

proposed by Angeli (1917,* 1930) and Pieroni (1922) for phenylazoxycarbonamides. The present analysis represents the first X-ray structure determination of an azoxycyano derivative and was undertaken in order to provide an unambiguous answer to these questions. The results are in agreement with the predictions of Gasco *et al.* (1974) as far as the position of the oxygen atom in the azoxycyano group is concerned; O(2) is actually bonded to the nitrogen atom adjacent to the benzene ring. The N(3)–O(2) distance is very short when compared with those found in azoxy compounds [1.279 Å in *p*-azoxyanisole (Krigbaum, Chatani & Barber, 1970), 1.291 Å in ethyl *p*-azoxybenzoate (Krigbaum & Barber, 1971)] and is of the same order as the N–O bonds in nitro groups or furoxans. The relative *anti* orientation of the benzene ring and the cyano group is confirmed. The geometry of the diazocycano group is similar to that found in *p*-chloro- (Gram & Rømming, 1967) and in *o*-bromobenzene-*anti*-diazocyanide (Bø, Klewe & Rømming, 1971), with the exception of the C(4)–N(3) distance which is longer in our case (1.471 compared with 1.403 Å in the more accurately determined *o*-bromo compound). The structure of the DMSO solvate presents no exceptional feature when compared with the structure of DMSO alone (Thomas, Shoemaker & Eriks, 1966). The molecule of DMSO is connected to the carboxyl group of the carboxyphenylazoxycyanide moiety by a rather strong hydrogen bond O–H...O of 2.526(7) Å. The

* And other papers in the series.

molecule of *p*-carboxyphenylazoxycyanide as a whole is only roughly planar, whereas the three separate azoxycyanide, phenyl and carboxyl [including C(7)] groups show no significant deviation from planarity. The dihedral angle between the carboxyl and the phenyl planes is 2.6° as a consequence of a slight rotation about the C(7)–C(10) bond. The azoxycyanide group forms an angle of 2.8° with the benzene ring owing to a folding at C(4) and a slight rotation about C(4)–N(3).

No short intermolecular contacts exist and the packing of the molecules in the crystal is due to van der Waals interactions only.

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1-Methyl-4-thiouracil

BY STUART W. HAWKINSON*

The University of Tennessee – Oak Ridge Graduate School of Biomedical Sciences, and Biology Division, Oak Ridge National Laboratory,† Oak Ridge, Tennessee 37830, U.S.A.

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Abstract. C₅H₆N₂OS, monoclinic, *P*₂₁/*c*, *a* = 6.757(1), *b* = 13.618(2), *c* = 7.010(1) Å, β = 99.36(1)°, *Z* = 4, *D*_c = 1.484, *D*_m = 1.488 g cm⁻³, *V* = 636.45 Å³, F.W. 142.2, λ(Cu Kα₁) = 1.5405 Å, μ = 36.7 cm⁻¹, *F*(000) = 296. The intensity data were collected on an automated diffractometer and the structure was solved by the heavy-atom technique. Full-matrix least-squares refinement

yielded an *R* of 0.033 for 978 reflections. The molecules form dimers in the crystal *via* N(3)–H(3)...S hydrogen bonds (N–S distance 3.328 Å). The crystal structure is similar to that of the more stable form of 1-methylthymine [Hoogsteen, *Acta Cryst.* (1963). **16**, 28–38].

Introduction. 1-Methyl-4-thiouracil has been used in chemical studies as a model of the nucleoside 4-thiouridine (Pal, Uziel, Doherty & Cohn, 1969), and in a crystallographic study of the hydrogen-bonded base pair with 9-methyladenine (Saenger & Suck, 1971a). The importance of considering N–H...S hydrogen bonds in nucleic acid structures has been emphasized

* Postdoctoral Investigator supported by subcontract No. 3322 from the Biology Division of Oak Ridge National Laboratory to The University of Tennessee. Present address: Department of Biochemistry, The University of Tennessee, Knoxville, Tennessee 37916, U.S.A.

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by Donohue (1969) and an example of one such hydrogen bond has been found in the structure of the nucleoside 2,4-dithiouridine (Saenger & Suck, 1971*b*).

