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Bis(2-nitrophenyl) Trisulfide

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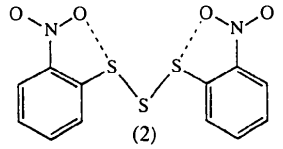
Abstract

The S—S bond lengths in 2-$O_2NC_6H_4SSSC_6H_4NO_2$-2, the title compound, are 2.0543 (13) and 2.0508 (13) Å, with the S1—S2—S3 valence angle 106.35 (5)°. There are two short intramolecular S···O contacts: O1···S1 = 2.598 (3) and O3···S3 = 2.592 (3) Å. The values of the angles O1···S1—S2 and O3···S3—S2 are 175.04 (8) and 178.70 (8)°, respectively.

Comment

Intramolecular non-bonded sulfur–oxygen contacts shorter than the sum of the van der Waals radii, 3.25 Å (Pauling, 1960), have been determined by diffraction methods for a number of compounds (Kucsman & Kapovits, 1985, and references therein). A typical group of such compounds is represented by 2-$O_2NC_6H_4SX$, (1) [*e.g.* *X* = aryl or alkyl (Howie, Wardell, Zanetti, Cox & Doidge-Harrison, 1992; Howie & Wardell, 1996; Kucsman, Kapovits, Parkanyi, Argay & Kálmán, 1984; Kucsman & Kapovits, 1985); *X* = Cl (Schultz, Hargittai, Kapovits & Kucsman, 1984); *X* = OMe (Schultz *et al.*, 1984); *X* = SCN (Howie & Wardell, 1995) and *X* = $SC_6H_4NO_2$-2 (Ricci & Bernal, 1970)].

The compounds (1), as well as possessing short S···O separations, also exhibit *X*—S···O angles close to 180°. This is well illustrated by the title compound, 2-$O_2NC_6H_4SSSC_6H_4NO_2$-2, (2) (*X* = $SSC_6H_4NO_2$-2), for which the relevant values are O1···S1 = 2.598 (3), O3···S3 = 2.592 (3) Å, O1···S1—S2 = 175.04 (8) and O3···S3—S2 = 178.70 (8)° (Fig. 1). Each of the nitro groups in the title compound is essentially coplanar with the aryl group to which it is attached.



(2)

The S···O non-bonded separations in the compounds (1) are dependent on the bonding atom within *X*; *e.g.* when *X* = Cl, the S···O distances are 2.379 (5) and 2.408 (5) Å (Schultz *et al.*, 1984); when *X* = OMe, 2.458 (2) Å (Schultz *et al.*, 1984) and when *X* = SCN, 2.504 (7) Å (Howie & Wardell, 1995). In the disulfide where *X* = $SC_6H_4NO_2$-2, two S···O short separations [2.588 (7) and 2.636 (8) Å (Ricci & Bernal, 1970)] were found to have similar distances to those determined in the title compound. In contrast, in the corresponding monosulfide where *X* = $C_6H_4NO_2$-2, only one nitro group, as a consequence of the skew conformation of the molecule, is suitably positioned to allow a significant S···O interaction: the two sets of S···O/C—S···O values are 2.656 (1) Å/171.7 (1)° and 2.900 (2) Å/134.3 (1)° (Kucsman *et al.*, 1984).

The aryl groups in the title compound have a *trans* arrangement about the S—S—S bridge, the angle between the normals of the best planes through the two aryl rings being 113.1 (5)° (Fig. 1). There are no intermolecular S···S contacts less than the sum of the van der Waals radii [3.70 Å (Pauling, 1960)]. The S—S bond lengths [S1—S2 = 2.0543 (13) and S2—S3 = 2.0508 (13) Å] and S1—S2—S3 bond angle [106.35 (5)°] are comparable with those determined for the only other diaryl trisulfide, (5-Bu-3-^{t}Bu-2-$HOC_6H_2)_2S_3$, for which a structure has been reported (Chetkina *et al.*, 1986).

