 169°], in which both acceptors are in the same nitro group. Comparisons are made with the hydrogen bonding in other nitrobenzenesulfenate esters.

Comment

We have recently discussed the interplay of intra- and intermolecular forces in 2-nitrobenzenethiolates of type 2- $O_2N-C_6H_4SX$ in examples where the α -atom of the group X is variously C (Low, Storey *et al.*, 2000; Glidewell *et al.*, 2000c), N (Low, Storey *et al.*, 2000; Glidewell *et al.*, 2000b), S (Low, Glidewell & Wardell, 2000; Glidewell *et al.*, 2000a) or Pd (Aupers *et al.*, 2000). In particular, we have been concerned with the correlation between the conformational behaviour of the 2-nitro group and that of the thiolate fragment, and with the influence upon this of intermolecular forces, especially soft hydrogen bonds of the C—H···O type. We have now extended this study to an example where the α -atom of X is O; we report here the structure of methyl 2,4-dinitrobenzenesulfenate, 2,4-(O_2N) $_2C_6H_3SOCH_3$, (I), and we compare the C—H···O hydrogen bonding in (I) with that in structures of related nitrobenzenesulfenate esters, retrieved *via* the Cambridge Structural Database (CSD; Allen & Kennard, 1993).

The ester O atom and the 2-nitro group are both very slightly twisted out of the plane of the aryl ring (Table 1), consistent with the correlation discussed in previous papers; on the other hand, the 4-nitro group is essentially coplanar

with the ring. The C—S—O—C torsion angle is close to 90°, determined primarily by the expected near-orthogonality of the adjacent lone-pair orbitals on S and O. The dimensions of the ring indicate a modest degree of *o*-quinonoid bond fixation, consistent with a small contribution from the canonical



form (Ia); there is, however, no evidence for the very marked development of *p*-quinonoid bond fixation as observed in 2- $O_2N-4-CH_3C_6H_3SCH=CHPh$ (Low, Storey *et al.*, 2000). Consistent with a contribution from (Ia), the C—S bond length is somewhat less than is typical for C(aryl)—S bonds [mean value 1.773 Å, lower quartile value 1.765 Å; Allen *et al.*, 1987].

The molecules of (I) (Fig. 1) are linked by two soft C—H···O hydrogen bonds (Table 2) into two-dimensional sheets; although neither hydrogen bond has particularly short H···O or C···O distances, the values in (I) are well within the ranges accepted for such bonds (Desiraju, 1991, 1996), and the C—H···O angles are both close to the optimally observed 160°.

† Postal address: Department of Electronic Engineering & Physics, University of Dundee, Nethergate, Dundee DD1 4HN, Scotland.

Unexpectedly, the shorter H···O and C···O distances are associated with the less acidic C—H bond. Aromatic C3 in the molecule at (x, y, z) acts as donor to nitro O41 in the molecule at $(1 - x, 1 - y, 1 - z)$, while C3 at $(1 - x, 1 - y, 1 - z)$ acts as donor to O41 at (x, y, z) , so generating a centrosymmetric $R_2^2(10)$ motif within a dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The second C—H···O hydrogen bond then links these dimeric units into continuous sheets parallel to (103), which take the form of (4,4) nets (Batten & Robson, 1998), in which the dimer units act as the nodes of the net. Methyl C7 in the molecule at (x, y, z) acts as hydrogen-bond donor, *via* H72, to nitro O42 at $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$; the symmetry-related C7 in the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is at $(1 - x, 1 - y, 1 - z)$ and this

