

by the substitution. Substitution of a Br atom at the *para* position of the second ring results in a gross change in crystal structure in which the layered structure is lost and the inter-ring angles revert to more normal values.

The comparison of the 4-bromo and linear polyphenyl structures suggests that the type of layered packing arrangement found in these compounds is associated with relatively small inter-ring dihedral angles. Apparently, sufficient energy is gained in this type of structure relative to some hypothetical arrangement having less planar molecules to offset the increase in intramolecular energy. The studies of C₁₂H₉Br and of the low-temperature forms of *p*-terphenyl and *p*-quaterphenyl indicate that the average value for the inter-ring angle of molecules crystallizing in this type of structure is 20° and consequently suggest that the angle in biphenyl itself may be of this magnitude.

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2,3-Dihydro-3-hydroxy-5*H*-thiazolo[3,2-*a*]pyrimidin-5-one. A 3,*S*²-‘Hydroxyethano’ Derivative of 2-Thiouracil

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Abstract. C₆H₆N₂O₂S, monoclinic, *P*2₁/*n*, *a* = 6.4676 (7), *b* = 8.268 (1), *c* = 13.617 (1) Å, β = 100.53 (1)°, *V* = 716.0 (1) Å³, *Z* = 4, *D*_c = 1.59, *D*_m = 1.58 Mg m⁻³. The final *R* was 0.034 for 846 reflexions. The cyclization through the hydroxyethano bridge changes the geometry of the thiouracil moiety. The pyrimidine ring is nearly planar while the thiazolidine ring adopts a half-chair conformation.

Introduction. Systematic studies on the mechanism of chloroacetaldehyde reactions with nucleic-acid components carried out by Wiewiórowski, Krzyżosiak and

their co-workers (Biernat, Ciesiołka, Górnicki, Adamiak, Krzyżosiak & Wiewiórowski, 1978; Biernat, Ciesiołka, Górnicki, Krzyżosiak & Wiewiórowski, 1978; Krzyżosiak, Biernat, Ciesiołka, Górnicki & Wiewiórowski, 1979*a*) have recently led to the conclusion that the thio analogues of pyrimidines and pyrimidine nucleosides also react with chloroacetaldehyde (Krzyżosiak, Biernat, Ciesiołka, Górnicki & Wiewiórowski, 1979*b*) under conditions in which adenosine or cytidine is converted into the so-called ‘etheno’ derivative (Barrio, Secrist & Leonard, 1972). Following a suggestion made by Wiewiórowski and

Krzyżosiak, one of the compounds obtained in the reaction of 2-thiouracil with chloroacetaldehyde has been chosen for X-ray analysis. Although spectroscopic observations (Krzyżosiak *et al.*, 1979*b*) suggested that in this new molecule the additional thiazolidine ring is fused to give a 5-pyrimidinone rather than a 7-pyrimidinone system, this point still required further verification.

Suitable crystals were grown from butyl alcohol. The crystal used for data collection was cut to 0.15 × 0.25 × 0.40 mm and mounted on a Syntex P2₁ four-circle diffractometer. The cell dimensions were determined from a least-squares refinement of the setting angles from 15 reflexions centred on the diffractometer. Graphite-monochromated Cu K α radiation was used and 883 independent reflexions were measured out to 2 θ = 115°. The $\theta/2\theta$ scanning technique was used and the scan speed was varied from 1.9 up to 29.3° min⁻¹.

The background and integrated intensity for each reflexion were obtained by the Lehmann & Larsen (1974) profile-analysis method (program PRAN; Jaskólski, 1979). Those 853 reflexions for which $I/\sigma(I) \geq 1.96$ were regarded as observed. The intensities were corrected for Lorentz and polarization effects but no correction was performed for absorption [$\mu(\text{Cu K}\alpha) = 3.5 \text{ mm}^{-1}$] or extinction. Anomalous-dispersion corrections were applied to the scattering factors of all non-hydrogen atoms.

