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The Crystal and Molecular Structure of Di-2-pyridyl Disulfide

By N. V. Raghavan* and Karl Seff

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822, *USA*

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The crystal and molecular structure of di-2-pyridyl disulfide has been determined by single-crystal X-ray diffraction using the 1578 unique and significant (at the 3σ level) reflections for which $2\theta < 50°$, and was refined to an unweighted R index of 0·048. Counter methods and monochromatized Mo $K\alpha$ radiation were employed. Crystals form in the monoclinic space group $P2_1/c$ (or $P2_1$) with cell dimensions a = 13·310 (3), b = 5·581 (2), c = 15·946 (5) Å, and β = 119·55 (2)°. All H atoms were located on a difference Fourier function and their positions were refined. The S–S bond length is 2·016 (2) Å and the average S–C distance is 1·785 Å. The C–S–S–C torsion angle is 87·1°. The S–S bond is nearly in the plane of each pyridine ring, one of which is disordered in $P2_1/c$.

Introduction

The crystal structure of di-2-pyridyl disulfide, alternatively named 2,2′-dithiodipyridine, was determined so that its geometry could be compared with that observed in its complexes with Co^{II}, Cu^{I}, and Hg^{II}. The crystal structures of $HgLCl_2$ (Kadooka, Hilti, Warner & Seff, 1976), $CoLCl_2$ (Kadooka, Warner & Seff, 1976), and CuL_2ClO_4 (Kadooka, Warner & Seff, 1977) have been recently determined.

The structure of *cyclo*-di-μ-{bis[2-(*N,N*-dimethylamino)ethyl] disulfide}dicopper(I) tetrafluoroborate (Ottersen, Warner & Seff, 1974*a*) showed an increased S–S bond length of 2·075 (6) Å as compared to 2·037 (1) Å in the free ligand in bis[2-(*N,N*-dimethylamino)ethyl] disulfide dihydrochloride (Ottersen, Warner & Seff, 1973). That this difference due to complexation was real was supported by the structure of {bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate (Warner, Ottersen & Seff, 1974*a*) whose S–S bond length is 2·081 (1) Å. When a metal ion other than Cu^{I}, such as Ni^{II} (Warner, Kadooka & Seff, 1975; Riley & Seff, 1972), Fe^{III} (Bertrand & Breece, 1974) or Cu^{II} (Thich, Mastropaolo, Potenza & Schugar, 1974), complexes $R–CH_2–S–S–CH_2–R$, no change in the S–S bond from approximately 2·04 Å, the expected value in the free ligand, is observed.

An anomalously long S–S bond length for an organic disulfide coordinated to Ni^{II}, 2·089 (8) Å, was observed in chloro{α,α'-dithiobis(*o*-phenylenenitrilo)-di-2-picoline}nickel(II) perchlorate (Warner, Ottersen & Seff, 1974*b*) where each S atom is bonded to an aromatic group. In order to learn whether the S–S bond-length dependency on complexing ion depends also upon the degree of saturation of the C atoms bonded to S, these studies were initiated.

Experimental

Crystals of di-2-pyridyl disulfide, obtained commercially from Aldrich Chemical Co., were recrystallized from a solution of chloroform and heptane. A crystal of dimensions 0·32 x 0·37 x 0·19 mm, mounted in a capillary, was used in this work. A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ = 0·70926 Å; $K\alpha_2$, λ = 0·71354 Å) was used for preliminary experiments and for the measurement of diffraction intensities. Preliminary experiments indicated that the reflections $h0l$ for l odd and $0k0$ for k odd were systematically absent, uniquely defining the space group $P2_1/c$. The cell parameters and their standard deviations were obtained from the least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 20° (with $K\bar{\alpha}$, λ = 0·71069 Å) and are given in Table 1. The θ–2θ scanning mode was used with a constant scan speed of 1° min^{-1}. Background counting time was equal to half the scan time at each end of the scan range, which varied from 2·0° at low 2θ to 2·3° at 50°. The intensities of three standard reflections, measured after

