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Structure of 2-Nitro-1,3-bis(phenylthio)benzene, $C_{18}H_{13}NO_2S_2$

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Abstract. $M_r = 339{\cdot}44$, monoclinic, $P2_1/c$, $a = 7{\cdot}640\,(3)$, $b = 13{\cdot}499\,(2)$, $c = 15{\cdot}587\,(6)$ Å, $\beta = 96{\cdot}818\,(11)°$, $V = 1596{\cdot}2\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}41$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}27$ cm^{-1}, $F(000) = 704$, $T = 163$ K, $R = 0{\cdot}041$ for 2856 observed reflections. Close, non-bonded interactions of 2·733 (2) and 2·748 (2) Å are observed between the S atoms and the O atoms. The nitro group is twisted out of the plane of the central phenyl ring by 40·69 (7)°. The molecule has approximate twofold symmetry with the twofold axis lying along the C—N bond axis and, therefore, the terminal phenyl rings are equivalent.

Introduction. Analysis of the ^{13}C NMR spin lattice (T_1) relaxation measurements of 3-nitro-2-(2-pyridylthio)-pyridine (Kimura, Simonsen, Caldwell & Martin, 1981) showed the non-nitro-substituted pyridine ring to reorient anisotropically by free rotation about the C—S bond while the nitro-substituted ring did not. A subsequent X-ray structure determination showed a close S···O contact and asymmetric C—S bond distances with the shorter distance being to the C atom of the substituted ring. It was concluded that this S···O contact inhibited free rotation of the substituted ring in solution and was responsible for the difference in the motional behavior of the rings. Preliminary ^{13}C NMR studies on the title compound indicated that the terminal phenyl rings were non-equivalent and an X-ray structure determination was undertaken to see if such asymmetry persisted in the solid state as well.

Experimental. The title compound was synthesized by the method of Miller (1976), and a yellow, plate-like crystal of approximate dimensions 0·40 × 0·66 × 0·15 mm was cut from a larger crystal obtained by slow evaporation from an ethanol solution. Data collected on a Syntex $P2_1$ diffractometer with a graphite monochromator and equipped with Syntex LT-1 low-temperature delivery system. Lattice parameters obtained by least-squares refinement of setting angles of 45 reflections with 2θ between 21·2 and 30·0°. ω-Scan technique, 3668 unique reflections, 2θ range 4–55°, scan range 1° θ, scan rate 3–6° min^{-1}, $h = 0$ to 9, $k = 0$ to 17, $l = -20$ to 20. Six reflections (3,9,14, 5,0,11, 4,7,15, 596, 6,7,$\overline{10}$, 2,2,$\overline{16}$) deleted because of errors related to an intermittent counter malfunction undetected during data collection. Four reflections ($\overline{1}0\overline{4}$, $0\overline{6}0$, 204, 200) measured after every 96 reflections to monitor instrument and crystal stability. Data corrected for Lp effects, absorption (transmission-factor range 0·82–0·95; crystal faces {010}, {0$\overline{1}$0}, {001}, {00$\overline{1}$}, and fragmentary faces) and decay; maximum correction on $I < 0{\cdot}14$ (Henslee & Davis, 1975). Data reduction described in Riley & Davis (1976); 806 reflections with $F_o < 4\sigma(F_o)$ considered unobserved. Structure solved using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) which afforded positions of S atoms, atoms of nitro group and one phenyl ring. All other non-H atoms obtained from difference map. After cycles of full-matrix least-squares refinement with anisotropic thermal parameters, H atoms located from difference map and refined with isotropic thermal parameters. Function minimized $\sum[w(|F_o| - |F_c|)^2]$, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5(kI)^{-1/2}\{[\sigma(I)]^2 + (0{\cdot}04I)^2\}^{1/2}$: I is the intensity of the reflection given by $(I_{\text{peak}} - I_{\text{background}}) \times$ (scan rate), 0·04 is a factor used to downweight intense reflections and to account for the instrument instability and k is the correction due to Lp effects, absorption and decay. $\sigma(I)$ estimated from counting statistics; $\sigma(I)$ = (scan rate) $(I_{\text{peak}} + I_{\text{background}})^{1/2}$. Final $R = 0{\cdot}041$ by refining 260 parameters using 2856 reflections,* $wR = 0{\cdot}046$, goodness of fit = 1·35. Maximum least-squares shift/e.s.d. 0·012 in the final refinement cycle and minimum and maximum peaks in the final difference map −0·27 and 0·29 e Å^{-3} respectively. Scattering factors for non-H atoms from Cromer &

