Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Methyl 4-nitrophenyl sulfoxide: π-stacked chains of hydrogen-bonded $R_2^2(10)$ dimers

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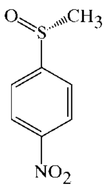
Received 27 November 2003
Accepted 1 December 2003
Online 20 December 2003

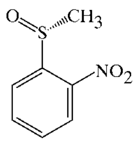
Molecules of the title compound, $C_7H_7NO_3S$, are linked into centrosymmetric $R_2^2(10)$ dimers by paired C—H···O hydrogen bonds, and these dimers are linked into [110] chains by a single aromatic π–π stacking interaction.

Comment

Molecules of the title compound, (I), are chiral, but the centrosymmetric space group accommodates equal numbers of the *R* and *S* enantiomers; the selected reference molecule (Fig. 1) is of the *R* configuration. Within the molecule, the ring C—C distances span the very narrow range 1.384 (2)–1.392 (2) Å. The two independent C—S distances (Table 1) are very similar but with the distance to the aryl C marginally the longer of the two. The reference mean values for C_{aryl}—S(O)– and Csp^3—S(O)– distances (Allen *et al.*, 1987) are 1.790 and 1.809 Å, respectively, while the reference mean value for the S═O distance in sulfoxides is 1.497 Å, so the S—O distance in (I) is entirely characteristic.



(I)



(II)

The internal C—C—C angles at C1 and C4 in (I), *ipso* to the electron-withdrawing NO_2 and $S(O)CH_3$ substituents, respectively, are both greater than 120°, as expected (Domenicano & Murray-Rust, 1979). At the pyramidal S atom, the bond angles involving sulfoxide atom O41 are both significantly larger than the C—S—C angle. The conformation of the S(O)—CH_3 fragment, with the sulfonyl O atom almost coplanar with the aryl ring, may be controlled by an intra-

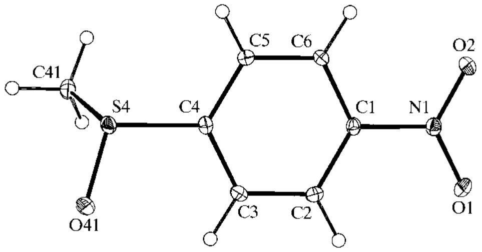


Figure 1
The *R* enantiomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

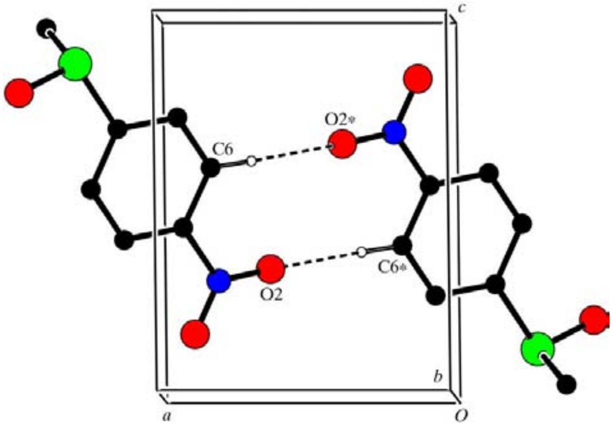


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric $R_2^2(10)$ dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

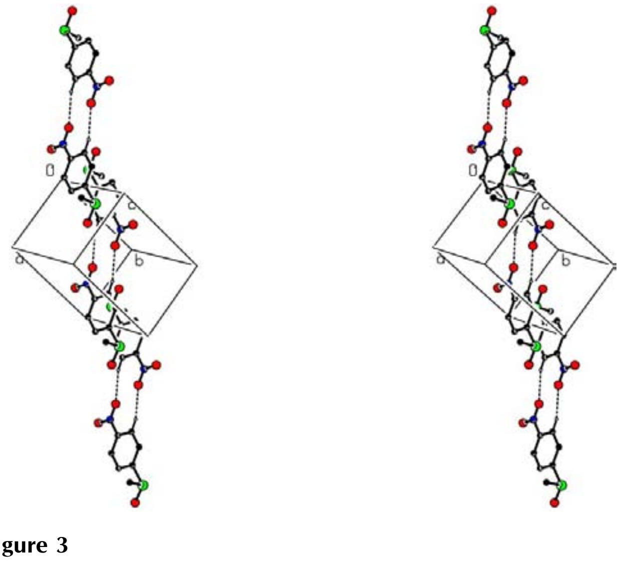


Figure 3
Stereoview of part of the crystal structure of (I), showing the formation of a [110] chain of π-stacked $R_2^2(10)$ dimers. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