Table 1. *Crystal data*

Di-2-pyridyl disulfide	$C_{10}H_8N_2S_2$
Monoclinic	F.W. 220·3
Space group $P2_1/c$ (or $P2_1$)	Z = 4
a = 13·310 (3) Å	F(000) = 456
b = 5·581 (2)	D_x = 1·420 (1) g cm^{-3}
c = 15·946 (5)	D_m = 1·410 (2)
β = 119·55 (2)°	V = 1030 (1) $Å^3$

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* Present address: Chemistry Department, Michigan State University, East Lansing, Michigan 48824, USA.

every 100 reflections, showed a small average decrease in intensity of 1% during the total data collection, for which the appropriate correction was applied.

Standard deviations were assigned to the individual reflections according to the formula $\sigma(I) = [\omega^2(\mathrm{CT} + B_1 + B_2) + (pI)^2]^{1/2}$, where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0·02 was assigned to the empirical parameter p to account for instrumental inaccuracies. Of the 3272 unique reflections measured (those for which $2\theta < 50°$), 1578 had intensities greater than three times their standard deviations. These were regarded as observed reflections, and only these were used in further calculations. The intensities were corrected for Lorentz–polarization effects, and for the absorption of X-rays ($\mu = 4\cdot6$ cm^{-1}) (Busing & Levy, 1957; Ottersen, 1974). The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction.

The atomic scattering factors of Doyle & Turner (1968) were used for S^0, N^0, and C^0 with modifications for the real and imaginary parts of the anomalous dispersion correction for S^0. The atomic scattering factors used for H were those of Stewart, Davidson & Simpson (1965).

Structure determination

The S atom positions could not be readily determined from a three-dimensional Patterson function. An overall isotropic thermal parameter ($B_{\mathrm{iso}} = 3\cdot1$ Å^2) was estimated from a Wilson (1942) plot, and normalized structure factor amplitudes of the 235 reflections with $|E| \geq 1\cdot30$ were used in in the computer program *MULTAN* (Germain, Main & Woolfson, 1971). A three-dimensional E function, phased as indicated by one of these solutions, revealed the positions of the two S atoms. Successive cycles of Fourier refinement, using the fast Fourier program *ALFF* (Hubbard, Quicksall & Jacobson, 1971), indicated the positions of all non-hydrogen atoms. Full-matrix least-squares refinement, using Ibers's modification of *ORFLS* (Busing, Martin & Levy, 1962) and treating all the atoms in the rings as C atoms, resulted in an R_1 of 0·25 $[R_1 = (\Sigma|F_o - |F_c||)/\Sigma F_o]$. The two atoms with lowest isotropic thermal parameters (2·8 and 2·9Å^2 respectively, *vs* an average of 3·6 Å^2 for the others) were chosen as N atoms. Isotropic least-squares refinement of this structural model allowed R_1 to decrease to 0·21, and subsequent anisotropic refinement resulted in an R_1 value of 0·09.

However, the bond lengths C(9)–N(10) (1·370 Å) and C(9)–C(14) (1·326 Å) in the ring attached to S(8) were inconsistent with the usual results for C–N and C–C aromatic ring bonds. Reversal of the C and N positions (atoms 10 and 14) did not result in a better model [C(9)–C(10), 1·339; C(9)–N(14), 1·377 Å]. The large positional shifts for atoms 10 and 14, and the resulting bond lengths (although full convergence was not achieved) indicated disorder in this pyridine ring.

A disordered model was therefore used in the final refinements, placing half a N atom and half a C atom at positions 10 and 14; this was accomplished by using the average N and C scattering function for the atoms placed at positions 10 and 14. The assumption of a 50% occupancy for each of the structural models used in the disordered model is consistent with the indications of space group $P2_1$ (see below).