A sample of 1-methyl-4-thiouracil was supplied by Dr Bimal C. Pal, Biology Division, Oak Ridge National Laboratory, and was recrystallized from aqueous solution. A pale-yellow prismatic crystal, bounded by pairs of faces $\{100\}$, $\{010\}$, and $\{10\bar{2}\}$ separated by distances of 0.07, 0.35, and 0.11 mm, respectively, was used in the diffraction study. The space group and approximate cell dimensions were determined from precession and Weissenberg photographs. More accurate cell dimensions were obtained by least-squares refinement with the use of the observed setting angles for eight $\text{Cu } K\alpha_1$ reflections measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was measured by flotation in mixtures of dichloromethane and carbon tetrachloride. Intensity

data were collected on the diffractometer with Ni-filtered $\text{Cu } K\alpha$ radiation. The intensities of 1014 unique reflections with $2\theta < 125^\circ$ were measured with the θ - 2θ scan technique. Of these, 979 had net positive intensities and were used in the subsequent analysis. Absorption corrections, calculated with the program *ORABS-2* (Busing & Levy, 1957), were applied to the data before averaging symmetry-related reflections. The calculated transmission factors were in the range 0.55 to 0.79. Each intensity was assigned a variance $\sigma^2(I)$ based on counting statistics plus a term $(0.04I)^2$, where I is the net intensity [see, for example, Wei (1971)].

A trial structure for the nonhydrogen atoms was derived from a three-dimensional Patterson map (program *FORDAPER* of A. Zalkin modified by G. Brunton). This model was confirmed by a Fourier synthesis phased on the sulfur atom position and by an initial R value ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.32 for all the nonhydrogen atoms. Full-matrix least-squares refinement

Table 1. *Positional and thermal parameters* ($\times 10^5$) *for nonhydrogen atoms*

The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Standard deviations in units of the last significant digits are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	100283 (8)	34580 (4)	56847 (9)	1893 (14)	390 (3)	2706 (15)	3 (5)	-604 (10)	119 (5)
O(2)	49196 (20)	56232 (10)	21514 (23)	1919 (36)	360 (9)	2880 (43)	105 (14)	-101 (31)	204 (15)
N(1)	39883 (23)	40156 (12)	22759 (24)	1386 (36)	434 (10)	1660 (34)	-89 (14)	-17 (28)	47 (14)
N(3)	71497 (23)	45283 (12)	37092 (24)	1495 (38)	289 (9)	1922 (38)	-88 (16)	-112 (30)	22 (15)
C(1)	19951 (34)	42329 (22)	11818 (40)	1556 (50)	680 (18)	2338 (60)	-29 (24)	-253 (43)	119 (26)
C(2)	53106 (27)	47850 (14)	26654 (27)	1521 (43)	404 (12)	1647 (40)	17 (17)	178 (34)	14 (18)
C(4)	77686 (28)	36173 (13)	43553 (27)	1726 (45)	318 (10)	1558 (39)	18 (16)	104 (35)	2 (16)
C(5)	63517 (32)	28603 (15)	38132 (29)	2194 (53)	305 (11)	1828 (44)	-79 (19)	72 (39)	8 (17)
C(6)	45446 (31)	30828 (15)	28236 (29)	1903 (50)	403 (12)	1828 (44)	-282 (20)	55 (38)	-91 (18)

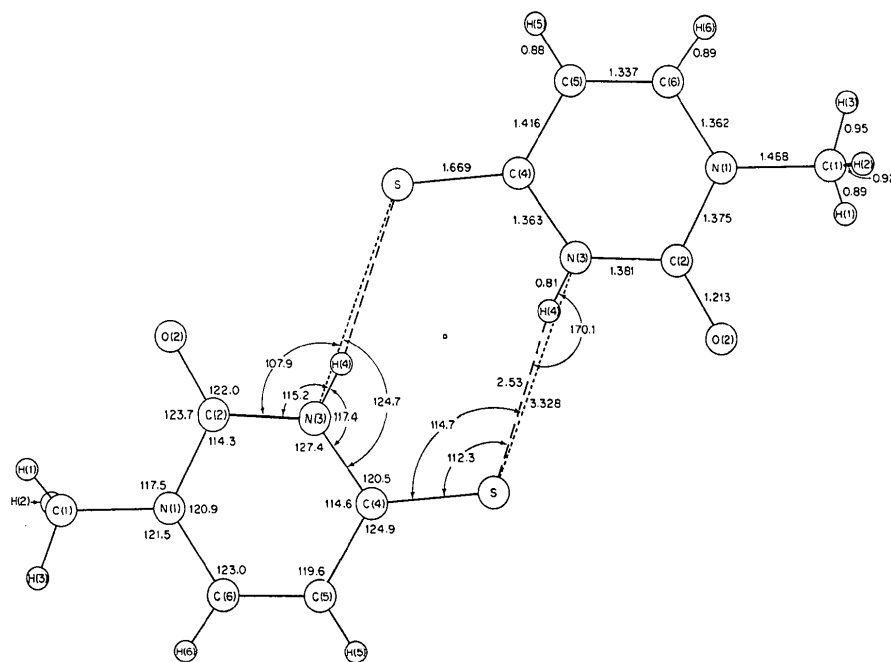


Fig. 1. Projection of the structure onto the $(10\bar{2})$ plane. The estimated standard deviations are about 0.3° for bond angles and 0.003 \AA for interatomic distances involving nonhydrogen atoms, and 1° for angles and 0.1 \AA for distances involving hydrogen atoms. This figure was produced with the aid of *ORTEP* (Johnson, 1965).