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* Lists of anisotropic thermal parameters, bond distances and angles for the H atoms, least-squares planes and a list of structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42211 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), scattering factors for H atoms from Stewart, Davidson & Simpson (1965); linear absorption coefficient calculated using values from *International Tables for X-ray Crystallography* (1974). Least-squares-planes' program supplied by Cordes (1983); other computer programs listed in reference 11 of Gadol & Davis (1983).

Discussion. An *ORTEP* drawing (Johnson, 1976) with the atom-labeling scheme is shown in Fig. 1. Positional and isotropic thermal parameters are listed in Table 1 while bond distances and angles for the non-H atoms are listed in Table 2.

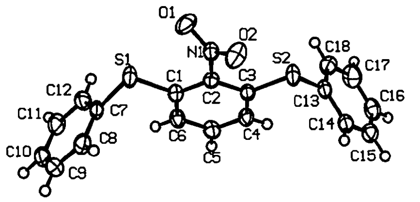

Fig. 1. View of the title compound showing atom-labeling scheme.

Table 1. *Positional and isotropic thermal parameters for the atoms of* 2-*nitro*-1,3-*bis*(*phenylthio*)*benzene*

	x	y	z	U_{eq}†/U_{iso}(Å^2)
S(1)	0·27788 (7)	0·22541 (4)	0·25936 (3)	0·0349 (2)
S(2)	0·68987 (7)	0·20105 (4)	−0·00795 (3)	0·0332 (2)
O(1)	0·4881 (2)	0·08288 (11)	0·20052 (9)	0·0454 (6)
O(2)	0·4585 (2)	0·07726 (11)	0·06168 (9)	0·0461 (6)
N(1)	0·4784 (2)	0·12309 (12)	0·12962 (10)	0·0276 (5)
C(1)	0·4012 (2)	0·28604 (14)	0·18513 (12)	0·0255 (6)
C(2)	0·4883 (2)	0·23101 (13)	0·12658 (11)	0·0229 (5)
C(3)	0·5847 (2)	0·27479 (14)	0·06532 (11)	0·0248 (5)
C(4)	0·5959 (3)	0·37795 (15)	0·06542 (13)	0·0284 (6)
C(5)	0·5108 (3)	0·43327 (15)	0·12231 (13)	0·0310 (6)
C(6)	0·4132 (3)	0·38879 (14)	0·18108 (13)	0·0295 (6)
C(7)	0·1552 (3)	0·32519 (14)	0·29794 (12)	0·0301 (6)
C(8)	−0·0176 (3)	0·3416 (2)	0·26280 (14)	0·0373 (7)
C(9)	−0·1149 (3)	0·4153 (2)	0·2980 (2)	0·0466 (8)
C(10)	−0·0412 (3)	0·4712 (2)	0·3667 (2)	0·0461 (8)
C(11)	0·1301 (3)	0·4546 (2)	0·40116 (15)	0·0430 (8)
C(12)	0·2286 (3)	0·3805 (2)	0·36777 (14)	0·0360 (7)
C(13)	0·8335 (3)	0·28922 (14)	−0·04789 (12)	0·0284 (6)
C(14)	0·7812 (3)	0·3352 (2)	−0·12643 (13)	0·0317 (6)
C(15)	0·8947 (3)	0·4021 (2)	−0·15948 (15)	0·0370 (7)
C(16)	1·0560 (3)	0·4226 (2)	−0·1146 (2)	0·0410 (8)
C(17)	1·1078 (3)	0·3758 (2)	−0·0369 (2)	0·0474 (8)
C(18)	0·9969 (3)	0·3081 (2)	−0·00332 (14)	0·0376 (7)
H(C4)	0·660 (3)	0·408 (2)	0·0301 (13)	0·031 (6)
H(C5)	0·518 (3)	0·505 (2)	0·1220 (13)	0·039 (6)
H(C6)	0·358 (3)	0·425 (2)	0·2188 (13)	0·034 (6)
H(C8)	−0·063 (3)	0·302 (2)	0·2126 (15)	0·049 (7)
H(C9)	−0·230 (3)	0·427 (2)	0·274 (2)	0·054 (7)
H(C10)	−0·109 (3)	0·525 (2)	0·393 (2)	0·056 (7)
H(C11)	0·183 (3)	0·492 (2)	0·449 (2)	0·058 (8)
H(C12)	0·344 (3)	0·370 (2)	0·3940 (14)	0·043 (6)
H(C14)	0·671 (3)	0·320 (2)	−0·1583 (13)	0·036 (6)
H(C15)	0·859 (3)	0·432 (2)	−0·2149 (13)	0·031 (5)
H(C16)	1·129 (3)	0·473 (2)	−0·140 (2)	0·056 (7)
H(C17)	1·218 (4)	0·391 (2)	−0·007 (2)	0·077 (10)
H(C18)	1·032 (3)	0·275 (2)	0·0492 (14)	0·041 (6)

