

The Crystal Structure of α -Bis(*p*-nitrophenyl) Disulfide

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Abstract: The crystal and molecular structure of bis(*p*-nitrophenyl) disulfide has been determined by three-dimensional single-crystal X-ray diffraction techniques. The compound crystallizes in the monoclinic system, space group C2/c, with four molecules at special positions in a unit cell having the following dimensions: $a = 7.30 \text{ \AA}$ ($\sigma = 0.03$), $b = 14.18 \text{ \AA}$ ($\sigma = 0.02$), $c = 12.76 \text{ \AA}$ ($\sigma = 0.04$), and $\beta = 95.0^\circ$ ($\sigma = 0.5^\circ$). The molecule consists of two identical halves related by a twofold axis passing midway between the two sulfur atoms. The S–C bond length is 1.767 \AA ($\sigma = 0.010$), the average N–O length is 1.207 \AA ($\sigma = 0.013$), and the O–N–O angle is 124° ($\sigma = 1^\circ$). The dihedral angle about the S–S bond is 72° ($\sigma = 2^\circ$), and the angle between the plane of the phenyl ring and the plane of the nitro group is 8.2° ($\sigma = 0.5^\circ$). The length of the C–N bond is 1.488 \AA ($\sigma = 0.013$), which implies that the amount of resonance between the benzene ring and the $-\text{NO}_2$ fragment is negligible. This result may be accounted for by repulsive forces between the oxygens of the nitro group and the substituted carbon of the benzene ring. The S–S distance, 2.019 \AA ($\sigma = 0.005$), implies some π character in this bond. This distance, the sulfur valency angle, and the dihedral angle about the S–S– fragment closely resemble those found in orthorhombic sulfur. The molecular packing produces no unusually close molecular contacts despite the fact that short O···S contacts are known to occur. The final discrepancy factor for 597 independent, nonzero, reflections is $R(F) = 10.1\%$.

As we have pointed out elsewhere,² the amount of structural data available for aromatic disulfides is very scarce. Our work on the reactions of metal carbonyls with aromatic disulfides led to our investigation of the steric characteristics of this class of sulfur compounds. It is our hope that structural studies will help us in understanding some of the problems encountered in our synthetic work with transition metal ions. Consequently, we have undertaken a systematic study of simple aromatic disulfides and some of their derivatives.

Aside from their chemical interest, the disulfides play a major role in the functioning of biological systems. Tetraethylthiuram disulfide, Antabuse, has long been known to be of value in the treatment of severe alcoholism.³ The enzyme ribonuclease contains four intrachain disulfide bridges, reduction of which results in a total loss of activity. Yet enzymic activity is restored and the structure spontaneously reproduced upon air reoxidation to form the original disulfide bonds. Insulin, which consists of two peptide chains held together and structured by disulfide linkages (the S–S bonds of cystine), is dependent on having its protein structure intact for its biological effects.^{4a} Mirsky^{4b} has shown that the liver possesses an enzymic system capable of deactivating insulin. The enzyme catalyzes cleavage of the disulfide bonds resulting in both of the interchain linkages being broken. Thus, it may be assumed that insulin's activity is an important function of its conformation as determined by the disulfide bridges.

The broad scope of disulfide chemistry makes structural investigation of the disulfides as a class of

compounds a highly interesting and useful undertaking. It is anticipated that the work presented here will serve as the beginning of a more extensive study of sulfur ligands and the nature of disulfide linkages.