H atoms – these were all noted on a difference Fourier function – were placed on calculated positions [one half H atom bonded to each of the C,N(10) and C,N(14) atoms] and included in the refinement with isotropic thermal parameters. Full-matrix least-squares refinement of all positional parameters, of the aniso-

Table 2. *Fractional atomic coordinates and thermal parameters with estimated standard deviations* (*all* $\times 10^4$)

The e.s.d. is in the units of the least significant digit for the corresponding parameter. The temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1046 (2)	7583 (5)	1422 (2)	91 (2)	384 (11)	68 (2)	−1 (4)	42 (1)	22 (4)
C(2)	−85 (3)	7401 (7)	840 (3)	99 (3)	424 (15)	81 (2)	43 (6)	44 (2)	38 (5)
C(3)	−745 (3)	5536 (7)	865 (3)	86 (3)	472 (17)	76 (2)	−1 (6)	36 (2)	−17 (5)
C(4)	−183 (3)	3751 (8)	1528 (3)	110 (4)	384 (15)	80 (2)	−51 (6)	47 (2)	−10 (5)
C(5)	973 (3)	3867 (6)	2125 (2)	95 (3)	378 (15)	56 (2)	5 (6)	33 (2)	22 (4)
C(6)	1551 (2)	5816 (6)	2051 (2)	83 (2)	370 (12)	46 (1)	−11 (5)	39 (2)	−11 (4)
S(7)	3057 (1)	6406 (2)	2797 (1)	85 (1)	747 (6)	51 (0)	−45 (2)	34 (0)	29 (1)
S(8)	3735 (1)	3383 (2)	3563 (1)	100 (1)	829 (6)	48 (0)	90 (2)	42 (0)	14 (1)
C(9)	3576 (2)	3648 (6)	4607 (2)	60 (2)	458 (13)	38 (1)	3 (5)	23 (1)	−3 (4)
C,N(10)	4044 (3)	1767 (6)	5225 (2)	86 (3)	499 (16)	56 (2)	54 (5)	35 (2)	33 (4)
C(11)	3964 (3)	1868 (7)	6043 (2)	91 (3)	509 (16)	54 (2)	22 (6)	30 (2)	56 (5)
C(12)	3400 (3)	3669 (7)	6212 (2)	111 (3)	544 (17)	49 (2)	−35 (6)	44 (2)	−11 (5)
C(13)	2933 (3)	5472 (7)	5553 (2)	113 (3)	387 (15)	66 (2)	0 (6)	58 (2)	−37 (5)
C,N(14)	3002 (2)	5512 (6)	4726 (2)	81 (2)	393 (13)	48 (1)	14 (5)	33 (2)	−13 (4)

tropic thermal parameters for nonhydrogen atoms, and of isotropic thermal parameters for H atoms, converged at $R_1 = 0{\cdot}048$ and $R_2 = 0{\cdot}049$ $\{R_2 = [\Sigma\, w(F_o - |F_c|)^2/\Sigma\, wF_o^2]^{1/2}\}$. The goodness-of-fit, $[\Sigma\, w(F_o - |F_c|)^2/(m-s)]^{1/2}$, is 2·79, where $m = 1578$ observations and $s = 163$ parameters. In the final cycle of least-squares refinement the largest parameter shift for a nonhydrogen atom was less than 30% of its corresponding e.s.d.; for H atoms this value was 50%. The rapid convergence observed indicated that these shifts would have decreased by nearly an order of magnitude in the next cycle. The largest peak on the final difference Fourier function, whose e.s.d. was calculated to be 0·04 e $Å^{-3}$, was less than 0·4 e $Å^{-3}$. Four low-angle reflections, $11\bar{3}$, $20\bar{4}$, $20\bar{2}$, and 300, were removed from the final cycles of least-squares refinement because they suffered from apparent extinction. The final parameters of the nonhydrogen atoms are given in Table 2, and those for H atoms are in Table 3.*

This model gives a C(9)—C,N(10) distance of 1·362 Å and an insignificantly different C(9)—C,N(14) distance of 1·358 Å. The C,N(10)—H′(10) and C,N(14)—H′(14) bond lengths refined to 0·77 (5) and 0·84 (6) Å respectively. The H′(10) and H′(14) thermal parameters were reasonable (see Table 3) and approximately equal. These three results support the validity of a model with 50% disorder in its higher-sequence-numbered pyridine ring.

