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# Phenanthro[9,10-*c*]-1,2,5-thiadiazole 1-Oxide Hydrate

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**Abstract.** $C_{14}N_2OSH_8.H_2O$, M.W. 270·31, orthorhombic, *Pnma* (systematic absences $0kl$, $k+l=2n$, $hk0$, $h=2n$; $h00$, $h=2n$; $0k0$, $k=2n$; $00l$, $l=2n$), $a=4·817$ (1), $b=13·882$ (2), $c=18·796$ (4) Å, $Z=4$, $D_c=1·425$, $D_m=1·421$ g cm$^{-3}$ (flotation in $CCl_4/C_6H_6$), $\mu=23·2$ cm$^{-1}$ [$\lambda$(Cu $K\alpha$)$=1·54178$ Å]. The structure was refined to a final $R$ of 0·059 for 894 reflexions. The molecule is approximately planar except for the sulfur and oxygen atoms of the S–oxide bond. The N–S–N bond angle is 97·2°. The water molecule is triply disordered.

**Introduction.** Of the four possible classes of thiadiazole derivatives (i) 1,2,3-thiadiazoles, (ii) 1,2,4-thiadiazoles, (iii) 1,3,4-thiadiazoles, and (iv) 1,2,5-thiadiazoles, the first three have been known for many years. But it was not until 1957 that a mononuclear derivative of 1,2,5-thiadiazole was reported. The N–S–N bond system in 1,2,5-thiadiazoles is very unusual. Electron diffraction (Momany & Bonham, 1961, 1964) and microwave spectroscopic studies (Dobyns & Pierce, 1963) on the parent compound have given bond lengths and bond angles, and shown the coplanarity of all of the atoms. The highly crystalline phenanthro[9,10-*c*]-1,2,5-thiadiazole 1-oxide has been recently prepared (Pilgrim, 1970). Since no structural parameters are available for an oxide derivative of this type of heterocycle, it was decided to determine its crystal and molecular structure.

The compound was synthesized and given to us by Dr Kurt Pilgrim of Shell Development Laboratory. Yellow, needle-shaped crystals were grown from ethanol/water by slow evaporation.

The cell parameters were determined by least-squares fit to the settings for the four angles of eight reflections on a Picker FACS-I diffractometer. A crystal measuring 0·4 × 0·3 × 0·2 mm cross-section, mounted along the *a* axis was used for recording crystal data and intensities.

Data were collected on a Picker FACS-I system with monochromatic radiation and the $\theta$–$2\theta$ scan technique. When the count rate exceeded 10000 counts s$^{-1}$, attenuators were inserted. The diffracted intensities were measured with a scintillation counter equipped with a pulse-height analyzer. The scan rate was 2·0° min$^{-1}$ with 10 s backgrounds measured at the two extremes of each scan. The scan range had a base width of 2·2°, with a dispersion factor allowing for $\alpha_1$–$\alpha_2$ splitting being applied to large $2\theta$ values. One independent set of data was measured, which consisted of 1252 reflections of which 894 were considered to be observed by the criterion $I > 3\sigma(I)$. Three standard reflections were monitored every 50 measurements to check the crystal alignment and stability; no decrease in the intensities

Table 1. *Final positional and thermal parameters of phenanthro*[9, 10-*c*]-1,2,5-*thiadiazole* 1-*oxide with estimated standard deviations in parentheses*

The temperature factor (× 10⁴) for the nonhydrogen atoms is of the form $\exp[-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+\beta_{23}kl)]$. The hydrogen atoms were given the isotropic thermal parameters of the atoms to which they were attached.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| S | 1·0919 (4) | 0·2500 (0) | −0·0670 (1) | 322 (8) | 74 (1) | 25 (1) | 0 (0) | 2 (1) | 0 (0) |
| N | 0·9830 (9) | 0·1586 (3) | −0·0144 (2) | 367 (19) | 69 (3) | 34 (2) | 13 (6) | 2 (4) | 1 (1) |
| O(1) | 1·3980 (10) | 0·2500 (0) | −0·0725 (2) | 315 (24) | 100 (4) | 39 (2) | 0 (0) | 13 (6) | 0 (0) |
| C(1) | 0·8193 (9) | 0·1967 (4) | 0·0325 (2) | 319 (24) | 67 (3) | 25 (1) | 2 (7) | −16 (5) | −1 (1) |
| C(2) | 0·6392 (10) | 0·1443 (4) | 0·0807 (3) | 363 (24) | 66 (3) | 25 (2) | 0 (8) | −12 (5) | −1 (1) |
| C(3) | 0·6343 (13) | 0·0444 (5) | 0·0803 (3) | 489 (31) | 76 (4) | 31 (2) | 8 (10) | −5 (6) | 2 (2) |
| C(4) | 0·4622 (14) | −0·0070 (5) | 0·1251 (3) | 555 (35) | 78 (4) | 40 (2) | −25 (11) | −1 (7) | 8 (3) |
| C(5) | 0·2946 (14) | 0·0432 (5) | 0·1716 (3) | 580 (37) | 91 (5) | 37 (2) | −46 (11) | −6 (7) | 15 (3) |
| C(6) | 0·2975 (12) | 0·1427 (5) | 0·1730 (3) | 453 (30) | 100 (5) | 29 (2) | −1 (10) | 12 (6) | 4 (2) |
| C(7) | 0·4704 (10) | 0·1966 (4) | 0·1273 (2) | 353 (24) | 78 (3) | 24 (1) | −7 (8) | −19 (5) | 2 (2) |
| O(2)* | 0·7109 (62) | 0·2500 (0) | −0·2500 (11) | 4873 (616) | 49 (9) | 11 (3) | 0 (0) | −1 (35) | 0 (0) |
| O(3)† | 0·6964 (42) | 0·1755 (8) | −0·2530 (7) | 1675 (136) | 46 (6) | 30 (4) | −7 (30) | 25 (20) | 6 (5) |

| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H(C3) | 0·788 (12) | 0·010 (4) | 0·052 (3) | H(C5) | 0·177 (14) | 0·003 (5) | 0·204 (3) |
| H(C4) | 0·453 (13) | −0·084 (4) | 0·119 (3) | H(C6) | 0·184 (13) | 0·170 (4) | 0·201 (3) |

* Occupancy factors of 0·33.

† Occupancy factor of 0·167.

of the standards was observed. Lorentz and polarization corrections were applied to the data, but no correction was made for absorption. The omission of absorption corrections will affect the final thermal parameters, but not the positional coordinates (Srivastava & Lingafelter, 1966).

The crystal structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The *E* map revealed all nonhydrogen atoms except the disordered water oxygen. Full-matrix least-squares refinement in which positional and isotropic thermal parameters were varied reduced *R* to 0·192. At this stage a difference map was calculated and an unexpected feature of the structure was that there was triply disordered water oxygen. By giving on occupancy factor of 0·33 to each disordered water oxygen, one more cycle of least-squares with anisotropic temperature factors reduced *R* to 0·088. A difference map at this stage revealed all the hydrogen atoms, except those of the disordered water molecule. One more cycle of least-squares refinement with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors (of the nonhydrogen atoms to which the hydrogen atoms are attached) for hydrogen atoms reduced *R* to 0·059. The refinement was terminated at this stage since the ratios of shifts in parameters to estimated standard deviations were all less than 0·3. The refinement was based on $F_o$, the quantity minimized being $\sum w(F_o - F_c)^2$. The weighting scheme used was based on counter statistics as defined by Corfield, Doedens & Ibers (1967); the value of *p* was 0·04. The scattering factors used were those of Hanson, Herman, Lea & Skillman (1964). The average standard deviation for an observation of unit weight is 2·5. The deviation from unity seems to be partly because of low-angle data being overweighted and partly because of disorder in the water molecules.*

**Results and discussion.** The final atomic coordinates are given in Table 1. The standard deviations for atomic positions were taken from the least-squares matrix. The bond lengths and angles and estimated standard deviations (in parentheses) in the molecule are given in Fig. 1. The average C–H distance is 0·98 Å and C–C–H angle, 120·2°. Fig. 2 shows the thermal ellipsoid plot of the molecule and Fig. 3, the crystal packing. The molecule has a mirror plane passing through it and S and O(1) lie on this plane. Only two other 1,2,5-thiadiazole derivatives (i) 1,2,5-thiadiazole-3,4-dicarboxamide (McDonald, 1962), (ii) acenaphtho[1,2-*c*]-1,2,5-thiadiazole (Schaefer & Arora, 1971) have been studied by X-rays. In both these structures the thiadiazole ring is planar and S–N (1·62 and 1·66 Å) and C–C (1·43 and 1·437 Å) bonds in the ring show a considerable amount of double-bond character. In the present structure the sulfur atom deviates 0·305 Å from the plane of other four atoms in the thiadiazole ring. The reason could be that in this structure the sulfur atom prefers $sp^3$

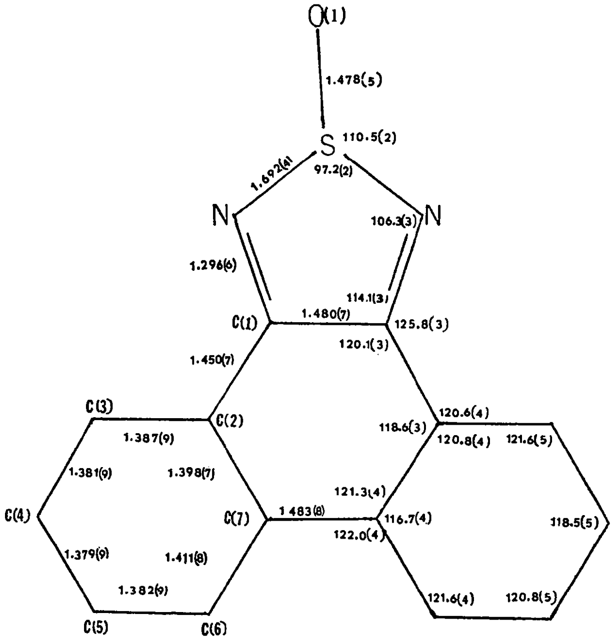

Fig. 1. Bond lengths (Å) and angles (°) in the molecule.