Experimental Section

Crystal Data. Bis(*p*-nitrophenyl) disulfide was obtained from Eastman (Technical Grade, T-1855) and recrystallized from a saturated acetic acid solution as light yellow, needle-shaped crystals which are stable in air and melt at $174\text{--}175^\circ$. During the melting point determination, it was noted that a phase change occurs at $132\text{--}134^\circ$ in which crystals burst (nonexplosively) without melting. This phenomenon was subsequently demonstrated and confirmed on a Du Pont 900 thermal analysis system. Since crystal data were taken at room temperature, this transition was not of immediate concern, and it was decided to call that phase existing below 132° the α phase. On the basis of precession, oscillation, and Weissenberg photographs it was established that the crystals belong to the monoclinic system and have unit cell dimensions $a = 7.30 \text{ \AA}$ ($\sigma = 0.03$), $b = 14.18 \text{ \AA}$ ($\sigma = 0.02$), $c = 12.76 \text{ \AA}$ ($\sigma = 0.04$), $\beta = 95.0^\circ$ ($\sigma = 0.5^\circ$); $V = 1316 \text{ \AA}^3$. A density of 1.556 g cm^{-3} calculated for four molecules in the unit cell agrees satisfactorily with that of $1.50 \pm 0.05 \text{ g cm}^{-3}$ measured by flotation in aqueous KI solution. The systematic extinctions observed on precession photographs of $0kl$, $1kl$, $h0l$, and $h1l$ zones are hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$). Possible space groups are Cc and C2/c, the latter demanding that the molecules lie at special positions in the lattice since $Z = 4$.

Intensities. A nonintegrated set of Weissenberg data consisting of levels $hk0$ through $hk11$ in the angular range $\theta \leq 60^\circ$ was obtained from a crystal ($0.2 \times 0.2 \times 0.3 \text{ mm}$) mounted and oriented along c (the needle axis). At the end of data collection, there was a noticeable darkening of the crystal due apparently to radiation damage. However, a successful attempt at reproducing the original precession and Weissenberg photographs led to the conclusion that the damage was not serious. A second set of reflections was collected as integrated Weissenberg data about the b axis of a new crystal of approximately the same dimensions. Intensities were observed out to $\theta \leq 60^\circ$ from levels $h0l$ through $h12l$. Interscaling⁵ of both sets of reflections gave 597 independent nonzero data which represent approximately 60% of those which can occur within this range for $\text{Cu K}\alpha$ radiation. Data was estimated visually from multiple films (five layers) by the use of a calibrated intensity strip. The intensities were corrected for Lorentz and polarization factors but not for absorption ($\mu = 37.0 \text{ cm}^{-1}$).

(1) (a) Currently, Research Collaborator, Brookhaven National Laboratory; (b) Brookhaven National Laboratory.

(2) J. S. Ricci, I. Bernal, and W. C. Hamilton, submitted for publication; see Abstracts of the 7th International Union of Crystallography Congress, Moscow, 1966.

(3) J. Hald, E. Jacobsen, and V. Larsen, *Acta Pharmacol. Toxicol.*, **4**, 285 (1948).

(4) (a) A. White, P. Handler, and E. L. Smith, "Principles of Biochemistry," 3rd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 891; (b) A. I. Mirsky, *Recent Progr. Hormone Res.*, **13**, 429 (1957).

(5) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, **18**, 129 (1965).

Table I. Final Parameters for Bis(*p*-nitrophenyl) Disulfide

Atom	Positional Parameters		
	x	y	z
S	0.0709 (4) ^a	0.1975 (2)	-0.1785 (2)
O(1)	-0.2195 (14)	0.4686 (7)	0.1944 (8)
O(2)	-0.3178 (15)	0.5528 (7)	0.0628 (8)
N	-0.2421 (13)	0.4835 (7)	0.1013 (9)
C(1)	-0.0365 (13)	0.2820 (7)	-0.1026 (7)
C(2)	0.0019 (14)	0.2759 (7)	0.0048 (9)
C(3)	-0.0620 (16)	0.3395 (8)	0.0720 (8)
C(4)	-0.1705 (14)	0.4128 (7)	0.0291 (8)
C(5)	-0.2147 (14)	0.4226 (7)	-0.0778 (9)
C(6)	-0.1471 (16)	0.3567 (7)	-0.1445 (8)
H(2) ^b	0.082	0.222	0.035
H(3)	-0.040	0.333	0.149
H(5)	-0.287	0.474	-0.107
H(6)	-0.165	0.363	-0.220