† For anisotropic atoms, the U value is U_{eq}, calculated as $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{A}_{ij}$ where $\mathbf{A}_{ij}$ is the dot product of the i^{th} and j^{th} direct-space unit-cell vectors.

Table 2. *Bond distances and angles for the non*-H *atoms of* 2-*nitro*-1,3-*bis*(*phenylthio*)*benzene*

1	2	3	1—2	1—2—3
C(1)	S(1)	C(7)	1·776 (2) Å	102·24 (9)°
C(7)	S(1)		1·786 (2)	
C(3)	S(2)	C(13)	1·777 (2)	101·23 (9)
C(13)	S(2)		1·781 (2)	
N(1)	O(1)		1·225 (2)	
N(1)	O(2)		1·220 (2)	
C(2)	N(1)	O(1)	1·460 (2)	118·26 (15)
C(2)	N(1)	O(2)		118·6 (2)
O(1)	N(1)	O(2)		123·1 (2)
C(2)	C(1)	C(6)	1·404 (3)	117·3 (2)
C(2)	C(1)	S(1)		120·57 (14)
C(6)	C(1)	S(1)	1·392 (3)	122·1 (2)
C(3)	C(2)	N(1)	1·404 (3)	118·4 (2)
C(3)	C(2)	C(1)		123·2 (2)
N(1)	C(2)	C(1)		118·4 (2)
C(4)	C(3)	S(2)	1·395 (3)	121·8 (2)
C(4)	C(3)	C(2)		117·1 (2)
S(2)	C(3)	C(2)		121·00 (14)
C(5)	C(4)	C(3)	1·379 (3)	120·5 (2)
C(6)	C(5)	C(4)	1·385 (3)	121·5 (2)
C(1)	C(6)	C(5)		120·4 (2)
C(8)	C(7)	C(12)	1·386 (3)	120·2 (2)
C(8)	C(7)	S(1)		120·1 (2)
C(12)	C(7)	S(1)	1·383 (3)	119·5 (2)
C(9)	C(8)	C(7)	1·394 (4)	119·1 (2)
C(10)	C(9)	C(8)	1·374 (3)	120·7 (2)
C(11)	C(10)	C(9)	1·372 (3)	119·9 (2)
C(12)	C(11)	C(10)	1·390 (3)	120·3 (2)
C(7)	C(12)	C(11)		119·7 (2)
C(14)	C(13)	C(18)	1·388 (3)	120·7 (2)
C(14)	C(13)	S(2)		118·83 (15)
C(18)	C(13)	S(2)	1·378 (3)	120·4 (2)
C(15)	C(14)	C(13)	1·393 (3)	119·3 (2)
C(16)	C(15)	C(14)	1·371 (3)	120·2 (2)
C(17)	C(16)	C(15)	1·381 (3)	120·2 (2)
C(18)	C(17)	C(16)	1·391 (4)	120·4 (2)
C(13)	C(18)	C(17)		119·2 (2)

