$w = zc \sin \beta$. The deviations of all the ring atoms from this plane are given in Table 3.

The most striking feature of the structure is the short Pd–S bond of 2·23 Å. However, the Pd–O bond, although shorter than the 2·10 Å observed by Shkol'nikova *et al.* (1973), appears normal in comparison with the 2·02 Å reported by Ito, Marumo & Saito (1971) for a Pd–O bond *trans* to N. Compared with the structure of the present ligand with Ni (Coetzer & Boeyens, 1971), it is once again the short Pd–S bond that stands out. The 2·14 Å Ni–S bond is not far from corresponding lengths of bonds *trans* to either S or N, and hence the present effect finds no easy explanation in terms of backbonding and/or *trans* effects. The *cis* arrangement that occurs persistently in the chelates of monothiodiketones is probably related to this effect, and further studies are indicated.

The structural formula of the complex is best represented by
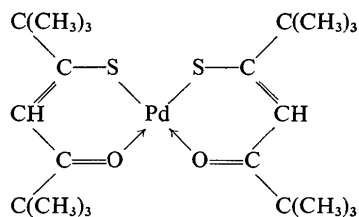
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2-Ethoxycarbonylimino-2*H*-1,2,4-thiadiazolo[2,3-*a*]pyridine Monohydrate

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Abstract. $C_9H_9N_3O_2S . H_2O$, a product of the oxidative cyclization of *N*-ethoxycarbonyl-*N'*-(2-pyridyl)thiourea by bromine in acetic acid [Koren, Stanovnik & Tišler, *Org. Prep. Proced. Int.* (1975), **7**, 55–59] is monoclinic, $P2_1/c$, $a = 6·310$ (4), $b = 37·269$ (22), $c = 4·568$ (4) Å, $\beta = 100·44$ (3)°, $V = 1056·5$ Å^3, $D_m = 1·52$ (5) g cm^{-3} (flotation), $Z = 4$, $D_x = 1·517$ g cm^{-3}, at 20 (1)°C. The molecule is almost planar, except for the ethoxy group which is bent out of the plane, and exhibits a very strong S···O interaction of 2·294 (5) Å, thus suggesting the presence of a single bond–no bond resonance structure.

Introduction. The compound crystallizes as transparent needles from toluene and dimethylformamide (3:1). The systematically absent reflexions ($0k0$; $k = 2n + 1$ and $h0l$; $l = 2n + 1$) on Weissenberg photographs and the centric distribution of $|E|$ values ($\langle E^2 \rangle = 1·000$; $\langle |E^2 - 1| \rangle = 1·020$; $\langle |E| \rangle = 0·776$) indicate space group $P2_1/c$. Unit-cell dimensions were obtained from a least-squares fit of the 2θ values of 15 reflexions measured on a CAD-4 diffractometer [Mo $K\alpha_1$ radiation, $\lambda = 0·70926$ Å, $t = 20$ (1)°C].

A single crystal with approximate dimensions $0·3 \times 0·1 \times 0·5$ mm was used for data collection on an automatic computer-controlled Enraf–Nonius CAD-4 four-

circle diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Reflexions were scanned in the ω–2θ mode (moving crystal–moving counter) at different rates to obtain a minimum net count of 5000 within a specified maximum scan time of 60 s. The background counts were taken at each of the scan limits for $\frac{1}{4}$ of the scan time. The 2θ scan width in degrees was $0·6 + 0·2 \tan \theta$ and the aperture was $2·4 + 0·9 \tan \theta$. The complete sphere of reflexions (7707 intensities in all) in the range $1·0 < \theta < 25·0°$ was measured. The symmetry-related reflexions were averaged (mean discrepancy on $I = 5·2\%$) to yield 1901 independent reflexions. Of these, 972 with $I > 3·0\sigma(I)$ were considered observed and were included in the refinement. The values of $\sigma(I)$ were based on counting statistics. Absorption corrections were not made [μ(Mo $K\alpha$) = 2·882 cm^{-1}]. The structure was solved by direct methods with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). An E map with the highest combined figure of merit CFOM (2·00) obtained with the unit weighting of ABSFOM (1·13), ψ_0 (2772) and RESID (31·13), computed with 300 phases ($|E| > 1·42$) gave initial coordinates for all the heavy atoms. The structure refinement was by full-matrix least squares, minimizing the function $\sum w(F_o - F_c)^2$, where the weighting function was determined empirically:

