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Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.059
 wR factor = 0.174
Data-to-parameter ratio = 17.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.*N,N*-Dibenzyl-3-nitrobenzenesulfenamide

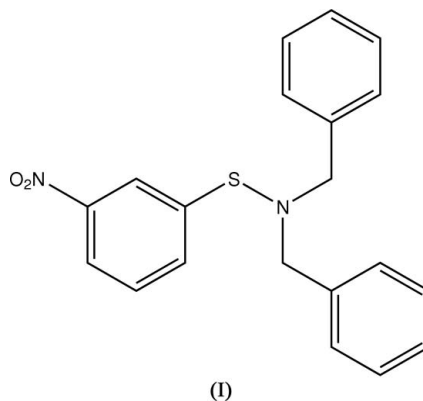
In the title molecule, $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$, all bond lengths and angles are within normal ranges. Weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions link the molecules into centrosymmetric dimers. The crystal packing is further stabilized by van der Waals forces.

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Comment

Sulfenamides are important intermediates in organic synthesis. They have been useful in investigations of lone-pair interactions, bond-polarization effects and (*p-d*) π conjugation (Craine & Raban, 1989; Makosza & Bialecki, 1992; Blanca *et al.*, 1997). Sulfenamides have important industrial applications, being used as additives in the rubber industry, and as insecticides, fungicides or ovicides in the agrochemical industry. They may be used as growth regulators in plants, and some of them have potential medicinal value (Kuhle, 1973). 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. In continuation of our ongoing study of the synthesis and structural characterization of divalent sulfur compounds, we present here the crystal structure of the title compound, (I) (Fig. 1).



The molecular dimensions in (I) (Table 1) are within normal ranges (Allen *et al.*, 1987). The nitrobenzene group is essentially planar, as is the nitropyridine group in 5-nitropyridine-piperidinesulfenamide (Brito *et al.*, 2002). The C—S distance of 1.792 (2) Å is comparable to 1.784 Å observed in bis(3-nitrophenyl) disulfide (Cannon *et al.*, 2000). For the rings C1—C6 (*A*), C9—C14 (*B*) and C15—C20 (*C*), the dihedral angles *A/B*, *A/C* and *B/C* are 68.4 (1), 69.8 (1) and 10.1 (1)°, respectively. The S—N distance (Table 1) is shorter than the normal

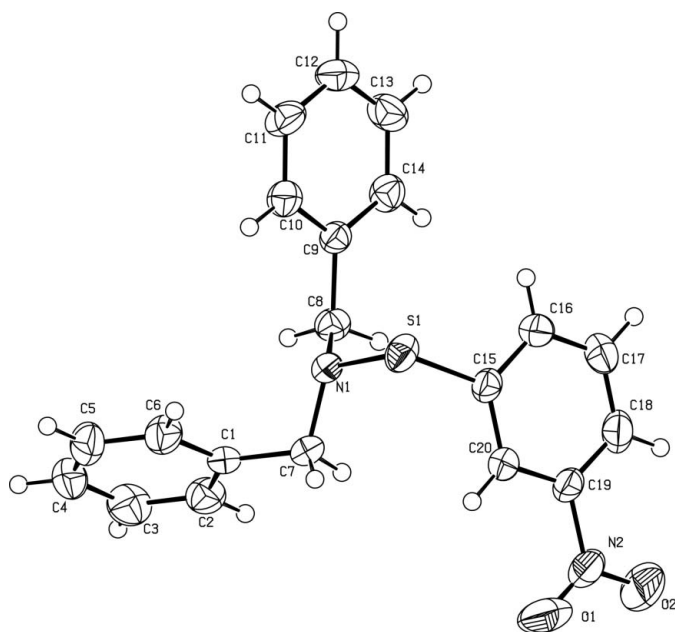


Figure 1
View of (I) with the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