Atom	Anisotropic Thermal Parameters ^c					
	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
S	0.060 (2)	0.055 (2)	0.058 (2)	0.007 (1)	0.001 (1)	-0.001 (9)
O(1)	0.122 (9)	0.099 (7)	0.066 (6)	-0.021 (6)	0.027 (4)	-0.027 (5)
O(2)	0.110 (5)	0.062 (5)	0.0116 (7)	0.014 (5)	0.028 (6)	-0.004 (5)
N	0.062 (6)	0.055 (6)	0.084 (7)	0.014 (4)	0.028 (5)	-0.024 (5)
C(1)	0.047 (6)	0.058 (6)	0.043 (6)	0.007 (4)	0.004 (4)	0.004 (4)
C(2)	0.060 (6)	0.046 (5)	0.063 (6)	0.004 (4)	0.000 (5)	0.004 (4)
C(3)	0.078 (9)	0.057 (6)	0.053 (7)	-0.001 (5)	-0.001 (6)	0.015 (5)
C(4)	0.051 (6)	0.050 (6)	0.073 (6)	-0.006 (4)	0.016 (4)	0.007 (4)
C(5)	0.047 (5)	0.050 (6)	0.074 (7)	-0.001 (4)	0.018 (4)	0.012 (5)
C(6)	0.070 (9)	0.059 (7)	0.053 (6)	0.011 (5)	0.008 (4)	0.003 (5)

^a Numbers in parentheses are standard deviations in the last significant figure. ^b Hydrogens were placed at idealized positions which meet these conditions: (a) they lie in the plane of the benzene ring; (b) C-H distance = 0.97 Å. Their temperature factors were arbitrarily made isotropic, with a value of 5.0 Å². ^c The anisotropic *U*'s are given by $\exp[-2\pi^2(h^2a^2U_{11} + 2hka^*b^*U_{12} + \dots)]$.

Structure Determination

After obtaining a single scale factor and an over-all temperature factor from a Wilson plot, the coordinates of the sulfur atom (the asymmetric unit consists of one-half the molecule) were obtained from a sharpened, origin-removed Patterson synthesis. The positions of the remaining light atoms were readily located from successive Fourier and difference Fourier syntheses based on initial phasing from the sulfur atoms and using the space group C2/c, the general positions of which are $(0, 0, 0; 1/2, 1/2, 0) \pm (x, y, z; \bar{x}, y, 1/2 - z)$.

The structure was refined by the least-squares method. An initial refinement using individual isotropic temperature factors for the atoms and rejecting reflections with $F^2 < 300$ led to a conventional $R(F)$ factor of 0.17. After allowing for anisotropic thermal motion, a difference Fourier map was computed eliminating the sulfur, carbons, and nitro group in an attempt to find the hydrogen atoms. Only two of the four hydrogens could clearly be distinguished; therefore, it was decided to place all four of them at idealized positions using a carbon-hydrogen bond distance of 0.97 Å and an isotropic temperature factor of 5.0 Å².

Weights for all reflections were obtained from an analysis of the residuals (Δ/σ) using the program NANOVA.⁶ For all observed reflections $\sigma = 0.37 + 0.08(F_c)$. The final anisotropic refinement including fixed hydrogen parameters and using all observed reflections gave a conventional $R(F)$ factor of 0.101 and a weighted $R_w(F)$ of 0.148. A difference Fourier showed no peaks higher than 0.49 e/Å³ (about 12% the height of a carbon atom). The final parameters

(6) This is the Brookhaven National Laboratory version of a generalized analysis-of-variance program.

together with their standard deviations are given in Table I. A table of structure factors for the 597 observed reflections is available from the National Auxiliary Publication Service of the American Society for Information Science (NAPS-00319).

