

The Crystal Structure of (*E*)-4-Nitrobenzenediazo-4'-methoxythiophenolate

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4-Nitrobenzenediazo-4'-methoxythiophenolate crystallizes with four molecules in a monoclinic cell with $a = 13.979$ (2), $b = 11.560$ (2), $c = 8.470$ (1) Å, $\beta = 90.03$ (1)°. The space group is $P2_1/c$, $Z = 4$. The structure was solved by direct methods and refined by the least-squares technique, with graphite-monochromatized Mo $K\alpha$ diffraction data. The final R and R_w values are 5.51 and 6.19%. The configuration with respect to the diazo bond is *E* (*trans*). The N=N and S-N bonds have lengths of 1.245 (6) and 1.728 (6) Å (corrected for vibrational effects). The S-C bond [1.762 (4) Å (c.f.v.e)] is rather small and indicates that resonance stabilization occurs within the phenolate moiety. A comparison with reported values indicates that this phenomenon may also occur in the second aromatic ring. The two aromatic rings are planar within 0.008 Å, their mutual angle being 123.1°.

Introduction

Alkyl aryl diazosulphides, Ar-N=N-S-R, occur as *E* and *Z* (*trans* and *cis* respectively) isomers (Hantzsch & Freese, 1895). Since one of the isomers is unstable the phenomenon of isomerism was doubted by several generations of chemists. However, during the last decade a number of groups (van Zwet & Kooyman, 1967; Yamada, 1970; van Beek, van Beek, Boven & Schoot, 1971; Brokken-Zijp & van den Bogaert, 1973) succeeded in preparing *E* and *Z* isomers of several diazosulphides. The crystal structure determination of both isomers of *t*-butyl 4-nitrobenzenediazosulphide by Brokken-Zijp, Braun & Hornstra (1976) clearly demonstrates that the isomerism involved is, indeed, *cis/trans*.

Thermal as well as photochemical decomposition takes place *via* radical intermediates (van Zwet, Reiding & Kooyman, 1970; Brokken-Zijp, 1974; Reiding, 1976). The appearance of chemically-induced dynamic nuclear polarization (CIDNP) effects (Brokken-Zijp & van den Bogaert, 1974) in the NMR spectra of heated solutions of (*Z*)-*t*-butyl benzenediazosulphide supports these indications. Diazosulphides are light-sensitive

(van Beek, 1973*a, b*), and are now used in photographic systems.

The present crystal structure determination of the title compound (hereafter ENM) offers an opportunity to compare its molecular geometry with that of the two isomers of *t*-butyl 4-nitrobenzenediazosulphide (Brokken-Zijp, 1974), the first compound containing two instead of one aromatic substituent. Introduction of the second aromatic substituent enhances the instability of the *Z* isomer: Yamada could isolate the *Z* isomers of this type of diazosulphide only at temperatures below -60°C. Moreover, a second aromatic group being present the CIDNP effect is no longer observed (Reiding, 1976). It might be expected that differences would also occur in the ground state when a second aromatic ring is present. These differences are reflected in the higher rates and higher order of the decomposition of compounds with two aromatic rings and might be correlated with resonance phenomena in the second aromatic ring. The numbering of atoms of ENM is indicated in Fig. 1.

Experimental

Monoclinic crystals of ENM were obtained, by recrystallization from pentane, in the form of orange-yellow needles. The lattice dimensions were determined at 20°C with a three-circle diffractometer using Mo $K\alpha$

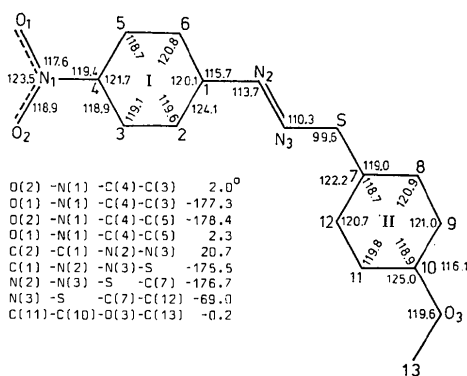


Fig. 1. The numbering of atoms, valency and torsion angles (°) of ENM. The estimated standard deviations are 0.3 and 0.4° respectively.

Table 1. Crystal data for 4-nitrobenzenediazo-4'-methoxythiophenolate

Molecular composition $C_{13}H_{11}N_3O_3S$, $M = 289.3$. Four molecules per unit cell, space group $P2_1/c$.

