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4-(2,4-Dinitrophenylsulfanyl)-morpholine

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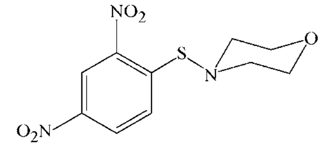
In the title compound, $C_{10}H_{11}N_3O_5S$, the 2,4-dinitrophenyl fragment is connected by an S atom to the morpholine ring, which is in a chair conformation. The *ortho*- and *para*-nitro groups are slightly twisted out of the plane of the benzene ring. The molecules are linked into *C*(7) and *C*(10) chains by two intermolecular C—H$\cdots$O hydrogen bonds.

Comment

Sulfenamides are important compounds with versatile industrial applications. Bond polarization in sulfenamide derivatives, resulting from the difference in electronegativity between sulfur and nitrogen, activates the S—N bond for attack by both nucleophiles and electrophiles, and appears to be the factor primarily responsible for the chemistry of these compounds. The title compound, (I), is the result of the condensation reaction of 2,4-dinitrophenylsulfanylphthalimide and morpholine. Its structure is decribed here as part of our work involving the study of the synthesis and structural characterization of divalent-sulfur compounds (Brito *et al.*, 2004, 2005, 2006). A search of the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002) for the morpholine fragment with an $S^{II}—X$ substituent (where *X* is alkyl, aryl or any adequate group) yielded only one example, *viz.* 1,3-bis(2-methylphenyl)-2-(4-morpholino)isothiurea (CSD refcode TEHDAL; Sudha *et al.*, 1996).

A view of the molecular structure of (I) is given in Fig. 1 and selected geometric parameters are listed in Table 1. The morpholine ring has a chair conformation [puckering amplitude Q_T = 0.573 (3) Å, θ = 180.0 (3)° and φ = 210 (25)° (Cremer & Pople, 1975)], with atoms N1 and O1 displaced by −0.659 (2) and 0.658 (2) Å, respectively, from the best plane through atoms C1, C2, C3 and C4 [maximum deviation ±0.0003 Å]. A survey of structures with morpholine rings shows wide variability, with the sum of the angles at the N atom ranging from 336 to 359° (Wong-Ng *et al.*, 1982). In the present case, the sum of the angles at N1 is 336.7 (2)°.



(I)

The morpholine ring in (I) is oriented in such a way that the N1 lone pair can accept an intramolecular hydrogen bond from the C10—H10 group. To achieve this favourable intramolecular interaction, the N1—S1—C5—C10 torsion angle has a value of −4.5 (2)°, while the best planes of the 2,4-dinitrophenyl and morpholino groups are almost perpendicular to one another [dihedral angle = 101.4 (2)°]. The average $Csp^3—Nsp^3$, $Csp^3—Csp^3$ and $Csp^3—Osp^3$ bond distances [1.474 (4), 1.449 (5) and 1.420 (4) Å, respectively] are comparable with the literature values (Allen *et al.*, 1987).

The benzene ring is slightly deformed, with atom C5 displaced out of the mean ring plane by 0.0095 (15) Å. The nitro groups in the *ortho* and *para* positions are rotated by 3.5 (4) and 6.1 (5)° from the aromatic ring, respectively. The C—S distance is shorter than the value of 1.777 (6) Å found in 4-[(dimethylamino)sulfanyl]-1,3-dinitrobenzene (Aupers *et al.*, 1999), but longer than the value of 1.735 (4) Å found in 2-(2,4-dinitrophenylthioamino)-2,3,4,5-tetraphenyl-2*H*-pyrrole benzene solvate (Atkinson *et al.*, 1985). The S—N distance is shorter than the normal S—N single-bond length (1.74 Å), but is normal for this type of structure, many of which have S—N single bonds in the range 1.63–1.68 Å as a result of the π character of the S—N bond.

The crystal structure of (I) is built up by an intramolecular C—H$\cdots$N hydrogen bond and two weak intermolecular C—H$\cdots$O hydrogen bonds. The intramolecular C10—H10$\cdots$N interaction forms a five-membered S1/N1/C10/C5/H10 closed ring (Fig. 2). The molecules are linked into chains by two intermolecular C—H$\cdots$O hydrogen bonds. Atoms C3 and C9

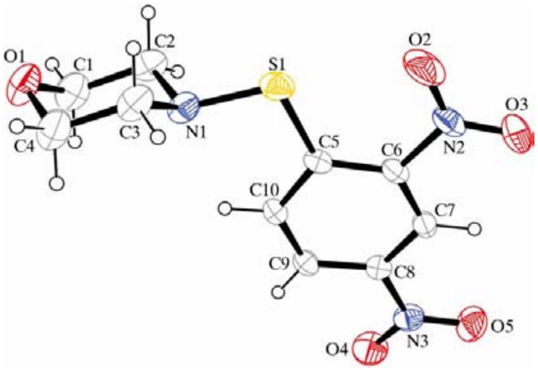


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donors *via* atoms H3*B* and H9 to sulfenamide atoms O5 and O3 in the molecules at ($x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$) and ($x + 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$), so generating by translation two *C*(10) and *C*(7) (Bernstein *et al.*, 1995) chains running parallel to the [100] direction (Fig. 3 and Table 2). Such interactions involving the nitro O atoms are generally the dominant feature of the crystal structures of compounds containing nitroarenethiolate ($O_2NC_6H_4SX$) fragments (Kucsman *et al.*, 1984; Aupers *et al.*, 1999; Low *et al.*, 2000; Glidewell *et al.*, 2000), as well as those of simple nitrobenzenes (Boonstra, 1963; Trotter & Williston, 1966; Choi & Abel, 1972; Herbstein & Kapon, 1990; Boese *et al.*, 1992; Sekine *et al.*, 1994).