Discussion

The formal structure and numbering system for the atoms in bis(*p*-nitrophenyl) disulfide are given in Figure 1. A stereoscopic drawing of the isolated molecule is

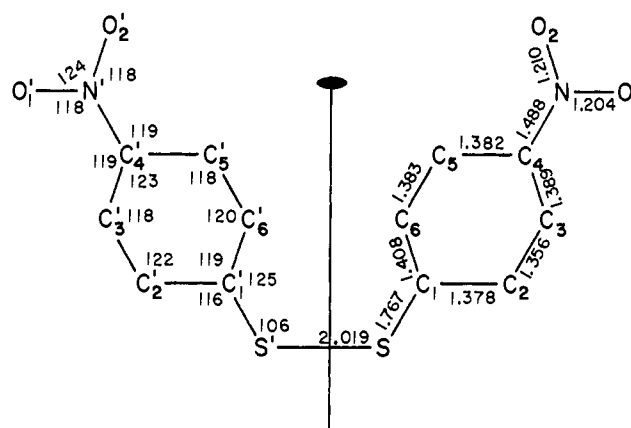


Figure 1. Bond distances (ångströms) and valency angles (degrees).

shown in Figure 2. From the positional parameters in Table I, the interatomic distances, bond angles, and their standard deviations were calculated and are presented in Table II. The S-S and S-C bond lengths are 2.019 (5) and 1.767 (10) Å, respectively. The

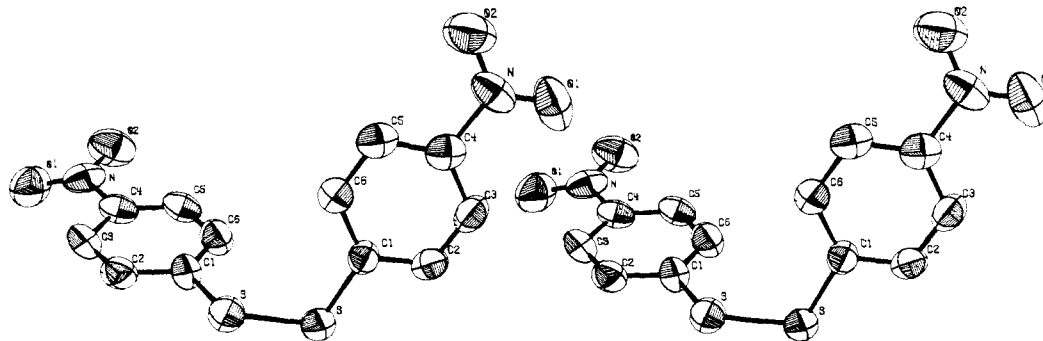


Figure 2. Molecular structure of bis(*p*-nitrophenyl) disulfide. The ellipsoids indicate the magnitudes of thermal vibration. This is a stereo pair and may be conveniently examined with the aid of a hand-held stereo viewer.

former is somewhat shorter (0.032 Å) and the latter somewhat longer (though perhaps not significantly since 0.013 Å = 1.3σ) than the corresponding distances in 2,2'-biphenyl disulfide.⁷ The sulfur-carbon distance

Table II. Selected Intramolecular Distances and Angles in Bis(*p*-nitrophenyl) Disulfide

Distances, Å		Angles, deg	
S-S	2.019 (5) ^a	S-C(1)-C(2)	116.1 (7)
S-C(1)	1.767 (10)	S-C(1)-C(6)	124.7 (7)
C(1)-C(2)	1.378 (15)	C(2)-C(1)-C(6)	119.0 (9)
C(2)-C(3)	1.356 (16)	C(1)-C(2)-C(3)	122.4 (9)
C(3)-C(4)	1.389 (15)	C(2)-C(3)-C(4)	117.6 (9)
C(4)-C(5)	1.382 (15)	C(3)-C(4)-C(5)	122.7 (10)
C(5)-C(6)	1.383 (14)	C(4)-C(5)-C(6)	118.3 (9)
C(6)-C(1)	1.408 (13)	C(5)-C(6)-C(1)	119.9 (9)
N-C(4)	1.488 (13)	O(1)-N-O(2)	124.2 (11)
N-O(1)	1.204 (13)	O(1)-N-C(4)	117.9 (11)
N-O(2)	1.210 (13)	O(2)-N-C(4)	117.9 (11)
		S-S-C(1)	106.2 (3)
		N-C(4)-C(5)	118.7 (10)
		N-C(4)-C(3)	118.6 (10)