$a = 13.979$ (2) Å	$d_{obs} = 1.38$ g cm ⁻³
$b = 11.560$ (1)	$d_{calc} = 1.40$
$c = 8.470$ (1)	$F(000) = 600$
$\beta = 90.03$ (3)°	$\mu(Mo K\alpha) = 2.5$ cm ⁻¹

Observed significant reflexions: 1585
 Reflexions less than twice the background: 740
 Non-observed reflexions within $\theta = 25^\circ$: 7

radiation ($\lambda_{\alpha_1}=0.71092$ and $\lambda_{\alpha_2}=0.71354$ Å), see Table 1.

The reflexion intensities of a crystal with dimensions $0.5 \times 0.5 \times 1.0$ mm were collected at room temperature with a PDP 8 computer-controlled three-circle diffractometer (CAD 3) using graphite-monochromatized Mo $K\alpha$ radiation. The θ - 2θ scanning mode with scan width $(0.64 + 0.84 \tan \theta)^\circ$ was employed with glancing angles varying between $\theta_{\min}=4.5$ and $\theta_{\max}=25^\circ$. One of the three standard reflexions $0\bar{2}3$, $\bar{2}20$ and $\bar{2}0\bar{2}$ was measured after each series of 29 reflexions. These standards were used for the computation of a polynomial function of the exposure time in order to correct for loss in scattering power of the crystal during extended periods of exposure.

Structure determination

The structure was determined by direct methods employing the program described by Motherwell & Isaacs (1971). Using the information of *all* reciprocal-lattice points within the scanned sphere with radius $\sin \theta/\lambda = 0.61$ Å⁻¹ the preliminary scale and temperature factors were modified in such a way that the normalized structure factors E fulfilled as well as possible the statistical criteria for centrosymmetric structures.

It was inferred from two very strong \sum_1 relations with probabilities larger than 0.9999 that the reflexions 604 and 044 have zero phases if the origin is fixed on a centre of symmetry. The assignment of zero phases to three qualified reflexions fixed the origin at 0, 0, 0. Trial values $\varphi=0$ or π were given to the reflexions 71 $\bar{7}$, 365 and 063. The combination $\varphi(71\bar{7})=\varphi(365)=\varphi(063)=0$ resulted in $R(\text{Karle})=37.5\%$ (Karle & Karle, 1969). The remaining seven combinations refined to $\varphi(71\bar{7})=\pi$ and $\varphi(365)=\varphi(063)=0$ with $R(\text{Karle})=18.5\%$. The latter combination proved to be correct. It resulted in 173 correctly phased reflexions with E values larger

than 1.75 and it produced an E -Fourier map in which the 20 highest peaks correspond to the positions of the heavy atoms.

The scattering factors of the heavy atoms were taken from *International Tables for X-ray Crystallography* (1962), those of hydrogen from Stewart, Davidson & Simpson (1965). The hydrogen atoms were not refined, but introduced at calculated positions with B values equal to those of the parent carbon atoms. The heavy atoms were refined with full-matrix blocks. The function minimized during the refinement was $\sum w(|F_o| - |F_c|)^2$, with weight $w=1$ during the isotropic stages and $w=\sigma^{-2}(F)$ during the anisotropic stages. The conventional and weighted R indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

Table 2. Fractional coordinates of the heavy atoms

Estimated standard deviations in units of the last decimal place are given in parentheses.

	x	y	z
C(1)	0.2995 (2)	0.6928 (2)	0.0254 (3)
C(2)	0.2750 (2)	0.8072 (3)	0.0476 (4)
C(3)	0.3286 (2)	0.8921 (2)	-0.0212 (4)
C(4)	0.4057 (2)	0.8612 (3)	-0.1133 (3)
C(5)	0.4302 (2)	0.7480 (3)	-0.1363 (4)
C(6)	0.3775 (2)	0.6646 (3)	-0.0652 (4)
C(7)	0.0079 (2)	0.5633 (3)	0.2876 (4)
C(8)	-0.0708 (3)	0.5130 (3)	0.2172 (4)
C(9)	-0.1602 (3)	0.5500 (3)	0.2506 (4)
C(10)	-0.1755 (3)	0.6394 (3)	0.3550 (4)
C(11)	-0.0971 (3)	0.6920 (3)	0.4262 (4)
C(12)	-0.0065 (3)	0.6527 (3)	0.3937 (4)
C(13)	-0.2894 (3)	0.7591 (4)	0.4882 (5)
N(1)	0.4619 (2)	0.9519 (3)	-0.1884 (4)
N(2)	0.2519 (2)	0.5976 (2)	0.1000 (3)
N(3)	0.1707 (2)	0.6221 (2)	0.1469 (3)
O(1)	0.5276 (2)	0.9221 (3)	-0.2741 (4)
O(2)	0.4407 (2)	1.0524 (3)	-0.1642 (4)
O(3)	-0.2675 (2)	0.6686 (2)	0.3808 (3)
S	0.12188 (8)	0.50681 (8)	0.24810 (12)