Table 1 (*cont.*)

Hydrogen atom parameters (positional parameters $\times 10^3$)				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
H(1)	145 (5)	474 (3)	172 (5)	7.8 (9)
H(2)	207 (5)	425 (2)	-11 (5)	7.3 (8)
H(3)	118 (5)	367 (3)	127 (5)	7.5 (8)
H(4)	794 (4)	498 (2)	396 (3)	3.3 (5)
H(5)	672 (3)	226 (2)	415 (3)	3.8 (5)
H(6)	356 (4)	265 (2)	246 (3)	4.3 (5)

of the positional and anisotropic thermal parameters of the nonhydrogen atoms by use of program *XFLSD*, a modification of *ORFLS* (Busing, Martin & Levy, 1962), reduced the *R* value to 0.058. The function minimized was $\sum w(F_o^2 - F_c^2)^2$ with *w* equal to the reciprocal of the estimated variances. From a three-dimensional difference synthesis calculated at this stage, all the hydrogen atom positions were located. No other peaks in this difference map were greater than one half the height of a hydrogen atom. Subsequent refinement with anisotropic thermal parameters for the nonhydrogen atoms, and isotropic thermal parameters for the hydrogen atoms, gave a final *R* of 0.033 for 978 observed intensities. The standard deviation of an observation of unit weight, defined as $[\sum w|\Delta F|^2/(n-p)]^{1/2}$ where *n* is the number of observations and *p* the number of adjusted parameters, was 1.35. The largest parameter shift during the last cycle of refinement was less than 15% of the estimated standard deviation. In the final stages of refinement the very strong reflection $10\bar{2}$ was given zero weight, since its measurement appeared to be severely affected by extinction.

Scattering factors for the nonhydrogen atoms were taken from *International Tables for X-ray Crystallography* (1962), and for hydrogen from Stewart, Davidson & Simpson (1965). Values for the real and imaginary parts of the dispersion correction of the atomic scattering factor for sulfur were taken from Cromer (1965). The final atomic parameters, along with their standard deviations estimated from the inverse of the normal equations matrix, are given in Table 1. The observed and calculated structure-factor magnitudes, and the standard deviations of the observed magnitudes, are given in Table 2.*

Discussion. A drawing of the structure, including some relevant distances and angles, is shown in Fig. 1. The bond distances and angles in the molecule are all normal for the 4-thio-substituted pyrimidines [see, for example, the reviews given in Saenger & Suck (1971*b*) and Lin, Sundaralingam & Arora (1971)]. The C(4)–S distance of 1.669(3) Å is typical of a thiopyrimidine in the diketo form. The pyrimidine ring is planar to within ± 0.02 Å (Table 3). The methyl carbon C(1) is

in the plane, in contrast to the pyrimidine nucleosides where atom C(1') of the ribose ring is usually forced out of plane because of intramolecular strain. The sulfur attached to C(4) is significantly (0.09 Å) out of the plane, although not so much as in 4-thiouridine (0.18 Å; Saenger & Scheit, 1970) where the deviation was attributable to crystal packing forces. The packing of the molecules is strikingly similar to that found in 1-methylthymine (Hoogsteen, 1963), with allowances for differences in ring substitutions. The molecules are approximately on the $(10\bar{2})$ plane with a spacing of 3.297 Å. The shortest in-plane contact is O(2)···C(5) at a distance of 3.207 Å from the molecule related by $1 - X, \frac{1}{2} - Y, \frac{1}{2} + Z$.

Table 3. Equation of best molecular plane and perpendicular out-of-plane distances (Å)

<i>x, y, and z</i> are fractional coordinates in the crystal system. $3.349x - 2.058y - 6.481z = -0.9471$			
N(1)	-0.019	C(6)	0.005
N(3)	0.005	S*	-0.091
C(2)	0.013	O(2)*	0.044
C(4)	-0.018	C(1)*	-0.020
C(5)	0.014		

* Atoms not included in plane calculation.