The bond distances and angles for the phenyl rings are normal. The phenyl rings are all planar and are approximately at right angles to each other. The nitro group is twisted substantially out of the plane of the central phenyl ring with atoms O(1) and O(2) −0·729 (2) and 0·673 (2) Å, respectively, out of this plane. This twist of 40·69 (7)° is in the upper end of the range observed for compounds with an S atom *ortho* to a nitro group. For example, in 1-nitro-2,4-bis(phenylthio)benzene (Korp, Bernal, Miller, Turley, Williams & Martin, 1978) the nitro group is essentially coplanar with the phenyl ring to which it is bound; in 3-nitro-2-(2-pyridylthio)pyridine (Kimura *et al.*, 1981) the nitro group is twisted by 16·7° and in 4-nitro-2-azathianthrene (Lynch, 1984, unpublished results) with two molecules per asymmetric unit, the nitro groups are twisted by 26·75 (14) and 38·82 (14)°. Surprisingly, while the range of dihedral angles varies widely, the C—N distances remain generally constant, in the region of 1·46–1·47 Å. Although for bis(*o*-nitrophenyl) disulfide (Ricci & Bernal, 1970) C—N distances of 1·425 (11) and 1·476 (13) Å and dihedral angles of 7·0 (5) and 18·6 (5)°, respectively, are observed, there appears to be little connection between the degree of twist of the nitro group and the C—N bond distance.

Although there is little difference in the C—S distances in the title compound, in compounds of this type asymmetric C—S distances are often observed with the shorter distance being to the C atom of the nitro-substituted ring (Kimura *et al.*, 1981; Korp *et al.*, 1978; Korp, Bernal & Martin, 1981). O···S—C angles close to 180° are generally observed and are 175·41 (8) and 175·31 (8)° for O(1)···S(1)—C(7) and O(2)···S(2)—C(13), respectively. A directional preference for atoms making close, non-bonded contacts with divalent sulfur has been suggested (Rosenfield, Parthasarathy & Dunitz, 1977). Nucleophiles (such as O in a nitro group) tend to approach S along the extension of one of the C—S bonds, which in the present case are the C(7)—S(1) and C(13)—S(2) bonds. It has been further suggested (Rosenfield *et al.*, 1977) that this directional preference is the result of an interaction between the nucleophile and a σ^* (C—S) orbital. Although the electron-withdrawing effects due to the nitro group cannot be overlooked, increasing the electron density in an anti-bonding orbital by such an interaction should result in a lengthening of the C—S bond and could explain the asymmetry in the C—S bond distances which is frequently observed.

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Structure of 5-(*p*-Methoxyphenyl)-3*H*-1,2-dithiole-3-thione, $C_{10}H_8OS_3$

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Abstract. $M_r = 240$, monoclinic, $P2_1/n$, $a = 10{\cdot}834\,(2)$, $b = 13{\cdot}446\,(2)$, $c = 7{\cdot}517\,(2)$ Å, $\beta = 104{\cdot}96\,(2)°$, $V = 1057{\cdot}9$ Å^3, $Z = 4$, $D_m = 1{\cdot}50$, $D_x = 1{\cdot}51$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7093$ Å, $\mu = 6{\cdot}39$ cm^{-1}, $F(000) = 496$, $T = 298$ K. Final $R = 0{\cdot}036$ for 1652 observed reflections. The molecule is composed of one methoxyphenyl ring and one five-membered heterocyclic ring containing an S—S single bond and an exocyclic C=S double bond. Each of the two individual rings is essentially planar, the angle between the two plane normals being 7·7 (1)°.

Introduction. Oltipraz, 4-methyl-5-(2-pyrazinyl)-3*H*-1,2-dithiole-3-thione, is a slow-acting schistosomidal drug which functions by reducing the glutathione stores of the worms (Bueding, Dolan & Leroy, 1982).

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