where

$$w = w_F w_S,$$

$$w_F(|F_o| < 10\cdot0) = (|F_o|/10\cdot0)^2$$
$$w_F(|F_o| > 50\cdot0) = (50\cdot0/|F_o|)^4$$
$$w_F(10\cdot0 < |F_o| < 50\cdot0) = 1\cdot0$$

and

$$w_S(\sin\theta < 0\cdot25) = (\sin\theta/0\cdot25)^2$$
$$w_S(\sin\theta > 0\cdot40) = (0\cdot40/\sin\theta)$$
$$w_S(0\cdot25 < \sin\theta < 0\cdot40) = 1\cdot0 .$$

Anisotropic temperature factors for the non-hydrogen atoms were adopted. Difference Fourier syntheses revealed all the H atoms at the expected positions. The H atom positions were refined, but their assumed isotropic thermal parameters were kept constant throughout. The final R value, $R = \sum|\Delta F|/\sum|F_o|$, and the weighted R value, $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$, were 0·056 and 0·067 respectively. The final difference electron-density map was featureless. Atomic scattering factors for H were those of Stewart, Davidson & Simpson (1965) and for other atoms those of Cromer & Mann (1968). The real and imaginary parts of the dispersion correction for S were those of Cromer (1965). All calculations were performed on the CDC CYBER 72 computer at RRC Ljubljana. The X-RAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used during the refinement and the final interpretation of the results.

Table 1 lists the final coordinates and thermal factors. Bond distances and angles are illustrated in Fig. 1. The numbering of atoms is different from the IUPAC convention.*

Discussion. Several crystal structures of heterocyclic compounds displaying S···O interactions have re-

cently been determined by X-ray diffraction [see Lynch, Mellor & Nyburg (1971) for a concise list]. Mellor & Nyburg (1971a, b), Amirthalingham & Muralidharan (1972) and Gilardi & Karle (1971) have also reported the structures of compounds with fairly strong S···O interactions. The intramolecular distance S···O in these compounds varies from 2·41 to 2·96 Å with only two exceptions; a value of 1·879 Å was found in the oxygen analogue of a thiathiaphthene (Gilardi & Karle, 1971) and a 2·034 Å distance was detected in
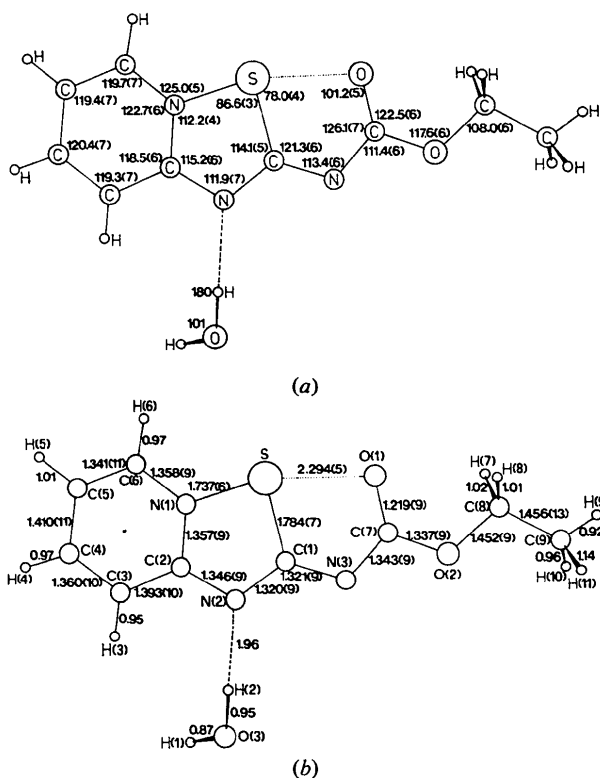

(a)

(b)

Fig. 1. (a) Bond lengths and (b) angles in the molecule with estimated standard deviations in parentheses.