Table 3. Observed and calculated thermal parameters U_{ij} ($\times 10^{-3}$ Å²) of the heavy atoms

Estimated standard deviations in units of the last decimal place are given in parentheses.

	U_{11}		U_{22}		U_{33}		$2U_{12}$		$2U_{23}$		$2U_{31}$	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
C(1)	71 (2)	69	58 (2)	61	52 (2)	53	-4 (3)	3	1 (3)	-7	-12 (3)	-13
C(2)	63 (2)	67	68 (2)	62	67 (2)	67	0 (3)	7	-5 (3)	-5	7 (3)	-1
C(3)	79 (2)	74	59 (2)	62	77 (2)	76	3 (3)	-2	-6 (3)	-3	-11 (4)	-2
C(4)	65 (2)	66	72 (2)	75	62 (2)	63	-20 (3)	-16	1 (3)	-4	-12 (3)	-14
C(5)	68 (2)	71	88 (2)	82	66 (2)	66	4 (4)	3	-18 (4)	-13	11 (3)	6
C(6)	84 (2)	79	62 (2)	68	67 (2)	65	15 (3)	14	-14 (3)	-15	-4 (4)	5
C(7)	96 (3)	98	64 (2)	59	63 (2)	62	-40 (4)	-41	25 (3)	28	12 (4)	7
C(8)	112 (3)	108	73 (2)	71	65 (2)	62	-48 (4)	-45	0 (3)	2	-2 (4)	-1
C(9)	97 (3)	101	85 (2)	85	70 (2)	71	-58 (4)	-54	-1 (4)	-9	-22 (4)	-13
C(10)	85 (3)	93	74 (2)	76	64 (2)	65	-51 (4)	-48	22 (3)	11	0 (4)	1
C(11)	105 (3)	97	65 (2)	70	71 (2)	70	-38 (4)	-47	-3 (3)	-3	13 (4)	2
C(12)	94 (3)	94	72 (2)	67	75 (2)	76	-54 (4)	-50	1 (4)	3	-15 (4)	-4
C(13)	126 (3)		115 (3)		117 (3)		-26 (6)		-35 (6)		52 (6)	
N(1)	83 (2)	83	95 (2)	94	84 (2)	84	-47 (4)	-49	8 (4)	10	-3 (3)	-5
N(2)	87 (2)	90	66 (2)	64	64 (2)	64	11 (3)	-6	-12 (2)	2	2 (3)	-1
N(3)	84 (2)		66 (2)		57 (2)		-14 (3)		1 (2)		-6 (3)	
O(1)	104 (2)		129 (2)		131 (3)		-56 (4)		11 (4)		74 (4)	
O(2)	129 (2)		80 (2)		139 (3)		-44 (4)		23 (3)		42 (4)	
O(3)	95 (2)	94	107 (2)	105	93 (2)	94	-42 (3)	-40	-19 (3)	-1	5 (3)	7
S	110 (1)	106	70 (1)	75	97 (1)	98	-16 (1)	-18	36 (1)	34	27 (1)	25

Finally the temperature factors are defined as $\exp[-2\pi^2 \sum_{i,j} h_i h_j a_i^* a_j^* U_{ij}]$, $i, j = 1, 2, 3$.

The final R and R_w values are 5.51 and 6.19%.[†] The positional and thermal parameters of the heavy atoms are given in Tables 2 and 3.

Thermal motion

It can be seen that the bond distances resulting from the least-squares refinement are approximately 0.015 Å smaller than one would anticipate. For this reason we analysed the thermal motion of different groups of atoms in terms of the rigid-body tensors of translation (T), libration (L), and screw motion (S) (Schomaker & Trueblood, 1968). The best results were obtained by assuming two rigid bodies, *i.e.* the moiety N(1), C(1) to C(6) and N(2) and the moiety S, C(7) to C(12) and O(3). The calculated U_{ij} values for these bodies are included in Table 3. The r.m.s. $\Delta(U_{ij})$ values are 0.0039 and 0.0040 Å² respectively. The rigid-body thermal parameters are collected in Table 4. With these values the bond lengths (Table 5) were corrected for thermal motion according to the method of Cruickshank (1956) using a peak-width parameter of 0.10 Å².

