2-Nitrobenzenesulfenyl Thiocyanate

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Abstract

A weak intramolecular S···O interaction is present in the title compound, $C_7H_4N_2O_2S_2$; S···O = 2.504 (7) Å and C—S···O = 176.8 (2)°.

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 in a number of compounds (Kucsman & Kapovits, 1985, and references therein). A typical group of such compounds can be represented by the formula $1\text{-}XS\text{-}2\text{-}O_2NC_6H_nR_{4-n}$, (1); as well as possessing short S···O contacts, the compounds (1) also exhibit X—S···O angles close to 180°. This is illustrated by the title compound [(1) $n = 4$, X = SCN], in which S···O = 2.504 (7) Å and (NC)S—S···O = 176.8 (2)°. The aryl and nitro groups are almost coplanar, the angle between the normals of the planes being 2.9°.

NCS—S benzene ring with NO₂

[(1) $n = 4, X$ = SCN]
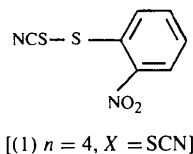
The majority of crystallographic studies on compounds of type (1) have involved 2-nitroaryl aryl or alkyl sulfides, *i.e.* (1) with X = aryl or alkyl. Generally, the S···O separations in (1) with X = aryl or alkyl are between 2.62 and 2.72 Å (Howie, Wardell, Zanetti, Cox & Harrison, 1992; Howie & Wardell, 1995; Kucsman & Kapovits, 1985, and references therein); no obvious correlation exists between the S···O distance and the electronic effects of the aryl or alkyl substituents.

The S···O distances in (1) with $X \neq$ aryl or alkyl are more clearly dependent on X, *e.g.* in (1) with R = H and X = Cl, the S···O distances are 2.379 (5) and 2.408 (5) Å (Schultz, Hargittai, Kapovits & Kucsman, 1984), in (1) with R = H and X = OMe they are 2.458 (2) Å (Schultz *et al.*, 1984), in (1) with R = H and X = SCN, *i.e.* the title compound, the S···O distance is 2.504 (7) Å, and in (1) with R = H and X = $SC_6H_4NO_2\text{-}2$ the distances are 2.588 (7) and 2.636 (8) Å (Ricci & Bernal, 1970).

In the title compound, the S2—C7—N2 valence angle is 178.2 (9)°, with bond lengths S2—C7 and C7—N2 of 1.702 (12) and 1.143 (12) Å, respectively; corresponding bond lengths in $Ph_3SnCH(SCN)CH_2SC_6H_4NO_2\text{-}2$ are 1.685 (4) and 1.140 (6) Å (Howie *et al.*, 1992), in $p\text{-}H_2NC_6H_4SCN$ 1.704 (4) and 1.132 (5) Å (Isakov, Rider & Zvonkova, 1976), and in $NCSCH_2SCN$ 1.677 (9) and 1.194 (12) Å (Konnert & Britton, 1971). The S1—S2 bond length in the title compound is 2.059 (3) Å, which is comparable with the S—S bond length [2.045 (3) Å] in $2\text{-}O_2NC_6H_4SSC_6H_4NO_2\text{-}2$ (Ricci & Bernal, 1970).
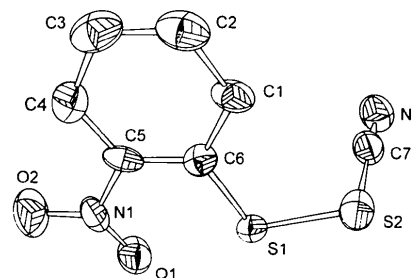

Fig. 1. The molecular structure showing atom labels and 40% probability ellipsoids.

Experimental

The title compound was prepared from $2\text{-}O_2NC_6H_4SCl$ and KSCN in benzene according to a published procedure (Kharasch, Wehrmeister & Tigerman, 1947) and was crystallized from ethanol; m.p. 363–364 K.