Further refinements were attempted in a lower space group in the hope that an ordered structure might be found. The local order in the disordered model indicates that the inversion center should be removed, and eight violations of the c glide condition [$10\bar{1}$, $I = 33\sigma(I)$; $30\bar{3}$, $I = 13\sigma(I)$; $30\bar{1}$, $I = 12\sigma(I)$; and five others for which $3\sigma(I) < I < 6\sigma(I)$] argue for the deletion of that element. The space group $P2_1$ is indicated, and subsequent cycles of least-squares refinement in $P2_1$ led to convergence with $R_1 = R_2 = 0{\cdot}045$. The R significance test of Hamilton (1965), applied to the ratio (1·08) of the R_2 values of the structure models refined in $P2_1/c$ and $P2_1$, indicates that the former can be rejected at the 99·5% confidence level. However, the discrepancies between chemically equivalent features of the molecules are unreasonably large in $P2_1$. For example, the S—S distances are 1·97 and 2·06 Å, and the C—S distances range from 1·75 to 1·82 Å. This is due, at least in part, to the high correlation coefficients observed in least-squares refinement between pseudosymmetry-related parts of the structure. For this reason, the results of this work are presented in the higher space group. This situation has been encountered before (Donohue & Caron, 1964; Templeton & Templeton, 1971; Gilje & Seff, 1972), and was handled in a similar way.

Table 3. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters* ($Å^2$) *for* H *atoms*

The e.s.d. is in the units of the least significant digit given for the corresponding parameter. The serial number of the atom name is the same as that of the nonhydrogen atom to which it is bonded. H′ indicates half occupancy.

	x	y	z	B
H(2)	−50 (3)	868 (7)	34 (2)	7·6 (10) $Å^2$
H(3)	−160 (3)	551 (6)	45 (2)	7·5 (9)
H(4)	−53 (3)	244 (7)	157 (2)	6·5 (9)
H(5)	139 (2)	276 (6)	257 (2)	4·9 (8)
H′(10)	441 (4)	84 (10)	514 (4)	3·3 (12)
H(11)	425 (3)	55 (6)	643 (2)	5·4 (8)
H(12)	331 (3)	376 (6)	678 (2)	7·6 (9)
H(13)	259 (3)	675 (6)	566 (2)	6·8 (9)
H′(14)	261 (5)	653 (11)	430 (4)	4·4 (15)

Discussion

The molecular structure of di-2-pyridyl disulfide is presented in Figs. 1 and 2. It can be seen that the entire molecule lies in two approximate planes which could be brought into register by a rotation about the S—S bond.

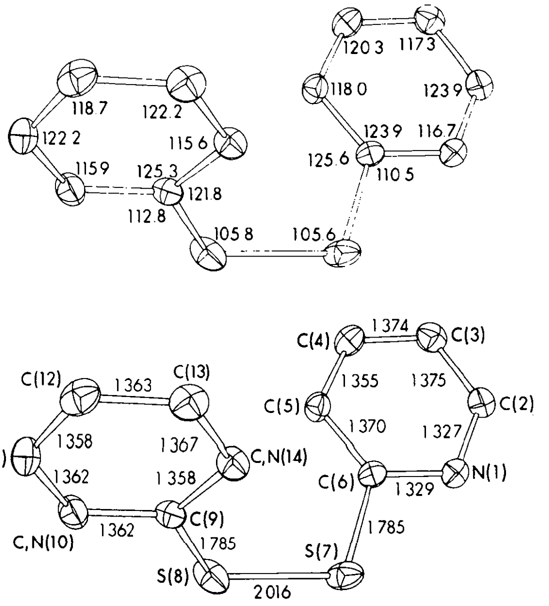

Fig. 1. The di-2-pyridyl disulfide molecule. Ellipsoids of 15% probability are used (Johnson, 1965). The e.s.d.'s are as follows: S—S, 0·002; S—C, 0·003; C—C and C—N, 0·004 to 0·006 Å; angles at S, 0·1; other angles, 0·2 to 0·4°. The C—H distances range from 0·77 to 1·00 Å, e.s.d. 0·03 to 0·05 Å. The CCH angles range from 114 to 125°, e.s.d. 2 to 4°.

