

Tableau 4. Distances Na—S (Å) dans le polyèdre de coordination de l'atome de sodium Na<sup>iv</sup>

Na <sup>iv</sup> —S(I <sup>i</sup> )	2,88 (1)	Na <sup>iv</sup> —S(2 <sup>iv</sup> )	2,96 (1)
Na <sup>iv</sup> —S(I <sup>iii</sup> )	2,88 (1)	Na <sup>iv</sup> —S(2 <sup>iv</sup> )	3,06 (1)
Na <sup>iv</sup> —S(I <sup>iv</sup> )	2,84 (1)	Moyenne	3,01
Na <sup>iv</sup> —S(I <sup>iv</sup> )	2,81 (1)		
Moyenne	2,85		

Du fait de sa coordination avec des atomes de soufre, appartenant à trois chaînes (AsS<sub>2</sub>)<sub>n</sub><sup>iv</sup> distinctes, l'ion Na<sup>+</sup> assure la cohésion entre elles.

On remarque que dans le polyèdre de coordination du sodium les distances Na—S, faisant intervenir les atomes de soufre 'libres', sont plus courtes (2,85 Å en moyenne) que celles faisant intervenir des atomes de soufre impliqués dans des ponts As—S—As (3,01 Å).

Pour NaAsS<sub>2</sub> on peut penser que, comme dans le cas de Na<sub>3</sub>AsS<sub>3</sub> (Palazzi, 1976), la paire non liée E de l'arsenic(III), pour une pyramide AsS<sub>3</sub>, est située du côté de l'atome d'arsenic, sur la normale au plan SSS passant par As. En effet, dans cette direction, la structure présente des 'vides' et il est possible d'imaginer qu'ils soient occupés par la paire E. Si l'on admet la distance As—E = 1,25 Å trouvée pour Na<sub>3</sub>AsS<sub>3</sub>, et donnée également par Galy, Meunier, Andersson & Åström

(1975), on trouve que, pour cette distance, les atomes de soufre qui entourent le doublet (ceux de AsS<sub>3</sub> compris) sont situés à environ 3,1 Å de celui-ci. Dans ces conditions l'ion sodium le plus proche est à 3,2 Å. Il paraît donc vraisemblable que dans le cas de Na<sub>3</sub>AsS<sub>3</sub> et NaAsS<sub>2</sub> le doublet soit situé à la même distance de l'atome d'arsenic bien que pour ce dernier, en raison de la disposition relative des pyramides AsS<sub>3</sub> dans les chaînes (AsS<sub>2</sub>)<sub>n</sub><sup>iv</sup> les doublets soient associés deux par deux.

#### Références

- ANGÉLI, J. & SOUCHAY, P. (1950). *C. R. Acad. Sci. Paris*, **250**, 713–715.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- CHAUS, I. S., DEMCHENKO, L. E. & SUKHENKO, V. D. (1974). *Ukr. Khim. Zh.* (Russian ed.), **40**, 473–476.
- GALY, J., MEUNIER, G., ANDERSSON, S. & ÅSTRÖM, A. (1975). *J. Solid State Chem.* **13**, 142–159.
- PALAZZI, M. (1972). *Bull. Soc. Chim. Fr.* pp. 528–531.
- PALAZZI, M. (1976). *Acta Cryst.* **B32**, 3175–3177.
- PALAZZI, M. & GUÉRIN, H. (1969). *Bull. Soc. Chim. Fr.* pp. 3815–3817.
- RIBES, M., OLIVIER-FOURCADE, J., PHILIPPOT, E. & MAURIN, M. (1974). *Acta Cryst.* **B30**, 1391–1395.

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### A Disorder Problem: 3,5-Diamino-4-hydroxyimino-4H-1,2,6-thiadiazine 1,1-Dioxide

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**Abstract.** C<sub>3</sub>H<sub>5</sub>N<sub>5</sub>O<sub>3</sub>S, *M<sub>r</sub>* = 191.1, orthorhombic, *Pbcn*, *a* = 9.3186 (6), *b* = 8.5485 (4), *c* = 8.5097 (4) Å, *Z* = 4, *V* = 677.9 Å<sup>3</sup>, *D<sub>m</sub>* = 1.71, *D<sub>c</sub>* = 1.87 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 4.46 cm<sup>-1</sup>. The two O atoms attached to the S atom are doubly and singly bonded. The molecule has an oxime group with intramolecular hydrogen bonds. The crystal structure consists of parallel chains of molecules linked together through NOH...O=S hydrogen bonds. There are some hydrogen bonds between chains and a supercell consisting of three consecutive cells along *b* is also present. There is molecular disorder along *b*.