Dihedral Angles between Planes, Each Defined by Three Atoms (1, 2, 3) and (4, 5, 6)

1, 2, 3	4, 5, 6	Dihedral angle, deg
O(1), N, O(2)	C(3), C(4), C(5)	8.2 (5)
S', S, C(1)	S, S', C(1)'	72 (2)
C(1), C(3), C(5)	C(1)', C(3)', C(5)'	68.2 (7)

^a Numbers in parentheses are standard deviations in the last significant figure.

lies between the suggested S-C single bond (1.82 Å) and double bond (1.62 Å) lengths.⁸⁻¹⁰ This would imply that sulfur d orbitals are participating in the π-electron systems of these compounds to the extent that the S-C bonds contain approximately one-third double-bond character. The average N-O bond length (1.207 (13) Å) and O-N-O angle (124 (1)°) are in good agreement with those found in *p*-dinitrobenzene (1.21 (3) Å and 124 (3)°), in the *p*-nitro group of 2,4,6-trinitrophenetole (1.218 (10) Å and 124.4 (7)°),^{11a} and in nitrobenzene (1.208 (14) Å and 124°).^{11b} The average C-C distance¹² is 1.383 (15) Å, as compared with the value

(7) J. S. Ricci, Doctoral Thesis, State University of New York at Stony Brook, 1969, Part I.

(8) S. C. Abrahams, *Quart. Rev.* (London), 10, 407 (1956).

(9) G. A. Jeffrey and R. Shiono, *Acta Cryst.*, 12, 447 (1959).

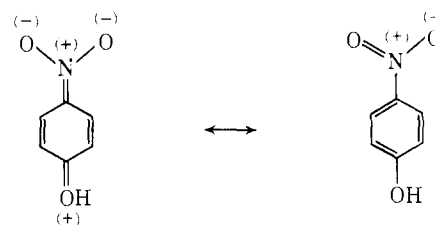
(10) I. L. Karle, J. A. Estlin, and K. Britts, *ibid.*, 22, 273 (1967).

(11) (a) C. M. Grammacioli, R. Destro, and M. Simonetta, *ibid.*, B24, 129 (1968); (b) J. Trotter, *ibid.*, 12, 884 (1959).

(12) Note that although bonds C(2)-C(3) and C(6)-C(1) differ in length by 0.052 Å, this is approximately $2.5(\sigma_1^2 + \sigma_2^2)^{1/2}$.

found in crystalline benzene (1.393 Å) by Cox, *et al.*¹³ The C-N bond length of 1.488 (13) Å is equivalent within experimental error¹⁴ to the average of 1.48 Å found for a number of aromatic nitro hydrocarbons as reported by Trotter¹⁵ and is significantly longer than the values reported by Coppens¹⁶ for the two forms of 4-nitrophenol, 1.442 (6) and 1.446 (2) Å.

None of the nitro derivatives considered by Trotter has substituents which are electron donating. A shortening of the C-NO₂ bond is associated with the addition of such substituents and can be accounted for in terms of valence-bond theory. For example, in 4-nitrophenol the quinonoid structures



are comparable in importance as determined from the shortened C-N bond. A C-N bond length of 1.460 Å at the nitro group in 4-nitroaniline might be attributed to the same electronic interaction and give rise to similar quinonoid resonance forms. A concomitant shortening of the C-NH₂, C(2)-C(3), and C(5)-C(6) bonds is also reported.^{16b}

A priori, one might expect inductive or resonance effects in conjugated molecules to result in a shortening of certain bond lengths as compared to those in non-conjugated systems. In the present study there is a distinct lack of any bond shortening among C-N, C-S, C(5)-C(6), or C(2)-C(3) distances (the somewhat smaller than average value for C(2)-C(3) not being statistically significant).

Two interpretations of these results will be given. The first explains the absence of shortening in terms of variations in the hybridization of the carbon and nitrogen atoms. Changes in C-C bond lengths in themselves do not imply that electron resonance is negligible because the magnitude of predicted shortenings¹⁷ may be less than the experimental error of

(13) E. G. Cox, D. W. J. Cruickshank, and J. A. S. Smith, *Proc. Roy. Soc. (London)*, A247, 1 (1958).