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* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32042 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

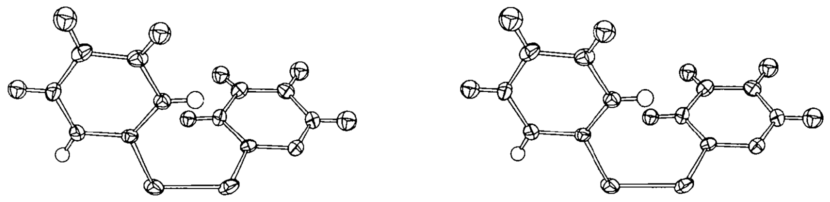

Fig. 2. Stereo view of di-2-pyridyl disulfide. Ellipsoids of 15% probability are used (Johnson, 1965). The disordered half H atoms are indicated by open circles.

Table 4. *Bond lengths* (Å) *and angles* (°) *in aromatic disulfides*

An 'aromatic disulfide' is one in which the S atoms of the disulfide groups are bonded to unsaturated C atoms. This tabulation supplements and updates a previous thirteen-entry compilation by Shefter (1970).

Compound	S—S	Av. C—S	Av. C—S—S	Av. C—S—S—C	Av. C—C—S—S	Reference
Di-2-pyridyl disulfide	2·016 (2)	1·785 (2)	105·7 (1)	87·1	7[a]	This work
Di-2-pyrimidyl disulfide dihydrate	2·016 (1)	1·781 (2)	104·7 (1)	82.5	4[a]	Furberg & Solbakk (1973)
Diphenyl disulfide	2·023 (1)	1·788 (3)	105·9 (1)	*ca* 90	*ca* 0	Sacerdoti, Gilli & Domiano (1975)
2,2′-Dicarboxydiphenyl disulfide[b] anion	2·047 (3)	1·790 (7)	106·3 (2)	86·7	15	Otterson, Warner & Seff (1974*b*)
2,2′-Diaminodiphenyl disulfide[c]	2·060 (3)	1·76 (1)	103·3 (3)	90·5	*ca* 90	Lee & Bryant (1970)

(*a*) One or both angles are N—C—S—S. (*b*) Alternatively named bis(2-carboxyphenyl) disulfide. (*c*) Alternatively named bis(2-aminophenyl) disulfide.

The torsion angle C(6)—S(7)—S(8)—C(9) is 87·1°, within the range of 90 ± 10° found in most organic disulfides. The geometry of the ordered pyridine ring is in close agreement with that observed in di-2-pyridylamine (Johnson & Jacobson, 1973), 2,2′-pyridil (Ashida, 1970), 2-(2′,4′-dinitrobenzyl)pyridine (Seff & Trueblood, 1968), and 4-(2′,4′-dinitrobenzyl)pyridine (Ottersen & Seff, 1974).

Shefter (1970) had previously noted that crystallographically observed C—C—S—S angles fall into two general classes, those where the S—S linkage is almost coplanar with the ring (*ca* 0°, equatorial) and those where it is approximately perpendicular to the ring (*ca* 90°, axial). All the compounds listed in Table 4, which updates Shefter's (1970) compilation, support that observation. In particular, the present compound belongs to the former class, as its torsion angles S(7)—S(8)—C(9)—C,N(14) and S(8)—S(7)—C(6)—C(5) are 5·1 and 10·2° respectively. This means that both S atoms lie approximately in the plane of each pyridine ring as can be seen in Table 5. The angle between the two ring planes is 80·3°.

Most S—S bond lengths in organic disulfides are within 0·02 Å of 2·03 Å in length (see Van Wart, Shipman & Scheraga, 1975). The 2·016 (2) Å distance in di-2-pyridyl disulfide is shorter than average but lies within the usual range.