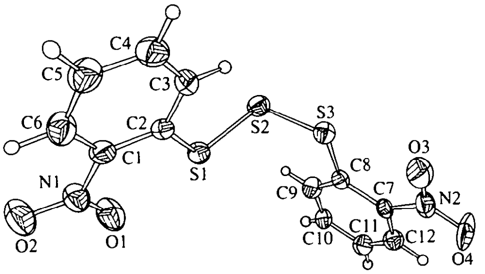


Fig. 1. The atom-numbering system for the title molecule. Displacement ellipsoids are shown at the 40% probability level. H atoms are shown as spheres of arbitrary radii.

Experimental

The title compound was prepared from 2-$O_2NC_6H_4SCl$ and $(Bu_3Sn)_2S$ in CCl_4, according to a published procedure, and was recrystallized from CCl_4; m.p. 448–449 K (Wardell & Clarke, 1971).

Crystal data

$C_{12}H_8N_2O_4S_3$
$M_r = 340.4$
Triclinic
$P\bar{1}$
$a = 7.839\ (7)$ Å
$b = 8.281\ (7)$ Å
$c = 13.113\ (9)$ Å
$\alpha = 92.77\ (6)°$
$\beta = 104.85\ (6)°$
$\gamma = 120.82\ (6)°$
$V = 690\ (1)$ Å^3
$Z = 2$
$D_x = 1.638$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 10.7–12.2°$
$\mu = 0.530$ mm^{-1}
$T = 298$ K
Block
0.6 × 0.4 × 0.28 mm
Yellow

Data collection

Nicolet *P*3 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4052 measured reflections
3668 independent reflections
2794 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.015$

$\theta_{\max} = 30°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 18$
2 standard reflections monitored every 50 reflections intensity variation: 2.5%

Refinement

Refinement on *F*
$R = 0.049$
$wR = 0.042$
$S = 1.45$
2794 reflections
191 parameters
H atoms: see below
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
S1	0.34065 (12)	0.74005 (11)	0.77778 (6)	0.0424 (2)
S2	0.53008 (13)	0.98355 (11)	0.72912 (6)	0.0446 (3)
S3	0.72929 (11)	0.93467 (11)	0.67815 (6)	0.0419 (2)
O1	0.0857 (4)	0.4468 (4)	0.8436 (2)	0.0734 (9)
O2	0.1080 (4)	0.3834 (3)	1.0016 (2)	0.0748 (10)
O3	0.9830 (3)	0.8792 (4)	0.6114 (2)	0.0674 (10)
O4	0.9407 (4)	0.7274 (4)	0.4611 (2)	0.0825 (12)
N1	0.1811 (4)	0.4842 (4)	0.9398 (2)	0.0516 (10)
N2	0.8764 (4)	0.7835 (4)	0.5201 (2)	0.0475 (10)
C1	0.3957 (4)	0.6568 (4)	0.9824 (2)	0.0369 (9)
C2	0.4835 (4)	0.7803 (4)	0.9166 (2)	0.0346 (8)
C3	0.6882 (4)	0.9386 (4)	0.9655 (2)	0.0429 (10)
C4	0.7954 (5)	0.9683 (5)	1.0724 (3)	0.0520 (11)
C5	0.7055 (5)	0.8443 (5)	1.1358 (3)	0.0537 (12)
C6	0.5030 (5)	0.6869 (5)	1.0899 (2)	0.0490 (11)
C7	0.6586 (4)	0.7329 (4)	0.4791 (2)	0.0337 (9)
C8	0.5770 (4)	0.7956 (4)	0.5435 (2)	0.0324 (8)
C9	0.3692 (4)	0.7394 (4)	0.4974 (2)	0.0380 (9)
C10	0.2505 (4)	0.6265 (4)	0.3944 (2)	0.0430 (1)
C11	0.3343 (5)	0.5640 (4)	0.3338 (2)	0.0444 (10)
C12	0.5394 (5)	0.6186 (4)	0.3765 (2)	0.0421 (10)