(14) The differences in bond lengths between the values reported by Coppens and ours (0.046 Å) is greater than $3(\sigma_1^2 + \sigma_2^2)^{1/2}$.

(15) J. Trotter, *Tetrahedron*, 8, 13 (1960).

(16) (a) P. Coppens and G. M. J. Schmidt, *Acta Cryst.*, 18, 62 (1965); (b) *ibid.*, 18, 654 (1965).

(17) J. Trotter, *Can. J. Chem.*, 37, 905 (1959).

X-ray methods. The C–N bond, however, is one for which the theory predicts considerable shortening from the ordinary single bond (nitromethane, 1.49 Å).¹⁸ A study by Trotter¹⁷ of several aromatic nitro compounds shows the following structural features. Nitrobenzene, a strictly planar molecule, has a C–N distance of 1.486 Å. Nitromesitylene, whose phenyl ring is noncoplanar with the NO₂ groups, has a C–N distance of 1.48 Å. The dihedral angle between the two groups is 66°, which implies a resonance interaction of $\cos^2 66^\circ$ (=0.17) of that in a coplanar structure. 9-Nitroanthracene¹⁹ also exhibits extreme noncoplanarity in that the plane of its nitro group is twisted 85° out of the anthracene plane. This molecule provides an example of an aromatic nitro compound with a nonconjugated C–N bond.

A comparison of the parameters found for bis(*p*-nitrophenyl) disulfide, whose nitro group is twisted 8.2° from the phenyl plane, shows many similarities to the above examples, especially nitrobenzene. The C–N bond length in the disulfide is 1.488 *vs.* 1.486 Å in nitrobenzene. Similarly, the average N–O distance is 1.207 *vs.* 1.208 Å. Trotter suggests that from the measured C–N distance in nitrobenzene any possibility of bond shortening as a result of resonance interaction is more than offset by a lengthening due to hybridization differences in the carbon and nitrogen atoms of nitrobenzene and 9-nitroanthracene. (According to Dewar and Schmeising²⁰ an increase in the valency angle at a given atom would shorten the bonds involving that atom because of an increase in the *s* character of the hybrid orbitals.) However, the exocyclic valency angles are the same within experimental error in both nitrobenzene and bis(*p*-nitrophenyl) disulfide. They are: O–N–O, 124 *vs.* 124°; O–N–C (av), 118 *vs.* 118°; C–C–N (av), 117 *vs.* 119°; and C(3)–C(4)–C(5), 125 *vs.* 123°. Trotter finds the corresponding valency angles in 9-nitroanthracene identical with those in nitrobenzene and concludes that hybridization effects should be the same for the C–N bonds in both molecules. Applying these results to the present study, it may then be concluded that resonance interaction across this bond is negligible to the extent that it is not sufficient to cause any observable C–N shortening.

A second interpretation of the longer-than-anticipated C–N distance may be made in terms of intramolecular nonbonded repulsions as discussed by Bartell.²¹ Using a hard-sphere model in which atomic positions depend on the sizes of spherical atoms packed around a given atom, he has been able to explain bond angles in a number of substituted ethylenes and carbonyl derivatives. Trueblood²² and Coppens²³ have found the dimensions of the nitro group in several aromatic nitro compounds to agree with this model. The model implies that if the atoms are taken as hard spheres, the nonbonded distances between the two oxygen atoms and those between the substituted carbon and each oxygen should be fixed in all nitro compounds independent of

(18) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(19) J. Trotter, *Acta Cryst.*, **12**, 237 (1959).

(20) M. J. S. Dewar and A. N. Schmeising, *Tetrahedron*, **6**, 68 (1959).

(21) L. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(22) K. N. Trueblood, E. Goldish, and J. Donohue, *Acta Cryst.*, **14**, 1009 (1961).

(23) P. Coppens, *J. Chem. Phys.*, **36**, 2523 (1962).