The structure was solved with MULTAN (Germain, Main & Woolfson, 1971). Full-matrix isotropic least-squares refinement of all 11 non-hydrogen atoms yielded $R = 0.103$. Three cycles of anisotropic refinement gave $R = 0.068$. The six H atoms were then located from a difference electron-density map by means of nineteen-point electron-density interpolation and a full-matrix least-squares refinement was carried

out for positional and thermal parameters of non-hydrogen atoms; H atoms were included as fixed contributions with isotropic temperature factors one unit greater than the isotropic values for their carriers. Statistical weights, $w = 1/\sigma_F^2$, were initially used, but in the last cycles of the refinement the following weighting scheme was applied $w = F_o^2/a^2$ if $F_o < a$; $w = 1$ if $a \leq F_o \leq b$; $w = b^2/F_o^2$ if $F_o > b$ where $a = 2.25$ and $b = 20.31$. The quantity minimized in the least-squares calculations was $\sum w(F_o - F_c)^2$. Seven of the most intense reflexions were judged to suffer from extinction and were excluded from the final stages of refinement. The final R value was 0.034 for 846 reflexions. All calculations were performed on a Nova minicomputer using original and locally modified Syntex XTL programs. Final positional and isotropic thermal parameters are listed in Table 1.*

Discussion. The X-ray analysis has shown that in the compound investigated the thiazolidine ring is fused to form a 5-pyrimidinone system. The structure contains two enantiomorphically distinct molecules related by the space-group symmetry. Bond lengths and angles are given in Fig. 1. The cyclization through the hydroxy-ethano bridge results in significant alteration of the geometry of the thiouracil moiety, as compared with that of 2-thiouracil (Tsernoglou, 1966). The greatest deviations in the bond distances and angles occur around the N(8)–C(9) and N(4)–C(5) bonds. The lack of an H atom at N(8) is reflected in the reduction of the C–N–C angle at N(8) to a value of 115.4° in accordance with the observations of Singh (1965).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34947 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

Fractional coordinates are $\times 10^4$, except those for H atoms, which are $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (Å ²)
S(1)	6969 (1)	5088 (1)	7928 (1)	3.3
C(2)	4628 (5)	4169 (4)	8234 (2)	3.0
C(3)	3147 (4)	3829 (3)	7258 (2)	2.4
N(4)	4551 (3)	3509 (3)	6533 (2)	2.1
C(5)	3831 (5)	2734 (3)	5615 (2)	2.7
C(6)	5386 (5)	2693 (4)	4990 (2)	3.2
C(7)	7279 (4)	3390 (4)	5280 (2)	3.3
N(8)	7887 (3)	4166 (3)	6176 (2)	2.7
C(9)	6502 (4)	4180 (3)	6759 (2)	2.3
O(1)	2036 (3)	2205 (3)	5430 (1)	3.5
O(2)	1886 (3)	5168 (2)	6948 (1)	2.6
H(21)	506	324	859	4.0
H(22)	396	491	863	4.0
H(3)	232	280	730	3.4
H(6)	504	220	436	4.2
H(7)	830	333	487	4.3
H(2)	61	478	667	3.6

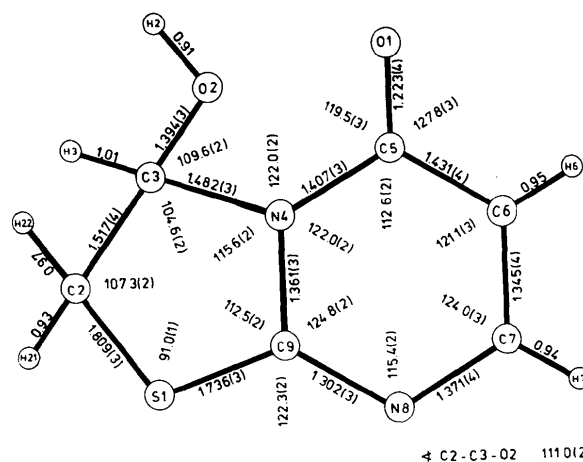


Fig. 1. Numbering scheme with bond distances (Å) and bond angles (°) and their e.s.d.'s.

Table 2. *Least-squares plane and deviations of atoms from this plane*

Atoms included in the calculation are marked with a dagger. *X*, *Y* and *Z* are orthogonal coordinates (in Å) along the *a*, *b* and *c** directions respectively.

Pyrimidine-ring equation:

$$-0.291X + 0.864Y - 0.411Z + 1.466 = 0.$$

N(4)†	-0.006 (2) Å	S(1)	0.001 (1) Å
C(5)†	0.014 (3)	O(1)	0.063 (2)
C(6)†	-0.008 (3)	C(3)	0.140 (3)
C(7)†	-0.005 (3)		
N(8)†	0.007 (2)		$\chi^2 = 52.6$
C(9)†	-0.001 (3)		

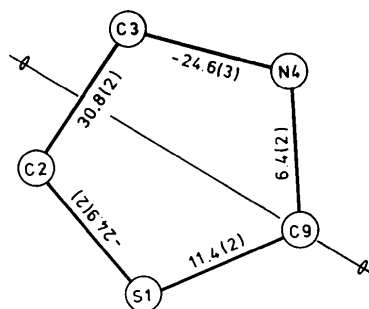


Fig. 2. Endocyclic torsion angles (°) in the thiazolidine ring.