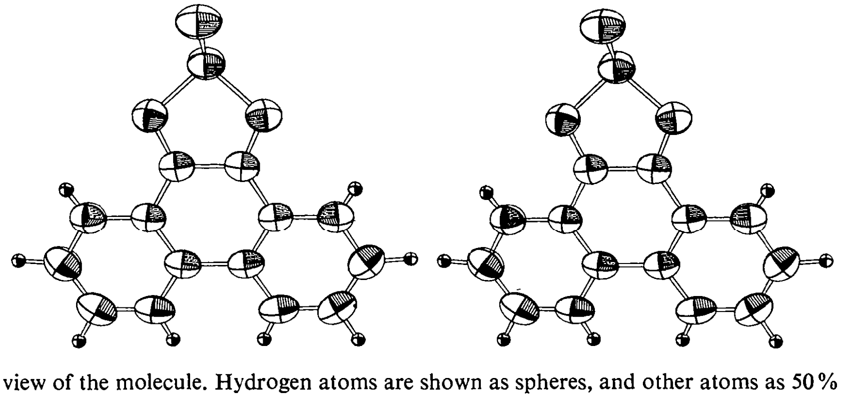

Fig. 2. Stereoscopic view of the molecule. Hydrogen atoms are shown as spheres, and other atoms as 50% propability ellipsoids.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30659 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

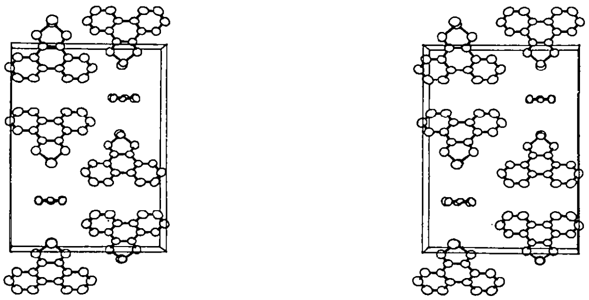

Fig. 3. Stereoscopic view of a unit cell, *a* axis projection, with *c* axis vertical and *b* axis horizontal.

hybridization to $sp^2$. The angle between the thiadiazole ring and the adjacent aromatic ring is 7·2°. Also the S–N (1·692 Å) and C–C (1·480 Å) bonds show more single-bond character than in the other two structures. The N–S–N bond angle has a value of 97·2° which is close to those of compounds (i) and (ii) (98·6° and 99·4°). The bond lengths and angles in the aromatic ring [C(2)–C(3)–C(4)–C(5)–C(6)–C(7)] are normal. There are four water molecules in the cell and each is triply disordered.

The S → O bond length of 1·478 ± 5 Å is normal for a sulfoxide. There is only one short intermolecular distance of significant value: N(*x,y,z*)–O(1) (1 + *x,y,z*), 2·65 Å.

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# 4-[2-(Methylthio)dibenzo[*b*,*f*]thiepin-11-yl]-1-piperazinylpropanol Hemihydrate (Oxyprothepine)

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**Abstract.** Monoclinic, $P2/c$, $a = 20{\cdot}648$ (5), $b = 5{\cdot}924$ (2), $c = 17{\cdot}627$ (5) Å, $\beta = 93{\cdot}67$ (1)°, 25°C, $C_{22}H_{28}N_2OS_2.\frac{1}{2}H_2O$, F.W. = 409·3, $Z = 4$.

**Introduction.** This compound is a potent neuroleptic usually known as oxyprothepine. Slow evaporation of a solution in ethanol yielded transparent crystals. Preliminary Weissenberg photographs showed systematic absences ($h0l$: $l = 2n + 1$) corresponding to space group $P2/c$ or $Pc$. The first was chosen on the basis of the intensity distribution.

The lattice parameters were obtained by the measurement of the Bragg angle of ten reflexions on a Nonius CAD-4 computer-controlled diffractometer. The experimental conditions used during the measurement of the intensities are given in Table 1.

Table 1. *Experimental conditions*

Source Cu $K\bar{\alpha}$; $\lambda = 1{\cdot}5418$ Å; $\omega$–$2\theta$ scan;
graphite monochromator; $\Delta 2\theta = 0{\cdot}7 + 0{\cdot}3 \operatorname{tg} \theta$;
$\theta_{\min} = 2°$; $\theta_{\max} = 70°$; aperture $= 3{\cdot}0 + 0{\cdot}5 \operatorname{tg} \theta$
Confidence level: 2·5
Total number of independent reflexions: 3585
Total observed: 2400

The structure was solved by direct methods with a modified version of *MULTAN* (Germain, Main & Woolfson, 1971) and refined by block-diagonal least-