**Introduction.** The structure of the title compound was undertaken as part of an investigation of a series of new heterocyclic systems with the N—SO<sub>2</sub>—N group.

There were some doubts about the presence of the oxime and nitroso groups and these could not be clarified by other techniques. This work was carried out in order to establish the correct structure.

The compound crystallizes in yellow prisms elongated along *c*. Preliminary survey photographs, taken by both the Weissenberg and precession methods, revealed an orthorhombic unit cell of dimensions *a* = 9.32, *b* = 25.65 and *c* = 8.51 Å with the following systematic absences: *Ok*l for *k* = 2*n* + 1 and *h*0l for *l* = 2*n* + 1, indicating *Pbc*2<sub>1</sub> or the corresponding centrosymmetric *Pbcm*. Nevertheless the diffraction pattern presents very special features; first the diffracted intensity concentrates (80% of the total intensity) on reflexions with *k* = 3*n* which indicates a strong pseudotranslation of 8.55 Å along *b*. This new subcell

presents another interesting feature: the  $hk0$  reflexions with  $h+k = 2n+1$  are very weak (20% of the averaged intensity), which indicates pseudosymmetry corresponding to the  $Pbcn$  space group for the smaller cell. In the supercell all the systematically weak reflexions are diffuse, probably because of some molecular disorder.

All the quantitative results of this work refer to the small pseudocell with  $Pbcn$  symmetry defined in the *Abstract*.

A crystal with dimensions  $0.28 \times 0.26 \times 0.40$  mm was selected for the data collection on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. There are 3156 independent reflexions up to  $\theta = 30^\circ$  in the large cell ( $b = 25.65$  Å), of which 984 belong to the small  $Pbcn$  cell. Of these reflexions, 1849 and 822 respectively were selected as observed, having  $I \geq \sigma(I)$ . Intensity data for the subcell were collected in the  $\omega/2\theta$  scan mode, while for the larger supercell the  $\omega$  scan was used. Lorentz and polarization corrections were applied but no absorption correction was made.

With the 822 observed reflexions of the small cell defined in the *Abstract*, the crystal structure has been solved by the heavy-atom method. Fig. 1 shows the molecule. A twofold axis passing through S(1) and C(4) implies populations of 50% for O(1a), O(1b), N(5) and O(6). Clearly this model is not the real molecule but a molecular overlap along  $b$  generating the twofold symmetry of  $Pbcn$ . After anisotropic least-squares refinement of all non-H atoms, a difference map revealed the two H atoms of the amino group as the highest peaks.

The final refinement included isotropic temperature factors for the H atoms and converged to values of 0.052 and 0.051 for the unweighted and weighted  $R$  values. The weighting scheme used for the refinement was:  $w = w_1 w_2$  where  $w_1 = K/\sigma_1^2$ ,  $w_2 = 1/\sigma_2$  and  $K = 0.05$ , with  $\sigma_1 = a + b|F_o|$  and  $\sigma_2 = c + d(\sin \theta/\lambda)$  (the coefficients are in Table 1). A final difference map displayed no significant peaks. The positional and thermal parameters are given in Table 2.\*

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32293 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

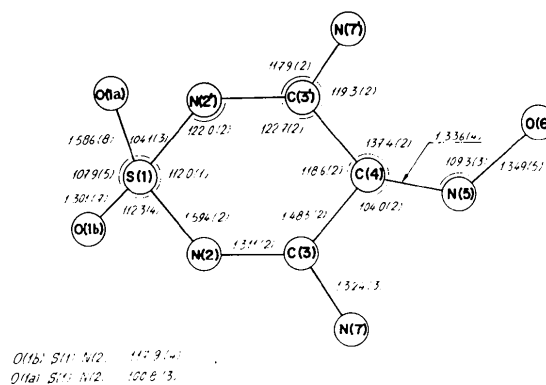


Fig. 1. Bond distances (Å) and angles ( $^\circ$ ) in the molecule.