Table III. Equations of Best Least-Squares Planes and Deviations of the Atoms from Planarity (Å)

(1) Plane through S plus phenyl ring			
	$5.931x + 8.239y - 1.493z = -2.311$		
S	0.003 (3) ^a	C(4)	0.036 (10)
C(1)	-0.051 (10)	C(5)	0.014 (10)
C(2)	-0.034 (11)	C(6)	-0.029 (12)
C(3)	0.011 (12)		
(2) Plane through phenyl ring			
	$6.032x + 7.929y - 1.741z = -2.193$		
C(1)	0.002 (10)	C(4)	0.001 (10)
C(2)	-0.002 (11)	C(5)	-0.001 (10)
C(3)	0.000 (12)	C(6)	0.000 (12)
	Displacement of the S atom from this plane = 0.011 Å		
(3) Plane through C(4) plus nitro group			
	$6.388x + 6.829y - 4.089z = -1.717$		
C(4)	0.001 (10)	O(1)	0.002 (10)
N	-0.003 (9)	O(2)	0.002 (10)
(4) Plane through N plus phenyl ring			
	$6.035x + 7.921y - 1.750z = -2.190$		
N	0.001 (10)	C(4)	0.000 (10)
C(1)	0.003 (10)	C(5)	-0.002 (10)
C(2)	-0.002 (11)	C(6)	0.000 (12)
C(3)	-0.001 (12)		

^a Standard deviations are given in parentheses.

the C–N bond length such that the O–N–O angle should increase as the C–N distance increases. Specifically, the amount of double-bond character which makes nitro N–O bonds shorter than the single N–O distance (1.30 Å) pulls the oxygen inward toward the nitrogen to the extent that the C–N bond is lengthened due to repulsive van der Waals forces between the oxygens and the substituted carbon. Bartell's hard-sphere radii as derived for carbon and oxygen are 1.25 and 1.13 Å, respectively. For an O–N–O angle of 124° and a C–N distance of 1.486 Å, as found in the present study, the average nonbonded C(4)···O distance is 2.312 Å and the O···O distance is 2.133 Å. If one assumes a 5% decrease in the derived oxygen hard-sphere radius to 1.07 Å, one obtains an excellent fit with the present results. (The decreased O···O distance clearly exhibits a deviation toward a "soft-sphere" model.²¹) Thus this rather oversimplified model appears to account very well for the angles and bond lengths of the nitro group in this molecule.

Within experimental error the benzene ring and the nitro group are each planar but not coplanar. In Table III are given the equations of the best least-squares planes through several molecular planes together with the displacements of the atoms from their respective planes. The nitro group, as shown in Figure 2, is twisted out of the plane of the phenyl ring by 8.2 (5)°. The magnitude of the twisting about the C–N bond approximates closely that found by Abrahams²⁴ for *p*-dinitrobenzene (9.5°) and by Trotter²⁵ for *m*-dinitrobenzene (11°). The out-of-plane twist about the sulfur–sulfur bond is 71.8 (1.7)° and is the same as the dihedral angle between the planes of the benzene rings, 71.6 (7)°.

Table IV compares the important structural feature of bis(*p*-nitrophenyl) disulfide with other relevant disulfides. The disulfide linkages found in these species are remarkably similar in terms of bond dis-

(24) S. C. Abrahams, *Acta Cryst.*, **3**, 194 (1950).

(25) J. Trotter, *ibid.*, **14**, 244 (1961).

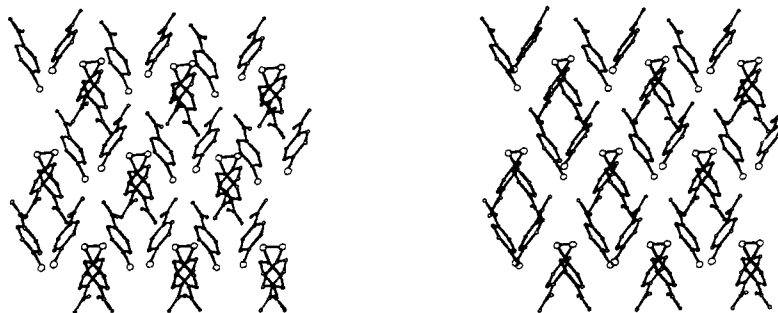


Figure 3. Molecular packing of bis(*p*-nitrophenyl) disulfide. This represents a view along the *c* axis (from + to -) with *a* parallel to the interocular direction (positive *a* from left to right), and with a small (12°) counterclockwise rotation about *b* (stereo pair).

tances, dihedral angle about S-S (twist), and the sulfur valency angle.