Molecular geometry

The bond lengths and their estimated standard deviations (e.s.d.'s) resulting from the refinement are listed

[†] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31733 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. Bond lengths (Å) in ENM resulting from the least-squares refinement and corresponding values corrected for thermal motion

The fourth column contains reported values. E.s.d.'s are given in parentheses.

C(1)—C(2)	1.380 (4)	1.393 (6)	1.395 (3) (a)
C(2)—C(3)	1.366 (4)	1.374 (6)	—
C(3)—C(4)	1.377 (4)	1.389 (6)	—
C(4)—C(5)	1.367 (4)	1.381 (6)	—
C(5)—C(6)	1.355 (4)	1.364 (6)	—
C(1)—C(6)	1.373 (4)	1.383 (6)	—
C(7)—C(8)	1.380 (5)	1.395 (7)	—
C(8)—C(9)	1.350 (5)	1.358 (7)	—
C(9)—C(10)	1.378 (5)	1.390 (7)	—
C(10)—C(11)	1.390 (5)	1.405 (7)	—
C(11)—C(12)	1.373 (5)	1.384 (7)	—
C(7)—C(12)	1.385 (5)	1.398 (7)	—
N(1)—C(4)	1.457 (5)	1.461 (7)	1.482 (3) (b)
N(1)—O(1)	1.221 (4)	1.226 (6)	1.225 (2) (c)
N(1)—O(2)	1.216 (4)	1.229 (6)	—
C(1)—N(2)	1.433 (4)	1.440 (6)	1.435 (3) (d)
N(2)—N(3)	1.236 (4)	1.245 (6)	1.248 (2) (d)
N(3)—S	1.726 (3)	1.729 (6)	—
C(7)—S	1.755 (3)	1.762 (6)	1.800 (8) (e)
C(10)—O(3)	1.347 (5)	1.351 (7)	1.384 (6) (f)
C(13)—O(3)	1.420 (5)	1.419 (7)	—

(a) *Molecular Structures and Dimensions* (1972). (b), (c) Average of six and 12 values of C—N and N—O bond lengths, respectively, occurring in the 3,5-dinitrobenzoate moieties of pyrocalciferol (de Kok & Romers, 1975), isopyrocalciferol (de Kok, Hoogendorp & Romers, 1975) and toxisterol C₁ (de Kok, Boomsma & Romers, 1976). (d) Average O—N and N=N bond lengths observed in (*E*)-azobenzene (Brown, 1966a), (*Z*)-azobenzene (Mostad & Rømming, 1971), (*E*)-*p,p'*-dimethylazobenzene (Brown, 1966b), (*E*)-*O,O'*-dichloroazobenzene (Komeyama, Yamamoto, Nishimura & Hasegawa, 1973), (*E*)-*O,O'*-azo-*p*-cymene (Wetherington, Holmes & Moncrief, 1974) and (*E*)-*p,p'*-dichloroazobenzene (Hope & Victor, 1969). (e) Diphenyl disulphide (Lee & Bryant, 1969). (f) Average of 20 phenolic O—C distances reported in (a).

Table 4. Rigid-body thermal parameters of ENM

Axes of reference are **a**, **b** and **c***. E.s.d.'s are given in parentheses.