Table 1. Coefficients for the weighting scheme

	$a$	$b$	$c$	$d$
$F_o < 2.31$	0.70	0.06		
$2.31 \leq F_o < 4.77$	1.42	-0.22		
$4.77 \leq F_o < 8.96$	0.51	-0.02		
$8.96 \leq F_o < 14.18$	0.26	0.01		
$14.18 \leq F_o$	-0.02	0.02		
			$(\sin \theta/\lambda) < 0.45$	2.92 -5.11
			$0.45 \leq (\sin \theta/\lambda) < 0.56$	1.26 -1.12
			$0.56 \leq (\sin \theta/\lambda) < 0.62$	-5.83 11.39
			$0.62 \leq (\sin \theta/\lambda) < 0.65$	3.81 -4.13
			$0.65 \leq (\sin \theta/\lambda)$	-4.34 8.07

Table 2. Final positional and thermal parameters ( $U \times 10^3$  and  $U_{ij} \times 10^4$ ) and their standard deviations

Anisotropic temperature factors are expressed as  $(-2\pi^2 \sum U_{ij} a_i^* a_j^* h_i h_j)$ .

	$x$	$y$	$z$	$U$ or $U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S(1)	0	0.2001 (1)	0.25	632 (6)	116 (3)	466 (4)	0	-250 (4)	0
O(1a)	0.1080 (10)	0.1287 (11)	0.1251 (8)	586 (35)	444 (31)	477 (24)	-213 (29)	52 (24)	99 (23)
O(1b)	-0.0544 (9)	0.0850 (6)	0.3302 (9)	399 (32)	175 (18)	353 (28)	-21 (17)	46 (21)	29 (15)
N(2)	0.1065 (2)	0.3044 (2)	0.3525 (2)	383 (9)	205 (7)	453 (10)	-12 (7)	-32 (7)	-36 (7)
C(3)	0.1035 (2)	0.4577 (2)	0.3480 (2)	323 (9)	211 (7)	374 (10)	-52 (7)	95 (9)	-63 (7)
C(4)	0	0.5462 (3)	0.25	416 (15)	144 (9)	453 (16)	0	152 (14)	0
N(5)	0.0286 (4)	0.6958 (4)	0.2827 (4)	378 (25)	185 (14)	509 (27)	34 (14)	-141 (15)	-9 (13)
O(6)	-0.0634 (4)	0.7884 (4)	0.2032 (6)	602 (21)	107 (11)	1088 (35)	43 (13)	-442 (23)	2 (15)
N(7)	0.1944 (2)	0.5350 (2)	0.4391 (3)	437 (10)	270 (8)	555 (11)	-105 (8)	34 (9)	-69 (8)
H(7a)	0.261 (3)	0.472 (4)	0.498 (4)	22 (8)					
H(7b)	0.206 (4)	0.632 (4)	0.425 (4)	27 (8)					

Fig. 1 shows the bond distances and angles for the non-H atoms. N—H bond distances are 0.96 (3) and 0.85 (4) Å for H(7*a*) and H(7*b*) respectively; bond angles around N(7) have an average value of 119 (2)°. Table 3 shows the geometry around the main plane of the molecule.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

**Discussion.** As far as the study in *Pbcn* (small cell) is concerned, two main results are emphasized: (a) The SO<sub>2</sub> group is not symmetric, and while O(1*b*) is doubly bonded to S, the O(1*a*) atom is almost singly bonded. Moreover, averaged tetrahedral bond angles at S(1) involving O(1*b*) are greater (113°) than the averaged value for the rest (106°). This result supports the greater double-bond character of S(1)—O(1*b*). The SO<sub>2</sub> group is almost perpendicular (89.2°) to the thiadiazine ring. (b) An oxime group is present in the molecule, and not a nitroso group, which is also chemically possible. This result is based on the fact that there is a short interatomic distance between O(6) and O(1*b*) of 2.76 Å — a hydrogen bond, where O(6) has to be the proton donor because O(1*b*) is doubly bonded to S(1). This oxime group is almost coplanar with the thiadiazine ring, forming with it very different bond angles (137 vs 104°); we shall try to explain this fact later.