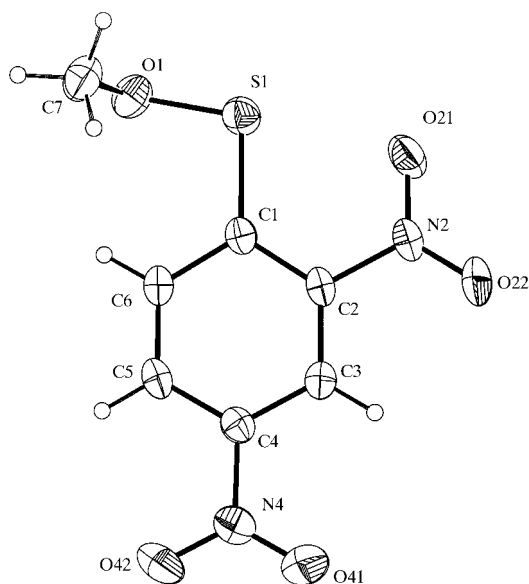


Figure 1
A view of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

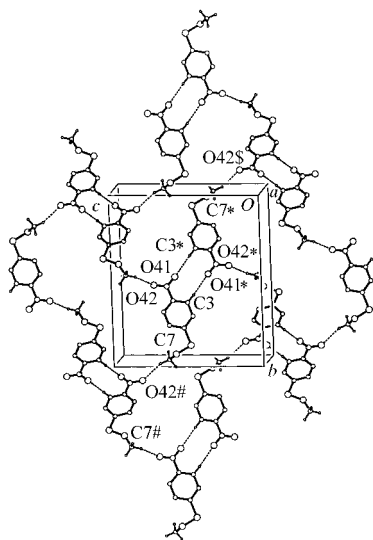


Figure 2
Part of the crystal structure of (I) showing the formation of a (103) sheet built from $R_2^2(10)$ and $R_6^6(42)$ rings. Atoms marked with an asterisk (*), hash (#) or dollar sign (\$) are at the symmetry positions $(1 - x, 1 - y, 1 - z)$, $(-\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(\frac{3}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

acts as donor to O42 at $(\frac{3}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$. Each $R_2^2(10)$ dimer thus acts as a double donor and as a double acceptor of hydrogen bonds of this type and, in this manner, the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is directly linked to the dimers centred at $(2, 0, 0)$, $(2, 1, 0)$, $(\bar{1}, 0, 1)$ and $(\bar{1}, 1, 1)$. Propagation of these hydrogen bonds by the space group generates the (103) sheet built from alternating $R_2^2(10)$ and $R_6^6(42)$ rings (Fig. 2); despite the presence of large rings, adjacent sheets are not interwoven.

It is noteworthy that while both O atoms of the 4-nitro group act as hydrogen-bond acceptors, neither of the O atoms in the 2-nitro group does so. Hence it is of interest to compare the hydrogen-bonding behaviour of (I) with that of the related compounds (II)–(VIII). In compound (II) (CSD code NUPPUJ; Green *et al.*, 1997), both O atoms of the 4-nitro group act as acceptors, with an adjacent pair of aromatic C atoms acting as the donors; in this manner, a $C(5)C(6)[R_2^2(7)]$ chain of rings (Bernstein *et al.*, 1995) is formed (Fig. 3) which contains the unusual synthon (IIa), not listed in Desiraju's compilation of supramolecular synthons (Desiraju, 1995). By contrast, in the closely related ester (III) (NUPPIX; Green *et al.*, 1997), neither of the nitro groups is involved in the hydrogen bonding; instead the ester O atom acts as the acceptor from an aromatic C atom, and a simple $C(5)$ spiral chain is formed (Fig. 4). However, there are no intermolecular C—H···O hydrogen bonds in either (IV) (MENBZS01;