Table 5. *Deviations from least-squares planes* (Å $\times 10^3$)

Bold-face deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 2 lies between that plane and the origin. The direction cosines ($\times 10^4$), q, are with respect to orthogonal axes. The r.m.s. deviation (Å $\times 10^3$) of the bold-face atoms from the plane is δ. D is the distance (Å) from the plane to the origin. The r.m.s. deviations of the H atoms from the planes is 0·041 Å.

Plane 1		Plane 2	
N(1)	**1**	C(9)	**9**
C(2)	**−7**	C,N(10)	**−16**
C(3)	**4**	C(11)	**13**
C(4)	**3**	C(12)	**−3**
C(5)	**−5**	C(13)	**−2**
C(6)	**3**	C,N(14)	**−2**
S(7)	70	S(8)	−11
S(8)	−215	S(7)	122
q_a	−5559		7193
q_b	4921		5064
q_c^*	6999		4756
D	3·25		4·88
δ	4		9

It is tempting to attribute the short S—S bond distances to the presence of a π interaction (ring π to S d, or S p to ring π^*) between the aromatic ring and the disulfide group. Maximization of π orbital overlap would also be the reason that the S—S bond lies nearly in the plane of each of its aromatic rings, as it does in most aromatic disulfides (C—C—S—S less than *ca* 20°). However, short distances are also found in organic disulfides where the S atoms are bonded to saturated C atoms, with which there can be no significant π interaction. Examples are dicinnamyl disulfide [2·020 (2) Å] (Donohue & Chesick, 1975) and dibenzyl disulfide [2·015 (3) Å] (van Dijk & Visser, 1971; Lee & Bryant, 1969). In addition, there is no apparent relationship between the geometry of the disulfide group and the electronegativity of an aromatic system even at approximately constant C—C—S—S angle. There is no indication of π delocalization between aromatic systems and disulfide groups.

There would seem to be considerable strain in the molecule caused by steric repulsion between S(7) and C,N(14), and between S(8) and C(5). This is shown by the large difference, averaging 12°, between the angles S(7)—C(6)—N(1) and S(7)—C(6)—C(5) and between S(8)—C(9)—C,N(10) and S(8)—C(9)—C,N(14). The distances S(7)· · · C,N(14) and S(8)· · · C(5) are 3·15 and 3·25 Å respectively, somewhat shorter than the sum of the van der Waals radii (approximately 3·4 Å); and the S(7)· · · H′(14) and S(8)· · · H(5) distances are 2·75 and 2·73 Å respectively, also somewhat short.

On the basis of semi-empirical molecular orbital CNDO/2 calculations on methyl *n*-propyl sulfide and methyl *n*-propyl disulfide, and compiled data on crystal structures of organosulfur compounds, Van Wart, Shipman & Scheraga (1975) suggest that there is an attractive nonbonded 1,4 C—S interaction. This is consistent with the short intramolecular approaches observed in many disulfides including di-2-pyridyl disulfide. The 1,4 interaction is suggested to be equal in strength to a weak hydrogen bond, but with less directionality. It would provide a reason for the S—S bond lying close to the plane of the aromatic ring to which it is bound, as is observed in most organic disulfides.

An alternative explanation, equally consistent with the CNDO/2 result, for the usually observed C—C—S—S near-coplanarity and the close 1,4 contacts (which may be viewed as dependent effects) involves a consideration of the lone pairs of electrons on S. According to Hordvik (1966), C—S—S—C torsion angles near 90° are commonly found because, in part, interatomic repulsive interactions between S lone pairs are minimized near that angle (near 60°, actually). The aromatic rings bonded to S may also orient so as to avoid unfavorable overlap with S lone pairs. Inspection of a model indicates that a coplanar arrangement of ring and S—S bond (C—C—S—S or N—C—S—S = 0° or 180°) minimizes these repulsions, and that a second shallower but sharper minimum should exist at a position related to the first by a torsional rotation of 90° about the C—S bond (C—C—S—S or N—C—S—S = 90 or −90°). This conclusion is supported by the distribution of crystallographically observed conformations (Shefter, 1970, and Table 4). A plot of these results (Van Wart, Shipman & Scheraga, 1975, Fig. 9*B*) indicates ten organic disulfide S—S—C—C torsion angles (absolute values) which are less than 25°, and six which