Table 2. *Selected geometric parameters (Å, °)*

S1—S2	2.0543 (13)	C2—S1	1.787 (3)
S2—S3	2.0508 (13)	C8—S3	1.785 (3)
N1—O1	1.220 (3)	N1—O2	1.222 (3)
N2—O3	1.216 (3)	N2—O4	1.213 (3)
C1—N1	1.470 (4)	C7—N2	1.468 (3)
O1···S1	2.598 (3)	O3···S3	2.592 (3)
C2—S1—S2	104.41 (11)	O2—N1—O1	123.1 (3)
C8—S3—S2	104.01 (11)	C1—N1—O2	118.8 (3)
C1—N1—O1	118.1 (3)	C7—N2—O3	118.3 (3)
O4—N2—O3	123.4 (3)	C2—C1—N1	121.1 (3)
C7—N2—O4	118.3 (3)	C1—C2—S1	121.9 (2)
C6—C1—N1	116.2 (3)	C7—C8—S3	121.9 (2)
C12—C7—N2	116.9 (3)	C8—C7—N2	120.7 (3)
C3—C2—S1	121.9 (2)	N1—O1···S1	102.9 (3)
C9—C8—S3	121.9 (2)	O1···S1—S2	175.04 (8)
N2—O3···S3	103.3 (3)	O3···S3—S2	178.70 (8)
S3—S2—S1	106.35 (5)		
O1—N1—C1—C2	3.7 (5)	O1—N1—C1—C6	−175.9 (3)
O2—N1—C1—C2	−177.6 (3)	O2—N1—C1—C6	2.9 (5)
O3—N2—C7—C8	0.8 (5)	O3—N2—C7—C12	−177.9 (3)
O4—N2—C7—C8	−179.3 (3)	O4—N2—C7—C12	2.0 (5)
S1—S2—S3—C8	81.7 (1)	C2—S1—S2—S3	87.8 (1)

H atoms were placed in calculated positions with C—H = 0.95 Å and refined with a riding model and common $U_{\rm iso}$. All computations were performed on the SUN SPARCserver of the Computing Centre of the University of Aberdeen.

Data collection: Nicolet *P*3 software (Nicolet XRD Corporation, 1980). Cell refinement: Nicolet *P*3 software. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *XPUB* (Low, 1980).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Chetkina, L. A., Zavodnik, V. E., Bel'skii, V. K., Arzamanova, I. G., Krisin, A. P., Gurvich, Ya. A. & Kuzubova, L. I. (1986). *Zh. Strukt. Khim.* **27**, 112–116.

Howie, R. A. (1980). *RDNIC. Data Reduction Program for Nicolet P3 Diffractometer.* University of Aberdeen, Scotland.

Howie, R. A. & Wardell, J. L. (1995). *Acta Cryst.* **C51**, 2651–2652.

Howie, R. A. & Wardell, J. L. (1996). *Acta Cryst.* **C52**, 1228–1230.

Howie, R. A., Wardell, J. L., Zanetti, E., Cox, P. J. & Doidge-Harrison, S. M. S. V. (1992). *J. Organomet. Chem.* **431**, 27–40.

Kucsman, A. & Kapovits, I. (1985). *Non-Bonded Sulfur–Oxygen Interaction in Organic Sulfur Compounds. Organic Sulfur Chemistry: Theoretical and Experimental Advances*, edited by F. Bernardi, I. G. Csizmadia & A. Mangini, pp. 191–245. Amsterdam: Elsevier.

Kucsman, A., Kapovits, I., Parkanyi, L., Argay, G. & Kálmán, A. (1984). *J. Mol. Struct.* **125**, 331–347.

Low, J. N. (1980). *XPUB. Program for the Preparation of Tabular Crystallographic Data.* University of Dundee, Scotland.

McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.

Nicolet XRD Corporation (1980). *Nicolet P3/R3 Data Collection Operators Manual.* Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, California 95014, USA.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell University Press.

Ricci, J. L. & Bernal, I. (1970). *J. Chem. Soc. B*, pp. 806–811.

Schultz, G., Hargittai, I., Kapovits, I. & Kucsman, A. (1984). *J. Chem. Soc. Faraday Trans.* 2, **80**, 1273–1279.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Wardell, J. L. & Clarke, P. L. (1971). *J. Organomet. Chem.* **26**, 345–352.