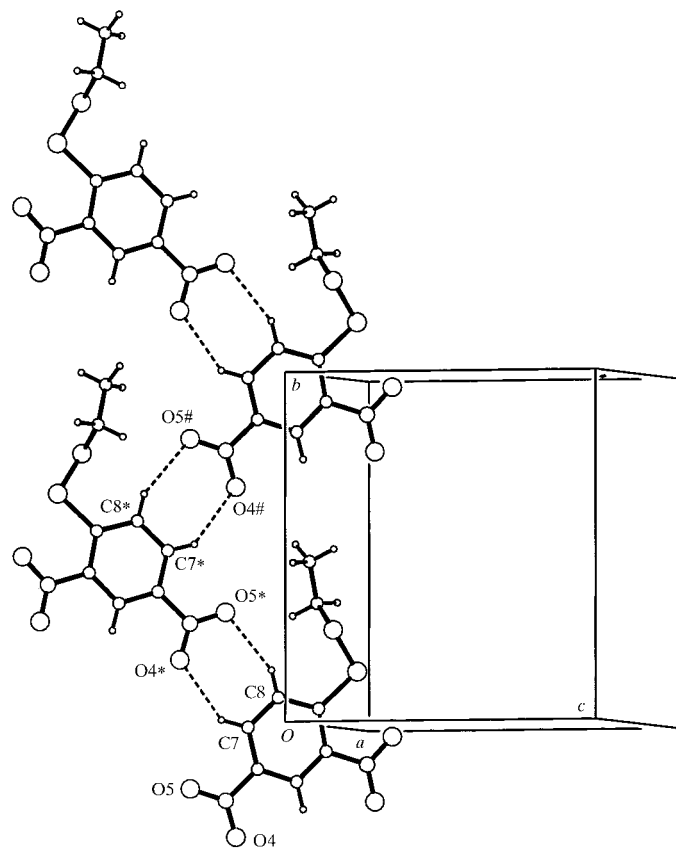


Figure 3
Part of the crystal structure of (II) showing the formation of a $C(5)C(6)[R_2^2(7)]$ chain of rings. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-x, \frac{1}{2} + y, -\frac{1}{2} - z)$ and $(x, 1 + y, z)$, respectively.

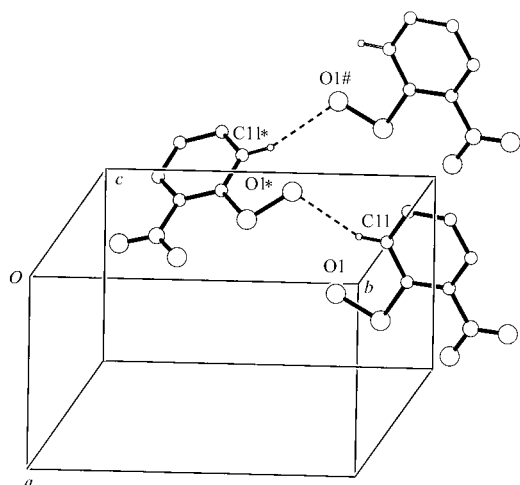


Figure 4
Part of the crystal structure of (III) showing the formation of a C(5) spiral chain. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z)$ and $(-1 + x, y, z)$, respectively.

Kuczman *et al.*, 1989) or (V) (EACBOZ; Craine *et al.*, 1993), both of which are evidently very closely related to compound (I); nor are there any such bonds in either the *trans* (TELKUQ; White *et al.*, 1996) or *cis* (TELKUQ01; Chan *et al.*, 1996; inadvertently described in the original report, and thence in the CSD, as *trans*) isomers of (VI), but in the isostructural pair (VII) (TOTRID; Chan *et al.*, 1996) and (VIII) (TOTREZ; Chan *et al.*, 1996), a C atom in the cyclohexyl unit acts as donor to one of the O atoms of the 4-nitro group, forming a C(11) spiral chain (Fig. 5). Thus, within the rather closely related series of esters (I)–(V), soft C–H...O hydrogen bonds generate a two-dimensional supramolecular structure in (I), and two quite different one-dimensional