Crystal data

$C_7H_4N_2O_2S_2$	Mo $K\alpha$ radiation
$M_r = 212.25$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 14
$P\bar{1}$	reflections
$a = 7.774$ (16) Å	$\theta = 5.4$–11.7°
$b = 7.973$ (12) Å	$\mu = 0.54$ mm^{-1}
$c = 8.053$ (17) Å	$T = 298$ K
$\alpha = 94.28$ (15)°	Plate
$\beta = 109.45$ (19)°	$0.5 \times 0.3 \times 0.04$ mm
$\gamma = 105.67$ (13)°	Yellow
$V = 445$ (2) Å^3	
$Z = 2$	
$D_x = 1.584$ Mg m^{-3}	

Data collection

Nicolet $P3$ diffractometer	$\theta_{max} = 25.0°$
$\theta/2\theta$ scans	$h = -8 \rightarrow 8$
Absorption correction:	$k = -9 \rightarrow 9$
none	$l = 0 \rightarrow 9$
1560 measured reflections	2 standard reflections
1297 independent reflections	monitored every 50
781 observed reflections	reflections
[$F > 4\sigma(F)$]	intensity variation: 3%
$R_{int} = 0.029$	

Refinement

Refinement on F
$R = 0.070$
$wR = 0.071$
$S = 1.38$
781 reflections
119 parameters
H atoms riding with common group U
$w = 1/[\sigma^2(F) + 0.002568F^2]$

$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ 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)

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

	x	y	z	U_{eq}
S1	0.4122 (4)	0.8415 (3)	0.1496 (3)	0.0524 (8)
S2	0.6223 (4)	0.8107 (4)	0.3704 (4)	0.068 (1)
O1	0.1709 (10)	0.8862 (9)	−0.1258 (9)	0.072 (3)
O2	−0.0423 (12)	0.7027 (11)	−0.3606 (10)	0.091 (3)
N1	0.0865 (11)	0.7359 (11)	−0.2140 (10)	0.051 (3)
N2	0.4227 (15)	0.7338 (12)	0.6082 (12)	0.081 (4)
C1	0.3248 (14)	0.4720 (11)	0.0925 (13)	0.051 (3)
C2	0.2257 (16)	0.3082 (13)	−0.0068 (15)	0.061 (4)
C3	0.0847 (16)	0.2801 (14)	−0.1690 (15)	0.065 (4)
C4	0.0383 (14)	0.4224 (13)	−0.2382 (13)	0.055 (3)
C5	0.1406 (12)	0.5878 (11)	−0.1382 (11)	0.040 (3)
C6	0.2872 (12)	0.6198 (11)	0.0278 (11)	0.041 (3)
C7	0.5007 (15)	0.7626 (12)	0.5107 (13)	0.058 (4)

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

S2—S1	2.059 (3)	C6—S1	1.791 (8)
C7—S2	1.702 (12)	N1—O1	1.229 (9)
N1—O2	1.221 (9)	C5—N1	1.465 (11)
C7—N2	1.143 (12)	C2—C1	1.352 (13)
C6—C1	1.386 (11)	C3—C2	1.352 (14)
C4—C3	1.382 (14)	C5—C4	1.367 (12)
C6—C5	1.389 (11)		
C6—S1—S2	103.4 (3)	C7—S2—S1	101.2 (3)
O2—N1—O1	123.5 (8)	C5—N1—O1	118.4 (7)
C5—N1—O2	118.1 (8)	C6—C1—C2	120.3 (9)
C3—C2—C1	122.5 (9)	C4—C3—C2	119.6 (10)
C5—C4—C3	117.7 (9)	C4—C5—N1	116.4 (8)
C6—C5—N1	120.0 (8)	C6—C5—C4	123.6 (8)
C1—C6—S1	123.3 (7)	C5—C6—S1	120.4 (6)
C5—C6—C1	116.3 (8)	N2—C7—S2	178.2 (9)

Data collection: Nicolet (1980) *P3* diffractometer software. Cell refinement: *P3* diffractometer software. Data reduction: *RDNIC* (Howie, 1980). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXS76* (Sheldrick, 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare material for publication: *XPUB* (Low, 1980).

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3-Methylphthalic Anhydride

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Abstract

Molecules of the title compound, $C_9H_6O_3$, are not wholly planar, having a dihedral angle of 2.0 (1)° between the two ring planes. The fused heterocyclic five-membered ring causes significant distortions in the bond angles within the benzene ring. The methyl group is displaced by 0.06 (1) Å from the least-squares plane through the aromatic ring.

Comment

A large number of derivatives of the title compound have been reported as a result of interest either in their use for the synthesis of epoxy resins and in the manufacture of ceramic and powder metallurgical products (Bayer & Nagl, 1993), or because they form charge-transfer complexes with a number of polycyclic compounds (Wilkerson, Chodak & Strouse, 1975; Baumer & Starodub, 1984; Bulgarovskaya, Zavodnik, Bel'skii & Vozzhennikov, 1989). In view of the potential utilization