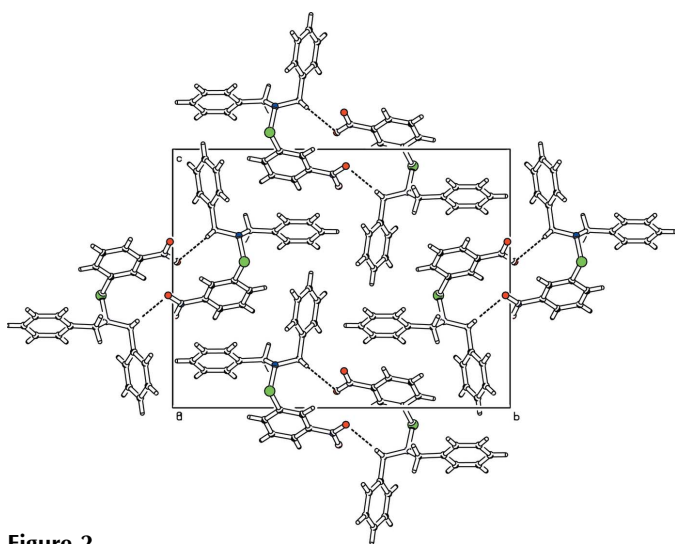


Figure 2
The packing of (I), viewed along the *a* axis and showing the formation of $R_2^2(18)$ hydrogen-bonded (dashed lines) dimers.

S—N single-bond length (1.74 Å), but is usual 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. Atom N1 deviates from the plane C7/S1/C8 by 0.393 (2) Å (Fig. 1), and the sum of the three bond angles around N1 is 341.3°. The internal bond angle at C19 (Table 1), *ipso* to the electron-withdrawing NO₂ substituent, is greater than 120°, as expected (Domenicano & Murray-Rust, 1979). The C15/S1/N1 plane makes a dihedral angle of 86.8 (1)° with the C7/N1/C8 plane, in good agreement with the value of 90.0° for the torsional ground state of the molecule.

In the crystal structure, weak intermolecular C—H...O interactions (Table 2) link the molecules into centrosymmetric dimers, which can be described by the graph-set motif $R_2^2(18)$ (Bernstein *et al.*, 1995). Such interactions involving the nitro O atoms are generally the dominant feature of the crystal structures of compounds containing nitroarenothiolate (O₂NC₆H₄S*X*) fragments (Kucsmán *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). The crystal packing of (I) (Fig. 2) is further stabilized by van der Waals forces.

Experimental

All reactions were carried out under an atmosphere of purified nitrogen. Solvents used were dried and distilled prior to use. The compound was obtained as yellow prismatic crystals using the metal-assisted technique (Davis *et al.*, 1977). Bis(3-nitrophenyl) disulfide was purchased from Aldrich. In a 1000 ml three-necked flask equipped with an overhead stirrer, silver nitrate (7.8 g, 0.045 mol) was dissolved in methanol (400 ml). After stirring for 1 h at room temperature, an equivalent amount of bis(3-nitrophenyl) disulfide was added and the reaction mixture cooled in an ice bath. An excess of *N,N*-dibenzylamine (5 equivalents) was added and the reaction mixture was stirred overnight. The silver mercaptide was removed by filtration and the filtrate was evaporated under reduced pressure at 303–313 K. The residue was extracted with diethyl ether, washed with water (4 × 100 ml) and dried over MgSO₄. Single crystals of (I) were obtained after one week by slow evaporation of the diethyl ether solution (m.p. 358 K, yield 55%). FT-IR (KBr, cm⁻¹): 3023 (*vw*), 2909 (*vw*), 2840 (*vw*), 1593 (*w*), 1527 (*vs*), 1495 (*m*), 1450 (*m*), 1348 (*vs*), 1095 (*w*), 1056 (*w*), 972 (*w*), 940 (*w*), 739 (*vs*), 711 (*s*), 698 (*vs*), 498 (*m*).

