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2-Nitro-*N*,*N*-bis(2-nitrophenylthio)-benzenesulfonamide

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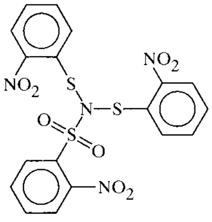
The central N atom of $C_{18}H_{12}N_4O_8S$ is essentially planar, lying 0.071 (2) Å out of the plane defined by the three S atoms. N—S distances are 1.712 (2) and 1.721 (2) Å to S—Ar, and 1.681 (2) Å to SO_2—Ar. The nitro group on the phenyl ring carrying the SO_2 group lies out of plane, with C—C—N—O– torsion angle 69.8 (3)°, while the other two nitro groups are near coplanarity, with torsion angle magnitudes 10.4 (3) and 14.0 (3)°.

Comment

The aim of the study was to synthesize *O*,*N*-bis(2-nitrobenzenesulfonyl)hydroxylamine, which could deliver its protected amino group to various nucleophiles *via* electrophilic amination. This is important in the synthesis of α-hyrazino acids for the synthesis of hydrazino peptides. When N,*N*-diisopropylethylamine, (DIEA) was used as a base in the reaction, the main product was the title compound. When collidine was used in place of DIEA, the desired product was obtained without formation of the title compound. We thus believe that the DIEA is acting as a reducing agent in the formation of the title compound, (I).



(I)

The central N atom is essentially planar, lying 0.071 (2) Å out of the plane defined by the three S atoms. Tris(thiophenyl)amine (Carruthers *et al.*, 1981) also has a near planar central N atom. N—S distances to thiol S are 1.712 (2) and 1.721 (2) Å, while the N1—S1 distance is shorter, 1.681 (2) Å. The nitro group on phenyl ring C1 through C6 lies out of plane, with C3—C2—N2—O3 torsion angle 69.8 (3)°. The other two nitro groups are nearer coplanarity with their respective phenyl rings, with torsion angles O6—N3—C8—C7 10.4 (3) and O8—N4—C14—C13 −14.0 (3)°.

Short intermolecular contacts exist between nitro groups of inversion-related molecules. O6 has distances of 2.772 (2) Å to O6^{i} and 2.827 (2) Å to N3^{i} [symmetry code: (i) 1 −*x*, 1-*y*, 2-*z*], as well as a distance of 2.785 (2) Å to O7^{ii} [symmetry code: (ii) 1-*x*, 1-*y*, 1-*z*]. An N3···O7^{ii} contact of distance 2.848 (2) Å also exists.

Experimental

Under an argon atmosphere, 2-nitrobenzenesulfonyl chloride (2.5 equivalents, 19.94 g, 0.09 mol) was added slowly to a stirred solution of DIEA (3 equivalents, 18.81 ml, 0.108 mol) and hydroxylamine hydrochloride (1 equivalents, 2.5 g, 0.036 mol) in dry acetonitrile (72 ml). The reaction mixture was stirred overnight at room temperature. The solvent was evaporated *in vacuo*. The residue was diluted with dichloromethane, extracted with 5% NaOH, dried over $MgSO_4$, and evaporated *in vacuo*. Solvent removal left a pale yellow semisolid, which was dissolved in hot toluene and kept in a freezer overnight. The resulting pale-yellow crystals were filtered and washed with cold toluene. The yield was 22%.

Crystal data

$C_{18}H_{12}N_4O_8S_3$
M_r = 508.51
Monoclinic, $P2_1/n$
a = 7.670 (3) Å
b = 19.766 (5) Å
c = 13.759 (3) Å
β = 90.63 (3)°
V = 2085.8 (11) Å^3
Z = 4
D_x = 1.619 Mg m^{-3}
Mo–Kα radiation
Cell parameters from 25 reflections
θ = 10.5–18.1°
μ = 0.412 mm^{-1}
T = 100 K
Prism, yellow
0.50 × 0.33 × 0.32 mm

Data collection

Enraf–Nonius CAD-4 diffractometer (with Oxford Cryostreams Cryostream cooler)
$\theta/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.835, $T_{\max}$ = 0.882
5118 measured reflections
4775 independent reflections
3426 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 9$
$k = -25 \rightarrow 0$
$l = -17 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 2.9%

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.040
S = 1.483
4775 reflections
298 parameters
H-atom parameters constrained
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.62 e Å^{-3}
$\Delta\rho_{\min}$ = −0.37 e Å^{-3}

H atoms were located in difference maps. For refinement, they were placed in calculated positions with C—H distance 0.95 Å and $B_{iso} = 1.3B_{eq}$ for the bonded C atom, and thereafter treated as riding.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SIR* (Burla *et al.*, 1989); program(s) used to refine structure: *LSFM* in *MolEN* (Fair, 1990); software used to prepare material for publication: CIFGEN in *MolEN* (Fair, 1990).

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