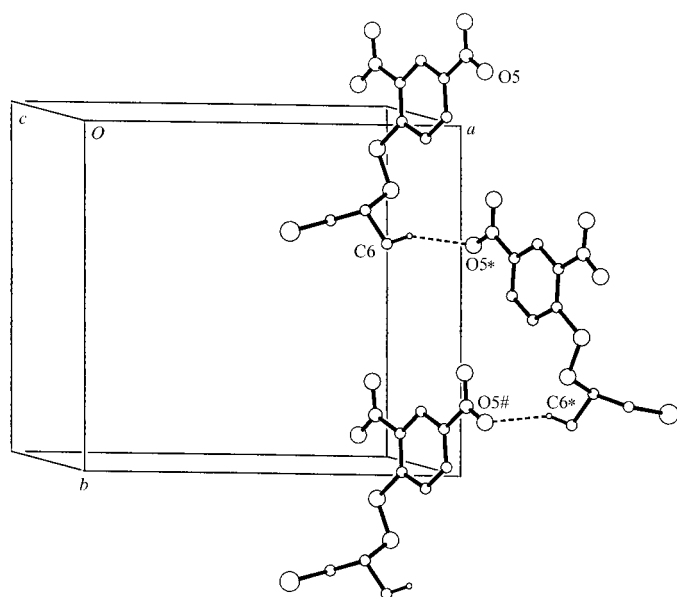


Figure 5
Part of the crystal structure of (VII) showing the formation of a C(11) spiral chain. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions $(2 - x, \frac{1}{2} + y, -\frac{1}{2} - z)$ and $(x, 1 + y, z)$, respectively.

arrays in (II) and (III) respectively, while there is no specific supramolecular aggregation in (IV) and (V); similarly, the closely related esters (VI)–(VIII) differ in their behaviour. In none of the original reports on compounds (II), (III) and (VI)–(VIII) was there any comment on this aggregation.

Experimental

A sample of compound (I) was prepared by reaction of 2,4-dinitrobenzenesulfonyl chloride with methanol. Crystals suitable for single-crystal X-ray diffraction were grown from a methanol solution.

Crystal data

$C_7H_6N_2O_5S$	$D_x = 1.625 \text{ Mg m}^{-3}$
$M_r = 230.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2643 reflections
$a = 4.0413 (2) \text{ \AA}$	$\theta = 2.85\text{--}29.74^\circ$
$b = 16.6702 (10) \text{ \AA}$	$\mu = 0.348 \text{ mm}^{-1}$
$c = 14.0749 (8) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 97.1830 (10)^\circ$	Block, yellow
$V = 940.77 (9) \text{ \AA}^3$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	3370 independent reflections
φ - θ scans	1920 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.903, T_{\text{max}} = 0.934$	$\theta_{\text{max}} = 32.6^\circ$
9619 measured reflections	$h = -6 \rightarrow 5$
	$k = -12 \rightarrow 25$
	$l = -21 \rightarrow 19$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0836P)^2]$
$wR(F^2) = 0.141$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3370 reflections	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
137 parameters	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

C1—C2	1.399 (2)	N2—O21	1.231 (2)
C2—C3	1.379 (2)	N2—O22	1.214 (2)
C3—C4	1.372 (2)	N4—O41	1.203 (2)
C4—C5	1.383 (2)	N4—O42	1.213 (2)
C5—C6	1.367 (2)	C1—S1	1.7471 (17)
C1—C6	1.407 (2)	S1—O1	1.6322 (13)
C2—N2	1.4445 (19)	O1—C7	1.448 (2)
C4—N4	1.464 (2)		
C1—S1—O1	100.38 (7)	S1—O1—C7	115.74 (11)
C2—C1—S1—O1	−177.65 (13)	C1—S1—O1—C7	89.37 (14)
C1—C2—N2—O21	−4.6 (2)	C3—C4—N4—O41	0.5 (3)
C1—C2—N2—O22	173.38 (17)	C3—C4—N4—O42	179.28 (17)

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C3—H3...O41 ⁱ	0.93	2.59	3.511 (2)	169
C7—H72...O42 ⁱⁱ	0.96	2.49	3.405 (3)	159

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

Compound (I) crystallized in the monoclinic system; space group $P2_1/n$ was uniquely assigned from the systematic absences. H atoms were treated as riding atoms with C—H distances of 0.93 (aromatic) or 0.96 Å (methyl).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1044). Services for accessing these data are described at the back of the journal.

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