Table 6. *Intermolecular approach distances* (Å)

All intermolecular distances less than $(\Sigma r_{\text{v.d.W.}}) + 0{\cdot}1$ are presented. The van der Waals radii (Å) used are: H, 1·2; S, 1·7; aromatic ring half thickness for C and N, 1·7 Å. The coordinates of the atoms are given in Tables 2 and 3; those of the second atom of each contact are related to those in tables by the symmetry operation indicated. The very close contacts involving H′(10) are avoided by the disorder found in the space group $P2_1/c$.

H(2)—C(13)	2·99	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
H(3)—C(11)	2·95	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
H(3)—C,N(10)	2·96	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
H(4)—H′(14)	2·46	$-x, \frac{1}{2}+y, \frac{1}{2}-z$
H′(10)—C,N(10)	2·80	$1-x, -y, 1-z$
H′(10)—H′(10)	2·05	$1-x, -y, 1-z$
H(12)—S(8)	2·87	$x, \frac{1}{2}-y, \frac{1}{2}+z$
H(13)—N(1)	2·88	$x, \frac{3}{2}-y, \frac{1}{2}+z$

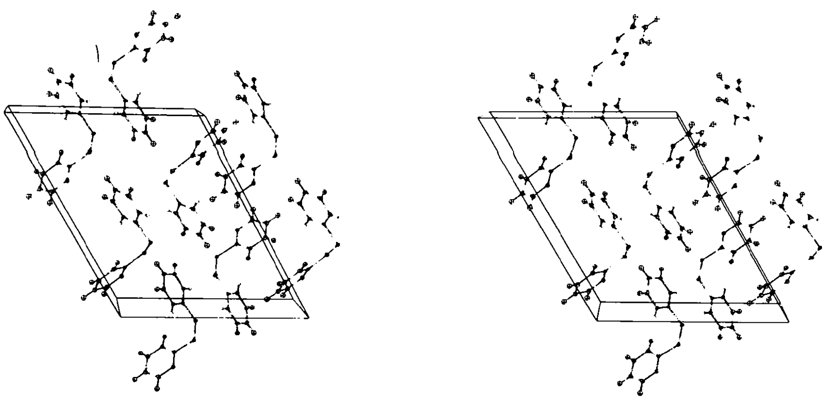

Fig. 3. A stereo view (Johnson, 1965) illustrating the packing of the molecules in the crystal. The *a* axis is horizontal and the *c* axis is vertical in the plane of the paper. Ellipsoids of 5% probability are used.

lie within 10° of 90°. No S—S—C—C torsion angle in that figure has a value between 25 and 90°. The 1,4 attraction discussed in the previous paragraph does not support this secondary clustering of S—S—C—C angles near 90°.

The disorder in the second pyridine ring has occurred to minimize the number of close H—H contacts. The contact between the 'half' H atoms, both H′(10), nearly at the very middle of the view given in Fig. 3, is unacceptably short, 2·05 Å (see Table 6). However, it can be avoided by requiring that no more than one H atom in total be present at these two positions, which are related by an inversion center. This can be accomplished if at least one of the two pyridine rings containing H′(10) is rotated 180° about its S(8)—C(9) bond, so that its N atom is at C,N(10), close to that inversion center. In fact, both pyridine rings could be so oriented, so that no disorder at all would exist. In that case, both H atoms, now at the 'half' H positions named H′(14), would be in close contact, 2·46 Å, with H(4) atoms of adjacent molecules (see Table 6 and Fig. 3). Apparently to avoid that contact, one ring, the maximum number in view of the constraint of the first H—H contact discussed, has rotated so that its H atom is at H′(10), in the cavity containing the inversion center mentioned above. By this reasoning, the two rotamers of the pyridine ring under discussion should be present in equal populations, consistent with the model used.

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