Table 1. *Final fractional coordinates and thermal parameters with standard deviations in parentheses*

Coordinates are multiplied by 10^4 for non-hydrogen and by 10^3 for hydrogen atoms. The anisotropic and isotropic temperature factors are expressed in the form $\exp\{-2\pi^2[U(11)h^2a^{*2} + 2U(12)hka^*b^* + ...] \times 10^{-3}\}$ and $\exp[-8\pi^2 U(\sin\theta/\lambda)^2 \times 10^{-3}]$ respectively.

	x	y	z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
S	8142 (3)	1028 (1)	1094 (4)	46 (1)	43 (1)	40 (1)	10 (1)	5 (1)	−6 (1)
O(1)	6288 (7)	639 (1)	3596 (10)	55 (3)	50 (3)	51 (3)	13 (2)	14 (2)	−1 (2)
O(2)	3464 (8)	725 (1)	5864 (11)	57 (3)	44 (3)	52 (3)	6 (2)	16 (2)	3 (2)
O(3)	4138 (9)	2300 (1)	2866 (11)	91 (4)	54 (3)	39 (3)	15 (3)	19 (3)	1 (2)
N(1)	9050 (8)	1405 (1)	−554 (11)	40 (3)	51 (4)	26 (3)	7 (3)	1 (2)	−3 (2)
N(2)	6297 (8)	1653 (2)	1378 (11)	43 (3)	45 (3)	33 (3)	3 (2)	2 (2)	−4 (3)
N(3)	4756 (9)	1192 (2)	3768 (12)	46 (3)	51 (4)	41 (3)	7 (3)	5 (3)	1 (3)
C(1)	6179 (10)	1316 (2)	2224 (13)	44 (4)	42 (4)	25 (3)	5 (3)	−2 (3)	−5 (3)
C(2)	7889 (10)	1702 (2)	−184 (13)	37 (3)	52 (5)	28 (3)	4 (3)	2 (3)	−3 (3)
C(3)	8431 (11)	2024 (2)	−1411 (15)	47 (4)	46 (4)	46 (4)	3 (3)	1 (3)	−6 (3)
C(4)	10087 (11)	2030 (2)	−2946 (15)	46 (4)	54 (5)	51 (4)	−4 (3)	5 (3)	5 (3)
C(5)	11255 (11)	1715 (2)	−3726 (16)	41 (4)	71 (6)	46 (4)	−4 (4)	4 (3)	−5 (4)
C(6)	10705 (10)	1407 (2)	−2086 (14)	40 (4)	66 (5)	33 (4)	8 (3)	0 (3)	12 (4)
C(7)	4952 (11)	839 (2)	4338 (14)	45 (4)	44 (5)	37 (4)	3 (3)	2 (3)	0 (3)
C(8)	3520 (13)	349 (2)	6724 (15)	67 (5)	50 (5)	48 (4)	11 (4)	9 (4)	1 (3)
C(9)	1636 (14)	277 (2)	8061 (19)	70 (5)	61 (6)	72 (6)	0 (4)	19 (4)	18 (4)

Table 1 (*cont.*)

	x	y	z	U
H(1)	413 (20)	243 (4)	126 (27)	89
H(2)	485 (15)	209 (3)	237 (20)	89
H(3)	757 (15)	223 (3)	−132 (20)	63
H(4)	1055 (11)	224 (2)	−388 (15)	63
H(5)	1252 (14)	172 (2)	−434 (18)	63
H(6)	1156 (14)	119 (2)	−197 (18)	63
H(7)	369 (11)	22 (2)	484 (18)	76
H(8)	496 (18)	28 (2)	791 (20)	76
H(9)	165 (18)	5 (3)	895 (25)	101
H(10)	26 (21)	32 (3)	686 (28)	101
H(11)	149 (15)	46 (3)	1003 (22)	101

3,5-epidithio-2-nitroso-1,5-diphenylpenta-2,4-dien-1-one (Johnson & Paul, 1969). The common feature of all these heterocyclic systems is the nearly planar sulphur environment and consequently the presence of conjugation in the five-membered ring closed by the S···O interaction.