Crystal data

C₂₀H₁₈N₂O₂S
M_r = 350.42
 Monoclinic, $P2_1/c$
a = 5.599 (2) Å
b = 20.30 (2) Å
c = 15.557 (6) Å
 β = 90.585 (12)°
V = 1768 (2) Å³
Z = 4

D_x = 1.317 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 4503 reflections
 θ = 1.7–27.0°
 μ = 0.20 mm⁻¹
T = 298 (2) K
 Prism, yellow
 0.35 × 0.23 × 0.19 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} = 0.943, T_{\max} = 0.960
 9951 measured reflections

3955 independent reflections
 3247 reflections with $I > 2\sigma(I)$
 R_{int} = 0.054
 θ_{max} = 27.5°
 h = -7 → 7
 k = -26 → 24
 l = -20 → 12

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.059
 $wR(F^2)$ = 0.174
 S = 1.19
 3955 reflections
 227 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.4961P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

S1–N1	1.7042 (19)	O2–N2	1.212 (3)
S1–C15	1.792 (2)	N1–C8	1.472 (3)
O1–N2	1.206 (3)	N1–C7	1.483 (3)
N1–S1–C15	105.39 (10)	C7–N1–S1	114.16 (14)
C8–N1–C7	111.97 (18)	C20–C19–C18	123.1 (2)
C8–N1–S1	115.19 (15)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C7-H7A\cdots O1^i$	0.97	2.57	3.443 (5)	150

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

H atoms were introduced at calculated positions, with C–H = 0.93 (CH) or 0.97 Å (CH₂), and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$.

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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References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

- Altomare, A., Burla, M. C., Camalli, M., Casciarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Aupers, J. H., Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Low, J. N. & Wardell, J. L. (1999). *Main Group Chem.* **3**, 23–42.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blanca, M. B. D., Maimon, E. & Kost, D. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 2216–2219.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Boese, R., Bläser, D., Nussbaumer, M. & Krygowski, T. M. (1992). *Struct. Chem.* **3**, 363–368.
- Boonstra, E. G. (1963). *Acta Cryst.* **16**, 816–823.
- Brito I., León, Y., Arias, M., Vargas, D., Carmona, F., Ramirez, E., Restovic, C. & Cárdenas, A. (2002). *Bol. Soc. Chil. Quím.* **47**, 159–162.
- Cannon, D., Glidewell, C., Low, J. & Wardell, L. (2000). *Acta Cryst.* **C56**, 1267–1268.
- Choi, C. S. & Abel, J. E. (1972). *Acta Cryst.* **B28**, 193–201.
- Craine, L. & Raban, M. (1989). *Chem. Rev.* **89**, 689–712.
- Davis, F. A., Friedman, A. J., Kluger, E. W., Skibo, E. B., Fretz, E. R., Milicia, A. P., LeMasters, W. C., Bentley, M. D., Lacadie, J. A. & Douglass, I. B. (1977). *J. Org. Chem.* **42**, 967–972.
- Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* **20**, 2283–2286.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Glidewell, C., Low, J. N. & Wardell, J. L. (2000). *Acta Cryst.* **B56**, 893–905.
- Herbstein, F. H. & Kapon, M. (1990). *Acta Cryst.* **B46**, 567–572.
- Kucsman, A., Kapovits, I., Parkanyi, L., Argay, G. & Kalman, A. (1984). *J. Mol. Struct.* **125**, 331–347.
- Kuhle, E. (1973). *The Chemistry of the Sulfenic Acids*, pp. 60–74. Stuttgart, Germany: G. Thime.
- Low, J. N., Storey, E. J., McCarron, M., Wardell, J. L., Ferguson, G. & Glidewell, C. (2000). *Acta Cryst.* **B56**, 58–67.
- Makosza, M. & Bialecki, M. (1992). *J. Org. Chem.* **57**, 4784–4785.
- Nonius (1998). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sekine, A., Ohashi, Y., Yoshimura, K., Yagi, M. & Higuchi, J. (1994). *Acta Cryst.* **C50**, 1101–1104.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Trotter, J. & Williston, C. S. (1966). *Acta Cryst.* **21**, 285–288.