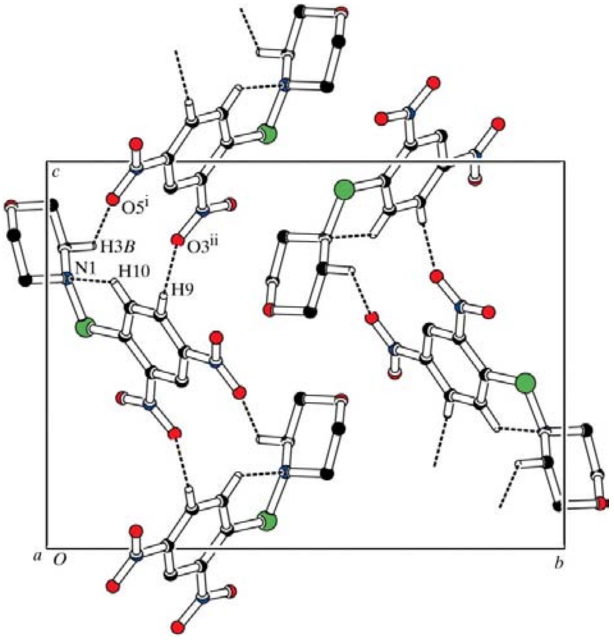

Figure 2
A view of the hydrogen-bonding interactions in (I). H atoms not involved in these contacts have been omitted for clarity. [Symmetry codes: (i) $x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (ii) $x + 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$.]

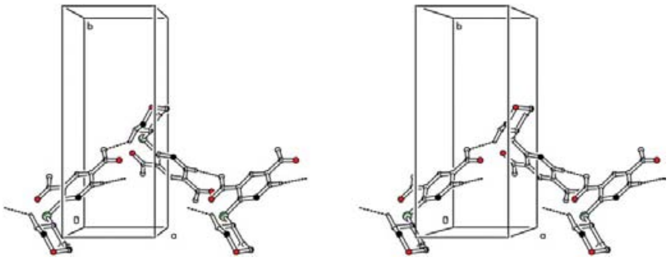

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of two *C*(7) and *C*(10) chains along [100]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled prior to use. 2,4-Dinitrophenylsulfenyl chloride and phthalimide were purchased from Aldrich. The precursor compound was prepared according to the method of Wunderly (1972). A solution of 2,4-dinitrophenyl chloride (2.487 g, 0.008 mol) in dry methanol (80 ml) was added dropwise to a stirred solution of phthalimide (1.176 g, 0.008 mol) and triethylamine (1.49 ml, 0.008 mol) in dimethylformamide (5 ml) under a nitrogen atmosphere. Stirring was continued for 30 min at 298 K. Cold distilled water (100 ml) was added and stirring was continued for a further 30 min. The yellow precipitate which formed was filtered off, washed with pentane and dried at room temperature. The title compound, (I), was prepared according to the method of Harpp & Back (1971). Orange crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a solution of the product in diethyl ether.

Crystal data

$C_{10}H_{11}N_3O_5S$
$M_r = 285.28$
Monoclinic, $P2_1/c$
$a = 6.4280$ (2) Å
$b = 16.0850$ (7) Å
$c = 12.1500$ (6) Å
$\beta = 97.4900$ (16)°
$V = 1245.52$ (9) Å^3
$Z = 4$
$D_x = 1.521$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.28$ mm^{-1}
$T = 298$ (2) K
Prism, orange
0.40 × 0.25 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.915$, $T_{max} = 0.950$
7918 measured reflections
2901 independent reflections
2311 reflections with $I > 2\sigma(I)$
$R_{int} = 0.086$
$\theta_{max} = 27.9°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.206$
$S = 1.12$
2901 reflections
172 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1026P)^2 + 0.3584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—N1	1.697 (2)	N2—C6	1.456 (3)
S1—C5	1.755 (2)	N3—C8	1.462 (3)
N1—S1—C5	100.41 (11)	C2—N1—S1	114.76 (19)
C1—O1—C4	109.8 (2)	C3—N1—S1	111.44 (19)
C2—N1—C3	110.5 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*B*···O5^{i}	0.97	2.54	3.224 (4)	127
C9—H9···O3^{ii}	0.93	2.52	3.446 (4)	174
C10—H10···N1	0.93	2.36	2.833 (3)	111

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

H atoms were positioned geometrically and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ (aromatic C—H = 0.93 Å and methylene C—H = 0.97 Å). The material was difficult to obtain in a suitable crystalline form and the best available specimen was lost late in the data collection, resulting in 97% completeness after merging equivalents.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3013). Services for accessing these data are described at the back of the journal.

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