	Rigid body of atoms N(1), N(2) and C(1) to C(6)				Rigid body of atoms S, O(3) and C(7) to C(12)			
	R.m.s. amplitude (Å)	Direction cosines			R.m.s. amplitude (Å)	Direction cosines		
Principal axes of reduced T [equations (20 a, b); Schomaker & Trueblood, 1968]								
$r_{T(i)(i)}$	0.26	-0.758	-0.385	0.526	0.32	0.881	-0.460	-0.113
$r_{T(i)(ii)}$	0.24	0.469	-0.883	0.029	0.25	-0.349	-0.470	-0.811
$r_{T(i)(iii)}$	0.22	0.454	-0.268	0.850	0.20	0.320	0.753	-0.575
Principal axes of L								
	R.m.s. amplitude (°)	Direction cosines			R.m.s. amplitude (°)	Direction cosines		
$L_{(i)(i)}$	7.0	0.573	0.614	-0.543	7.4	0.830	-0.467	-0.304
$L_{(ii)(ii)}$	3.8	0.339	0.427	0.839	4.0	0.389	0.877	-0.283
$L_{(iii)(iii)}$	3.2	0.747	-0.664	0.036	3.6	0.398	0.117	0.910
L tensor [$10^{-1}(\text{°})^2$]								
	235 (6)	143 (6)	-110 (6)		423 (11)	-155 (6)	-114 (6)	
	143 (6)	257 (11)	-116 (6)		-155 (6)	243 (6)	52 (6)	
	-110 (6)	-116 (6)	246 (6)		-114 (6)	52 (6)	161 (6)	
Effective screw pitch (Å radian ⁻¹)								
Parallel to $L_{(i)(i)}$		-0.091					-0.023	
Parallel to $L_{(ii)(ii)}$		0.440					-0.259	
Parallel to $L_{(iii)(iii)}$		-0.177					0.453	

in Table 5 together with the corresponding values corrected for thermal motion and the anticipated values derived from the literature. We assumed an e.s.d. of 0.005 Å for the thermal-correction terms and calculated estimates of the standard deviations of the expected average values. The valency angles and a number of dihedral angles characterizing the conformation of the molecule are indicated in Fig. 1. The e.s.d.'s of the latter entities are 0.3 and 0.4° respectively.

The bond distances collected in Table 5 give a number of indications that quinonoid resonance structures contribute to the molecular state. In order to verify this phenomenon we compare in Table 6 the relevant bond distances of ENM with the corresponding distances in α - and β -nitrophenol (Coppens & Schmidt, 1965*a, b*) and the *E* and *Z* isomers of *t*-butyl 4-nitrobenzenediazosulphide, thereby assuming C_s symmetry for the inspected molecular moieties and averaging over the symmetry-related distances.

In agreement with earlier work of Coppens & Schmidt (1965*b*) we may conclude that resonance plays a role in both modifications of *p*-nitrophenol and in the *p*-nitrophenyl ring in ENM. As already mentioned by Brokken-Zijp this effect is, however, doubtful or absent in the *p*-nitrophenyl ring in the *E* and *Z* isomers of *t*-butyl 4-nitrobenzenediazosulphide. On the other hand the effect is manifest in the thiophenolate ring in ENM and might be correlated with the finding of Yamada that the *Z* isomers of the di-aromatic diazosulphide compounds can only be isolated below -60°C .

The two benzene rings are planar within 0.008 Å and make an angle of 123.1° . Several minor distortions are present: (i) Neither the bonds N(1)–C(4) and C(1)–N(2) nor the bonds S–C(7) and C(10)–O(3) are collinear. The former pair makes an angle of 174.8° , the latter an angle of 172.4° . These deformations, often observed in aromatic rings, are caused by steric interactions of *ortho*-hydrogen atoms and have been discussed by Hirschfeld (1964). (ii) The bond N(1)–C(4) is slightly bent with respect to benzene ring I and the nitro group is twisted about N(1)–C(4) by the small amount of 2° (see torsion angles in Fig. 1).

The torsion angles about the bonds N(2)–N(3) and

N(3)–S (-175.5 and -176.6°) indicate that the bridge atoms C(1), N(2), N(3), S and C(7) form a nearly planar stretched chain. The benzene rings I and II make angles of 24 and 69° with this chain. Fig. 2 is a drawing of the overall shape of the molecule.

Packing

Fig. 3 is an illustration of the crystal structure viewed in projection along [001]. No short intermolecular

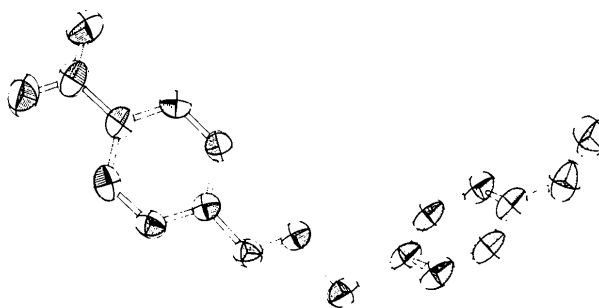


Fig. 2. An ORTEP (Johnson, 1965) projection of the molecule.