The crystal structure of the title compound (hereinafter CITP.H₂O) proved to be another example in the series of compounds with a very short S···O approach. The S···O(1) distance [2·294 (5) Å] and angles N(1)–S–C(1) [86·6 (3)°] and C(1)–S···O(1) [78·0 (4)°] suggest a very strong S···O interaction. However, the S···O distance is mainly influenced by the values of the angles S–C(1)–N(3) [121·3 (6)°], C(1)–N(3)–C(7) [113·4 (6)°] and N(3)–C(7)–O(1) [126·1 (7)°] as was shown by Kapecki, Baldwin & Paul (1968). Nearly the same geometry of a five-membered ring closed by an S···O interaction was found in 3,5-diacetamido-1,2-dithiolium bromide (Hordvik & Kjoge, 1966).

Table 2. *Least-squares planes*

(*a*) Deviations from the least-squares planes. Deviations (Å × 10³) printed in bold type indicate atoms which were not used to define the plane.

	Plane						
	I	II	III	IV	V	VI	VII
S	18	8	−3		0	−2	
O(1)	25	−5	−24			4	0
O(2)	12	−38	−61				0
N(1)	7	−11	7	2	1		
N(2)	21	8	3		2		
N(3)	32	0	−15			3	0
C(1)	25	6	−4		−1	0	
C(2)	4	4	2	0	−2		
C(3)	−13	−4	0	0			
C(4)	−34	−11	−5	−1			
C(5)	−28	−3	1	2			
C(6)	−15	0	−1	−3			
C(7)	24	−13	−32			−5	0
C(8)	44	−11	−39				
C(9)	−121	−191	−222				

(*b*) Equations of the least-squares planes. The equations are expressed in the form *lx+my+nz=p* where *x, y* and *z* are in Å.

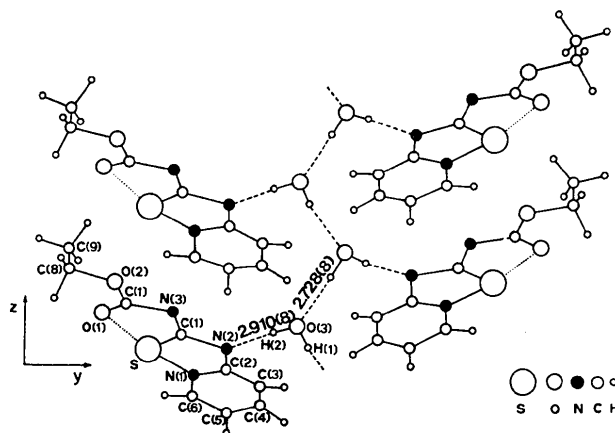| Plane	
I	$3·0342x + 7·4530y + 3·4372z = 3·5951$
II	$3·0817x + 7·5648y + 3·4086z = 3·6521$
III	$3·0911x + 7·6856y + 3·3999z = 3·6820$
IV	$3·0982x + 7·7407y + 3·3945z = 3·6999$
V	$3·0757x + 7·5991y + 3·4108z = 3·6594$
VI	$3·0519x + 7·4797y + 3·4270z = 3·6311$
VII	$2·9983x + 7·2355y + 3·4622z = 3·5933$

Fig. 2. A view down the *a* axis showing the packing of the molecules in the crystal. Hydrogen bonds are marked with broken lines.

Several least-squares planes (Table 2) were calculated through the three fused-ring systems of CITP.H₂O and through some atom groups to obtain detailed information of the molecular shape and conformational features. The whole molecule as well as the separate ring systems is almost planar except for the ethoxy group O(2)–C(8)–C(9) which is rotated about the bond O(2)–C(8). The torsional angles C(7)–O(2)–C(8)–C(9), O(1)–C(7)–O(2)–C(8) and N(3)–C(7)–O(2)–C(8) are 173·9, 2·0 and 178·1° respectively. The dihedral angles between planes IV and V, and V and VI are 0·4 and 0·3° respectively.

The general features of the hydrogen bonding are shown in Fig. 2 viewed along the [100] direction. The water molecules in each case donate one proton to N(2) of the CITP molecules and the other one to another water molecule thus making an infinite zigzag chain of water molecules in the c direction. There are no unusually close van der Waals contacts between the other parts of the molecules.

I am indebted to Professor B. Stanovnik and M. Tišler for suggesting this problem and supplying the crystalline sample, and Professor L. Golič for many helpful discussions.