DOI: 10.1107/S0108270103027616

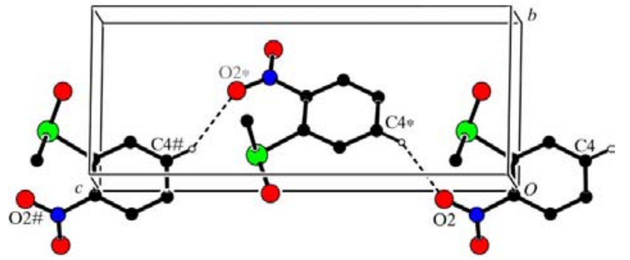


Figure 4
Part of the crystal structure of (II) (Ianelli *et al.*, 1992), showing the formation of a zigzag *C*(7) chain along [001]. Atomic coordinates and atom labels are as given in the original report. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions ($x, \frac{1}{2} - y, \frac{1}{2} + z$) and ($x, y, 1 + z$), respectively.

molecular dipolar attraction involving the positively charged atom H3 and the negatively charged atom O41. The nitro group is essentially coplanar with the aryl group, and a similar conformation was found in the isomeric compound methyl 2-nitrophenyl sulfoxide, (II) (Ianelli *et al.*, 1992).

The molecules of (I) are weakly linked into centrosymmetric dimers by a nearly linear C—H···O hydrogen bond, and these weak dimers are further linked into chains by a single aromatic π–π stacking interaction. Ring atom C6 in the molecule at (x, y, z), which is adjacent to the nitro group and hence has the most polarized C—H bond in the molecule, acts as hydrogen-bond donor to nitro atom O2 in the molecule at ($1 - x, 1 - y, 1 - z$), so forming an $R_2^2(10)$ dimer (Bernstein *et al.*, 1995) centred at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) (Table 2, Fig. 2). The aryl rings of the molecules at (x, y, z) and ($2 - x, 2 - y, 1 - z$), which are components of the $R_2^2(10)$ dimers centred, respectively, at ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and ($\frac{3}{2}, \frac{3}{2}, \frac{1}{2}$), are parallel, with an interplanar spacing of 3.367 (2) Å. The centroid–centroid separation is 3.666 (2) Å, corresponding to a nearly ideal centroid offset of 1.450 (2) Å. Propagation by inversion of this stacking interaction then generates a chain of π-stacked dimers running parallel to the [110] direction (Fig. 3).

The supramolecular structure of (II) was not discussed at all in the original report (Ianelli *et al.*, 1992). However, use of the atom coordinates for (II) retrieved from the Cambridge Structural Database (Allen, 2002; refcode KONKON) shows that, in contrast with the supramolecular structure of (I), that of (II) consists of isolated *C*(7) zigzag chains built from a single C—H···O hydrogen bond and generated by a glide plane in space group $P2_1/c$ (Fig. 4). π–π stacking interactions are absent from the structure of (II).

Experimental

A sample of compound (I) was prepared by oxidation of a commercial sample of methyl 4-nitrophenyl sulfide (Aldrich), using hydrogen peroxide and $TiCl_3$, following the published procedure of Watanabe *et al.* (1981). Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation of a solution in ethanol (m.p. 430–432 K).

Crystal data

$C_7H_7NO_3S$
$M_r = 185.20$
Triclinic, $P\overline{1}$
$a = 6.1522$ (2) Å
$b = 7.8550$ (3) Å
$c = 7.9939$ (3) Å
$\alpha = 83.684$ (3)°
$\beta = 89.320$ (2)°
$\gamma = 88.430$ (3)°
$V = 383.81$ (2) Å^3
$Z = 2$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1739 reflections
$\theta = 3.3$–27.5°
$\mu = 0.38$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.35 × 0.35 × 0.30 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.878$, $T_{max} = 0.894$
6313 measured reflections
1739 independent reflections
1588 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 8$
$k = -10 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.079$
$S = 1.11$
1739 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.1817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C4—S4	1.8003 (14)	S4—C41	1.7909 (15)
S4—O41	1.4937 (11)		
C2—C1—C6	123.20 (13)	C4—S4—O41	106.29 (6)
C3—C4—C5	121.67 (13)	O41—S4—C41	107.10 (7)
C4—S4—C41	96.61 (6)		
C3—C4—S4—O41	6.56 (13)	C2—C1—N1—O1	−0.87 (19)
C3—C4—S4—C41	−103.45 (12)	C2—C1—N1—O2	178.88 (12)

Table 2
Geometry of hydrogen bonds and short intramolecular contacts (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O41	0.95	2.49	2.907 (2)	106
C6—H6···O2^{i}	0.95	2.56	3.478 (2)	164

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Crystals of (I) are triclinic. Space group $P\overline{1}$ was selected and confirmed by the successful structure analysis. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic) and 0.98 Å (methyl).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1686). Services for accessing these data are described at the back of the journal.

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