Foss²⁶ lists a number of crystal structure determinations of disulfides including *N,N'*-diglycyl-L-cystine dihydrate, hexagonal L-cystine hydrochloride, and formamidinium disulfide diiodide and dibromide monohydrates. Nonplanar, unbranched disulfide groups occur in all of these compounds. Values reported for the S-S bond length are practically invariant at 2.042 Å. Sulfur valency angles lie in the range 99 – 107° , and the twist about S-S lies in the range 79 – 105° .

conclusion directly applicable to the present study. Besides bond lengths the valency angles of the central sulfurs also closely approach those of S_8 ; tetrathionate, 103.8° ; pentathionate, 105 , 106° ; and hexathionate, 101 , 113 , 109 , 100° . It is therefore concluded that nonplanar disulfide fragments are fairly inert to substitution and are the dominant influence in the conformation of all the above molecules.

The crystal structure consists of individual monomeric molecules, each of which contains two asymmetric units related by a twofold axis. The positions of the atoms and their anisotropic thermal parameters are

Table IV. Comparison of Important Bond Lengths and Angles^a

	I	II	III ^b	IV
S-S, Å	1.999 (5)	2.051 (4)	2.045 (4)	2.019 (5)
S-C, Å	1.815 (25)	1.754 (8)	1.797 (9)	1.767 (10)
N-C, Å	1.47 (2)	...	1.45 (1)	1.488 (13)
N-O, Å	1.222 (9)	1.207 (13)
Dihedral angle about S-S, deg	83.6 (3)	68.7 (3)	85.1 (4)	72 (2)
Sulfur valency angle, deg	103.5 (3)	96.3 (2)	104.4 (3)	106.2 (3)
O-N-O angle, deg	123 (1)	124.2 (11)

^a I = tetraethylthiuram disulfide,¹⁰ II = 2,2'-biphenyl disulfide,¹⁷ III = bis(*o*-nitrophenyl) disulfide,⁷ and IV = bis(*p*-nitrophenyl) disulfide.
^b Quantities listed for this compound are average values because the two halves of the molecule are not symmetry related.

It is interesting to compare all the above values with the corresponding ones in elemental orthorhombic sulfur, S_8 , a cyclic molecule whose structure has been determined by Abrahams.²⁷ The average S-S bond length in S_8 is 2.037 (5) Å, the mean dihedral angle is 80.7° , and the sulfur valency angle is 107.8° . The comparison may be extended to some inorganic polysulfides such as the S_4^{2-} moiety in BaS_4 whose central dihedral angle is 76° .²⁸ Polythionates of general formula $[O_3SS_nSO_3]^{2-}$, where $n = 1$ – 4 , contain sulfur chains whose configuration are very similar to those of segments of the S_8 ring. The S-S bonds in polythionates are of two types, namely, those between divalent sulfurs in the middle of chains and those between a divalent and a sulfonate sulfur atom. The average terminal sulfur bond in nine different salts²⁶ is 2.11 Å, while the average central S-S distance is 2.04 Å. This difference in bond lengths suggests that bonds between divalent sulfurs contain some π character, a

given in Table I. The stereo drawing of the packing diagram as shown in Figure 3 represents a view along the *c* axis with *a* parallel to the interocular direction, and with a small counterclockwise rotation (12°) about *b*. There are no unusually close intermolecular contacts, the shortest being sulfur-oxygen of 3.31 Å which is greater than the sum of the van der Waals radii for S and O (3.25 Å).²⁹ No other features of the packing appear to merit special comment.

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