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Monomethylurea: a Redetermination

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Abstract. C$_2$H$_6$N$_2$O, orthorhombic, space group $P2_12_12_1$, $a=8\cdot4767$ (6), $b=6\cdot9809$ (5), $c=6\cdot9227$ (6) Å at 20°C. $D_m=1\cdot204$ g cm^{-3} [Corey & Wyckoff, *Z. Kristallogr.* (1933), **85**, 132–142], $D_c=1\cdot2007$ g cm^{-3} with $Z=4$; Mo $K\alpha$ radiation ($\lambda=0\cdot7107$ Å); $R_w=0\cdot035$.

Introduction. An early investigation of the crystal structure of monomethylurea was carried out by Corey & Wyckoff (1933). As was concluded by these authors the structure they proposed might not be correct. This conclusion has been confirmed by the present work.

The crystal used was taken from commercially available monomethylurea (Fluka A. G., Switzerland). The linear dimensions of the crystal were about 0·4 mm. Data were collected at room temperature, 20°C, with a computer-controlled single-crystal diffractometer (Philips, PW 1100) using graphite-monochromated Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å. The built-in program for the accurate determination of lattice constants (Hornstra & Vossers, 1973) was used. Each of the four sets of equivalent reflexions $hkl,\bar{h}kl,h\bar{k}l,hk\bar{l}$ was recorded in the θ range of 3 to 35° using the θ–2θ scan mode, scan width 1·4°. Background counting was done during one half of the total scanning time at each side of the reflexion. In the refinement the weighted mean, $\bar{I}_{hkl}$, of each set of four equivalent

reflexions was chosen for the intensity of the reflexion hkl:

$$\bar{I}_{hkl}=\left(\sum_i I_i/\sigma_i^2\right)\Big/\left(\sum_i 1/\sigma_i^2\right),$$

where the summations extend over the four equivalent reflexions and σ_i are the individual errors due to counting statistics. The standard deviation in $\bar{I}_{hkl}$, σ, was calculated from the expression

$$1/\sigma=\left(\sum_i 1/\sigma_i^2\right)^{1/2}.$$

The structure was solved with the program *MULTAN* of Germain, Main & Woolfson (1971). The refinement was carried out with the program *ORFLS* of Busing, Martin & Levy (1962). First positional and anisotropic thermal parameters of the non-hydrogen atoms were refined. After the location of the hydrogen atoms in a difference Fourier map a complete refinement including atomic positions, anisotropic thermal parameters of the heavy atoms, isotropic thermal parameters of the hydrogen atoms, a scale factor and an isotropic extinction factor (Larson, 1969) was carried through. The function minimized was $\sum w(|F_o|-k|F_c|)^2$, where the summation extends over all reflexions having an intensity larger than twice their standard deviation due to counting statistics, k is the scale factor, $|F_o|$ and $|F_c|$ are the observed and calculated structure factors, respectively. The weight, w, for each reflexion

Table 1. *Atomic parameters for monomethylurea*

The anisotropic temperature factor is of the form: $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots 2hka^*b^*U_{12}+\ldots)]$ and the isotropic temperature factor: $\exp(-8\pi^2U\sin^2\theta/\lambda^2)$. The positional parameters are $\times10^4$ (for the H atoms $\times10^3$). The thermal parameters for non-hydrogen atoms are given in 10^{-3} Å^2, the values of U are in Å^2. Standard deviations are shown in parentheses and refer to the last digits.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	3305 (1)	8051 (2)	4727 (2)	37·8 (6)	39·7 (6)	43·6 (6)	−3·5 (5)	4·7 (5)	4·7 (5)
O(1)	2000 (1)	8784 (1)	4337 (1)	40·0 (4)	56·4 (5)	54·4 (5)	5·2 (4)	−1·4 (4)	2·0 (4)
N(1)	3982 (2)	8296 (2)	6459 (2)	48·7 (7)	74 (1)	49·1 (7)	12·8 (7)	−3·5 (6)	−10·0 (7)
N(2)	4087 (2)	6964 (2)	3460 (2)	50·3 (7)	61·6 (7)	51·3 (7)	11·6 (7)	−1·3 (6)	−7·7 (6)
C(2)	3476 (3)	6535 (3)	1571 (3)	101 (2)	75 (1)	56 (1)	23 (1)	−10 (1)	−19 (1)