Some attempts have also been made to use quantitatively more diffraction information. First we tried to

refine the model in the subcell with *Pbc*<sub>2</sub><sub>1</sub> symmetry (without a binary axis along *b*). This resulted in the molecule changing in such a way that the interacting surroundings of the oxime group (symmetry-related by the binary axis in *Pbcn*) become sufficiently different to favour one of the positions of the oxime group as being more stable. However, either the electron density or the population parameters of both groups are similar. This last fact is in contradiction to the first and reinforces the idea that molecular superposition exists along *b*, generating the pseudobinary axis. In the light of these two facts we prefer *Pbcn* for describing the structure.

Further attempts were made to use the total diffraction information, *i.e.* the 1849 observed reflexions in the large cell, to locate three independent molecules within *Pbcn*. The results were not encouraging, in that no significant differences between molecules could be detected, and the disorder in the oxime and SO<sub>2</sub> groups was still present.

We concluded that the significant quantitative results are those obtained from the small cell defined in the *Abstract*.

Nevertheless, from the above-stated discussion we suggest a diffracting model for the observed pattern consisting of parallel chains of molecules along *b*. Molecules in one chain link together by hydrogen bonds O(6)H...O(1*b*). Every three molecules there is a crystallographic translation of 25.65 Å; however, these three molecules are very similar (concentrating diffracted intensity on reflexions with *k* = 3*n*). The X-ray model fitting the latter reflexions would indicate that the three similar molecules along the 25.65 Å *b* axis have parallel thiadiazine rings, with the groups SO<sub>2</sub> and N—O differently oriented with respect to their rings, giving rise to the positional disorder detected in the overlapped molecule.

Table 3. *Main plane of the molecule*

Plane through atoms	Distance (Å)	Other atoms	Distance (Å)
S(1)	-0.002	O(1 <i>a</i> )	-1.472
N(2)	0.005	O(1 <i>b</i> )	0.862
C(3)	-0.005	N(7)	0.023
C(4)	0.002	H(7 <i>a</i> )	0.000
		H(7 <i>b</i> )	-0.138
		N(5)	0.039
		O(6)	0.095

Table 4. *The network of hydrogen interactions*

<i>X</i>	<i>Y</i>	H	<i>X</i> ... <i>Y</i> (Å)	H... <i>Y</i> (Å)	<i>X</i> -H... <i>Y</i> (°)
N(7)	N(5)	H(7 <i>b</i> )	2.459 (4)	2.12 (3)	103 (3)
N(7 <sup>i</sup> )	O(6)	H(7 <i>b</i> ) <sup>i</sup>	2.765 (4)	2.18 (4)	126 (3)
O(6)	O(1 <i>b</i> ) <sup>ii</sup>	—	2.758 (7)	—	—
O(6)	O(1 <i>b</i> ) <sup>iii</sup>	—	2.778 (7)	—	—
N(7)	O(1 <i>a</i> ) <sup>iv</sup>	H(7 <i>a</i> )	2.803 (9)	1.85 (3)	174 (3)
O(1 <i>a</i> )	O(6) <sup>v</sup>	—	2.912 (9)	—	—

Symmetry code

(i)	- <i>x</i> ,	<i>y</i> ,	$\frac{1}{2} - z$	(iv)	$\frac{1}{2} + x$ ,	$\frac{1}{2} - y$ ,	$1 - z$
(ii)	<i>x</i> ,	$1 + y$ ,	<i>z</i>	(v)	<i>x</i> ,	$1 - y$ ,	$\frac{1}{2} + z$
(iii)	- <i>x</i> ,	$1 + y$ ,	$\frac{1}{2} - z$				

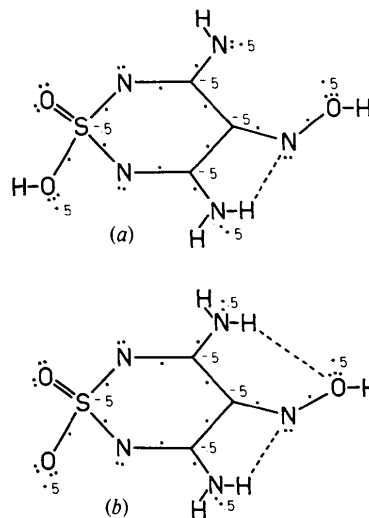


Fig. 2. The two proposed electron-distribution molecular models.