Table 3. *Hydrogen-bond distances (Å) and angles (°)*

O(2)—H(2)	0.91	O(2)⋯N(8 ^b)	2.736 (3)
H(2)⋯N(8 ^b)	1.84	∠O(2)—H(2)⋯N(8 ^b)	174

Symmetry code: (i) $-1 + x, y, z$.

Remarkable shortening of N(8)—C(9) to a value of 1.302 Å indicates its almost double-bond character. Moreover, the N(4)—C(5) bond (1.407 Å) is significantly longer than in 2-thiouracil (1.376 Å) and may indicate less pronounced delocalization of the π electrons in the pyrimidine ring. Similar lengthening of this bond was also observed in 3,*N*⁴-ethenocytidine hydrochloride (Wang, Barrio & Paul, 1976). The cyclization also produces some changes in bond angles around N(4) and C(5), *i.e.* the C(9)—N(4)—C(5) angle is 5.0° less, whereas O(1)—C(5)—C(6) is 3.8° greater than the corresponding values in 2-thiouracil. Also, the distribution of the bond angles around C(5) is quite irregular.

The geometry of the thiazolidine ring agrees well with that found in 2-carboxy-5-methylidihydrothiazolo[3,2-*a*]pyridinium-3-carboxylate (Groth, 1971). The largest difference is in the C_{sp^3} —S distance which is shorter in the present case (1.809 Å), but still

Table 4. *Shortest intermolecular contacts (Å)*

O(1)⋯C(7 ^b)	3.200 (4)	O(2)⋯C(7 ^v)	3.394 (3)
C(3)⋯N(8 ^b)	3.462 (3)	C(5)⋯C(7 ^v)	3.457 (4)
O(1)⋯C(2 ⁱⁱ)	3.388 (4)	S(1)⋯C(9 ^{vi})	3.529 (3)
O(1)⋯C(2 ⁱⁱⁱ)	3.310 (3)	S(1)⋯N(8 ^{vi})	3.581 (3)
O(2)⋯C(2 ^{iv})	3.447 (4)	S(1)⋯N(4 ^{vi})	3.606 (2)
O(2)⋯C(3 ^{iv})	3.216 (3)		

Symmetry code

(i)	$-1 + x, y, z$	(iv)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$
(ii)	$\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$	(v)	$1 - x, 1 - y, 1 - z$
(iii)	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$	(vi)	$\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$

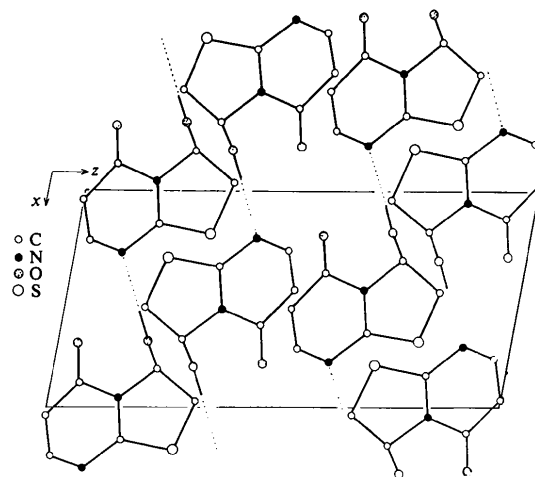


Fig. 3. Packing in the unit cell. Hydrogen bonding (involving N and O atoms) is represented by dashed lines.

comparable with the value of 1.812 Å for a pure single C—S bond (Pauling, 1960).

The displacements of the atoms from the least-squares plane of the pyrimidine ring are listed in Table 2. The pyrimidine ring is nearly planar, though χ^2 is 52.6. The S(1) atom lies in the plane of this ring.

The endocyclic torsion angles in the five-membered ring are given in Fig. 2. The ring is best described as a half chair with the approximate C_2 axis bisecting the C(2)—C(3) bond. The asymmetry parameters are: $\Delta C_2^{2-3} = 3.5$ and $\Delta C_s^2 = 10.2^\circ$ (Duax & Norton, 1975).