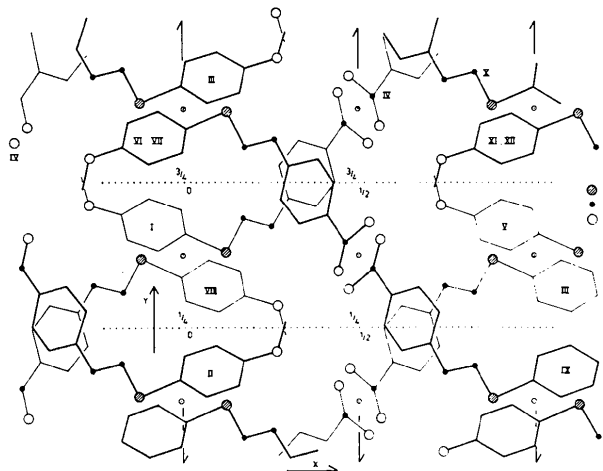
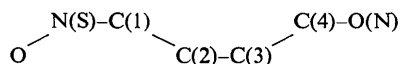


Fig. 3. Projection of the structure along [001]. The molecules with bold lines are closer to the reader.

Table 6. A number of bond lengths (Å) in ENM, α - and β -*p*-nitrophenol and the *E* and *Z* isomers of *t*-butyl 4-nitrobenzenediazosulphide

Comparison is made for the system:



	N–O	N(S)–C(1)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–O(N)
This work	1.227 (4)	1.461 (6)	1.385 (4)	1.369 (4)	1.388 (4)	1.440 (6)
α - <i>p</i> -Nitrophenol	1.234 (4)	1.442 (6)	1.386 (4)	1.379 (4)	1.390 (4)	1.351 (6)
β - <i>p</i> -Nitrophenol	1.242 (4)	1.450 (3)	1.394 (3)	1.380 (2)	1.397 (2)	1.361 (3)
<i>E</i> -Isomer	1.210 (2)	1.481 (3)	1.377 (2)	1.375 (2)	1.388 (2)	1.423 (3)
<i>Z</i> -Isomer	1.20 (1)	1.51 (2)	1.38 (1)	1.37 (1)	1.36 (1)	1.44 (2)
This work, phenolate ring	–	1.762 (6)	1.397 (5)	1.371 (5)	1.397 (5)	1.351 (7)
Expected values when resonance is absent	1.225 (2)	1.482 (3)	1.395 (3)	1.395 (3)	1.395 (3)	1.435 (3)
		1.800 (8)	1.395 (3)	1.395 (3)	1.395 (3)	1.384 (6)

Table 7. Intermolecular contacts (Å) of the type H...H (<3.0 Å), O...H, C...H and N...H (<3.15 Å)

Molecule	Operation	Type	Number	Average distance	Minimum distance
II, III	$-x, \mp\frac{1}{2}+y, \frac{1}{2}-z$	H...H	4	2.86	2.72
		O...H	4	2.83	2.64
		C...H	4	3.04	2.99
IV, V VI, VII	$\mp 1+x, \quad y, \pm 1+z$ $x, \quad \frac{1}{2}-y, \mp\frac{1}{2}+z$	O...H	2	3.13	3.13
		H...H	4	2.91	2.87
		O...H	2	2.73	2.73
		C...H	4	2.96	2.92
		N...H	4	2.98	2.94
VIII IX, X XI, XII	$-x, \quad 1-y, \quad -z$ $1-x, \quad \mp\frac{1}{2}+y, \quad -\frac{1}{2}-z$ $-x, \quad 1-y, \quad \mp\frac{1}{2}+z$	O...H	4	2.58	2.56
		H...H	2	2.89	2.89

distances are observed, the shortest contacts being two O...H interactions at distances of 2.56 and 2.59 Å. Surprisingly, molecule I at x, y, z is surrounded by only nine neighbours, the interactions of which are listed in Table 7.

The coordination number is 11 if we accept an interaction between O(1) of molecule I and H(133) of molecule V at $1+x, y, -1+z$, the distance between these atoms being 3.13 Å. This loose packing is reflected in the rather low density (1.38 g cm^{-3}) for an organic crystal containing relatively large fractions of oxygen, nitrogen and sulphur atoms. The outcome seems to contradict Kitaigorodsky's (1961, 1970) predictions that space group $P2_1/c$ allows a proper packing of molecules with a coordination number equal to or larger than twelve. The unusual shape of the molecule containing a bridge $-N=N-S-$ which connects two more bulky aromatic rings may be the reason for this exception.

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