The feature of the crystal structure which deserves special attention is the intermolecular hydrogen bond N(3)–H(4)···S with a N···S distance of 3.328 Å and an angle H–N···S of 7.5°. These parameters meet the criteria for a N–H···S hydrogen bond given by Donohue (1969): a N···S distance in the range 3.25 to 3.55 Å, and a departure from linearity of less than 25°. A N(3)–H···S hydrogen bond has been found in the structure of 2,4-dithiouridine (Saenger & Suck, 1971*b*), with a N···S distance of 3.331 Å. It should be noted that in crystals of the base pair 1-methyl-4-thiouracil and 9-methyladenine (Saenger & Suck, 1971*a*) the sulfur did not participate in any hydrogen bonding. Instead, the presumably more stable N–H···O type of hydrogen bonding was observed.

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* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31022 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Hydrogen Bond Studies. CIII.* Monomethylammonium Hydrogen Oxalate: an X-ray Structure Determination

BY JOHN O. THOMAS

Institute of Chemistry, Uppsala University, Box 531, S-751 21 Uppsala, Sweden

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Abstract. Monoclinic, $P2_1/n$, $a=9.143$ (1), $b=8.248$ (1), $c=7.548$ (1) Å, $\beta=96.30$ (1)°, $V=565.72$ Å³ at 25°C, $\text{CH}_3\text{NH}_3\text{HC}_2\text{O}_4$, $Z=4$, $D_x=1.420$ g cm⁻³. Single-crystal four-circle diffractometer data. The HC_2O_4^- ions are linked by 2.515 (2) Å O–H...O bonds to form infinite chains along [101]. Transverse linkage between these chains is *via* a complex network of N–H...O bonds from the CH_3NH_3^+ cation. Dihedral twist between COO planes within the oxalate group is 1.1 (1)°.

Introduction. $\text{CH}_3\text{NH}_3\text{HC}_2\text{O}_4$ was prepared by bubbling air through a mixture of $\text{CH}_3\text{NH}_3\text{Cl}$ and excess NaOH, and slowly adding water. Crystallization ensued on passing the resulting gas (an air– CH_3NH_2 mixture) through a concentrated solution of oxalic acid in alcohol. Recrystallization from 80% ethanol gave flat rectangular crystals. The crystals sublime above 150°C and melt while decomposing at ~180°C. The crystal selected for data collection measured 0.30 × 0.22 × 0.08 mm. A preliminary film investigation indicated absences $h0l$ for $h+l$ odd and $0k0$ for k odd (β angle for $P2_1/c$ was ~126°). Cell parameters were refined from 34 θ values measured on a Guinier–Hägg XDC-700 powder camera calibrated with silicon. Intensity data were collected on a Stoe–Philips four-circle X-ray diffractometer with graphite monochromatized Mo $K\alpha$ radiation [for further details see Thomas (1972)]. In all, 1754 reflexions were measured out to $\sin \theta/\lambda=0.593$ Å⁻¹. After removal of systematic absences and averaging of hkl and $h\bar{k}l$ reflexions, 991 reflexions remained of which 728 were greater than 2σ and used in the refinements. An absorption correction ($\mu=1.43$ cm⁻¹) was made, making use of an explicit description of the crystal shape and size.

The structure was solved by direct methods following the iterative procedure programmed by Long (1965). Hydrogen atoms were subsequently located unambiguously in a difference synthesis. The weighting function used in the full-matrix least-squares refinement (based on F) was: $w=1/\sigma^2(F)$; where $\sigma^2(F)=\sigma^2(F^2)/4F^2$ and $\sigma^2(F^2)=\sigma_{\text{count}}^2(F^2)+(0.05F^2)^2$.

The refined value of g , the isotropic extinction parameter (Coppens & Hamilton, 1970), was 4630 (1770). Final $R(F)$ and $R_w(F)$ values were 0.044 and 0.056, respectively, for 102 refined parameters. Atomic scattering factors for C, N and O were those of Hanson, Herman, Lea & Skillman (1964), and for H those of Stewart, Davidson & Simpson (1965).

Final positional and thermal parameters are given in Tables 1 and 2.†

Discussion. Hydrogen oxalate ions exhibit a strong tendency to form infinite chains in crystal structures. The internal geometry of the ion would nevertheless appear to be readily distortable. The dihedral angle between the COO planes has been found to be as large as 12.9° [in $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$: Tellgren & Olovsson (1971)]; significant variations have also been found in the C–O lengths [see, for example, $\text{N}_2\text{H}_5\text{HC}_2\text{O}_4$ (Ahmed, Liminga & Olovsson, 1968), KHC_2O_4 (Einspahr, Marsh & Donohue, 1972) and $\text{LiHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Thomas, 1972)]. The geometry of the HC_2O_4^- ion may thus be expected to respond sensitively to changes in the hydrogen-bond environment of the ion chain.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31015 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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