In Fig. 3 the projection of the structure along the *y* axis is given. The molecules form chains along the *x* axis *via* O(2)—H(2)⋯N(8) hydrogen bonds. The distances and angles involved in these bonds are summarized in Table 3. The remaining intermolecular contacts correspond to van der Waals interactions; the shortest of these are listed in Table 4.

I wish to thank Professor M. Wiewiórowski for suggesting this compound as an attractive subject for X-ray study and for his interest in this work. Thanks are also due to Dr W. Krzyżosiak for supplying the sample and for helpful discussions.

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Structure of Triphenylphosphine Oxide Hemiperhydrate

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Abstract. $2[\text{C}_{18}\text{H}_{15}\text{OP} \cdot \frac{1}{2}\text{H}_2\text{O}_2]$, $M_r = 590.6$, orthorhombic, $Fdd2$, $a = 32.277$ (1), $b = 19.786$ (4), $c = 9.546$ (2) Å, $Z = 8$, $V = 6096.4$ Å³, $D_c = 1.30$, $D_m = 1.33$ Mg m⁻³ (floatation), $\mu(\text{Mo } K\alpha) = 0.137$ mm⁻¹, $F(000) = 2256$, $R = 0.083$. The crystallographically dependent $(\text{C}_6\text{H}_5)_3\text{PO}$ units and H_2O_2 molecules are linked by hydrogen bonds. Some bond parameters are: $\text{P}-\text{O}(1) = 1.477$ (10), $\text{O}(1)\cdots\text{O}(2) = 2.759$ (24), $\text{O}(2)-\text{O}(2') = 1.443$ (14) Å, $\text{P}-\text{O}(1)-\text{O}(2) = 134.7$ (7), $\text{O}(1)-\text{O}(2)-\text{O}(2') = 99.9$ (12)°.

Introduction. Recently, we have found short hydrogen bonds in $\text{Ph}_3\text{PO} \cdot \text{HCl}$ (Haupt, Huber, Krüger, Preut & Thierbach, 1977), $\text{Ph}_3\text{PO} \cdot \text{HF}$ (Thierbach & Huber, 1979a) and $(\text{Ph}_3\text{PO})_2 \cdot \text{H}_2\text{O} \cdot \text{HBr}$ (Thierbach & Huber, 1979b). In our efforts to determine structures of other hydrogen-bonded derivatives of phosphine oxides, we first tried to prepare crystals of hydrates, described as 1:1 (Michaelis & Gleichmann, 1882; Michaelis & von Soden, 1885) and 2:1 adducts (Halman & Pinchas, 1958). We obtained, however, in all cases, only the monoclinic modification of Ph_3PO . We then turned to investigate other adducts of Ph_3PO with HOX ligands

and succeeded in determining the structure of $(\text{Ph}_3\text{PO})_2 \cdot \text{H}_2\text{O}_2$. This compound was first prepared by Temple, Tsuno & Leffler (1963), and was proposed as a polymerization catalyst (Rudolph & Reinking, 1967).

Suitable colourless single crystals were obtained by shaking a solution of 2.0 g $(\text{C}_6\text{H}_5)_3\text{PO}$ and 3.1 g 30% H_2O_2 in 24 g ethanol (yield 96%). Analysis: C (found/calc.) 73.18/72.21%, H 5.36/5.46%; TGA (maximum temperature 460 K): total weight loss 6.1% (calculated for loss of H_2O_2 5.8%).

Precession and Weissenberg photographs indicated an orthorhombic lattice with systematic absences (hkl , $h + k = 2n + 1$, $k + l = 2n + 1$ and $l + h = 2n + 1$; $0kl$, $k = 2n + 1$, $l = 2n + 1$ and $k + l = 4n + 1$; $h0l$, $h = 2n + 1$, $l = 2n + 1$ and $h + l = 4n + 1$; $hk0$, $h = 2n + 1$ and $k = 2n + 1$; $h00$, $h = 4n + 1$; $0k0$, $k = 4n + 1$; $00l$, $l = 4n + 1$) consistent with the space group $Fdd2$. The crystal used for data collection was $0.48 \times 0.24 \times 0.19$ mm. The intensity measurements were made on a Hilger & Watts four-circle diffractometer (Mo $K\alpha$ radiation, $\lambda = 0.70926$ Å, graphite monochromator and scintillation counter). The cell dimensions and orientation matrix were determined by least squares from the angular positions of 20 reflections. A complete set of symmetry-independent reflections was

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