Parallel chains also link through different hydrogen bonds. All the possible hydrogen bonds are in Table 4.

A last paragraph must be added about the geometry of the oxime group obtained from the results in the small *Pbcn* cell (which entails a binary axis along the molecule). The two C—C—NO bond angles are different, and there are two short intramolecular distances  $N(7) \cdots N(5) = 2.459(4) \text{ \AA}$  and  $N(7') \cdots O(6) = 2.765(4) \text{ \AA}$ . These results were interpreted in two ways yielding the following models:

(1) Atoms N(7) and N(7') in the real molecule are chemically different: one is  $\text{NH}_2$  and the other NH. The first forms a very strong hydrogen bond to N(5), the second directs its lone electron pair towards N(5) [see Fig. 2(a)]. Both cause the difference in C—C—NO bond angles. In this model O(1a) would be protonated.

(2) atoms N(7) and N(7') are chemically identical ( $\text{NH}_2$ ) and there is a two fold symmetry within the thiadiazine ring. The oxime group would be completely twofold disordered around this binary axis, both positions being energetically fixed by the cooperation of the two intramolecular hydrogen bonds  $N(7)\text{H} \cdots N(5)$  and  $N(7')\text{H} \cdots O(6)$  [see Fig. 2(b)]. This model would preclude protonation of O(1a).

Fig. 2 shows the probable electron-distribution molecular models for both molecules. Linnett's (1966) ideas about electron-repulsion theory have been followed.

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#### References

- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.  
 LINNETT, J. W. (1966). *The Electronic Structure of Molecules. A New Approach*. London: Methuen.  
 STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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### 9-Trimethylsilylphenanthrene\*

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**Abstract.**  $\text{C}_{17}\text{H}_{18}\text{Si}$ ,  $M_r = 250.42$ , orthorhombic, space group *Pbca*,  $a = 17.385(25)$ ,  $b = 12.728(9)$ ,  $c = 13.091(7) \text{ \AA}$  (from  $P\bar{1}$  Syntex diffractometer),  $Z = 8$ ,  $D_c = 1.15$ ,  $D_x = 1.14(2) \text{ g cm}^{-3}$  (by flotation), m.p. 61–63°C. The compound was recrystallized from *n*-hexane. The structure was solved primarily by the symbolic addition method. The final  $R$  value is 0.061. The effect of the trimethylsilyl group on the phenanthrene appears to be a partial reduction in  $\pi$ -electron delocalization.

**Introduction.** Preliminary crystal structure data of the compound have previously been reported (Lu, 1975). For further refinement, a single, transparent, roughly spherical crystal of diameter 0.3 mm was cut to re-col-

lect a total of 1251 ( $I > 3\sigma$ ,  $\sin \theta/\lambda < 0.56$ ) independent reflexions on a Syntex  $P\bar{1}$  auto-diffractometer with Cu  $K\alpha$  (Ni) radiation. Systematic absences ( $0kl$ ,  $k$  odd;  $h0l$ ,  $l$  odd;  $hk0$ ,  $h$  odd) uniquely determine the space group *Pbca* ( $D_{2h}^{15}$ ). The linear absorption coefficient for Cu  $K\alpha$  radiation is  $12.98 \text{ cm}^{-1}$ . Azimuthal rotations (North, Phillips & Mathews, 1968) about the three strong reflexions 333, 060 and 440 fluctuate within 5%. Intensities of three reflexions were remeasured periodically as a check on crystal and instrument stability. No time-decay correction was made since only random fluctuations (within 2.7%) in these check reflexions were observed. The Si atom, located by the conventional heavy-atom method, was found to be on a glide plane perpendicular to the  $a$  axis. Half the calculated structure factors have zero contribution from Si. An attempt to locate the C positions from a difference Fourier map (DFM) was unsuccessful. The non-

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