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# Structure of 5-(Diphenylphosphino)uracil

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**Abstract.** $C_{16}H_{13}N_2O_2P$, $M_r = 296{\cdot}27$, monoclinic, $P2_1/c$, $a = 12{\cdot}005\ (4)$, $b = 9{\cdot}804\ (2)$, $c = 12{\cdot}628\ (3)$ Å, $\beta = 106{\cdot}02\ (2)^\circ$, $V = 1429\ (2)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}38$ g cm$^{-3}$, $\lambda(\text{Mo}\ K\alpha) = 0{\cdot}70926$ Å, $\mu = 1{\cdot}91$ cm$^{-1}$, $F(000) = 616$, room temperature, final $R = 0{\cdot}042$ for 3294 unique reflections including unobserved. The title compound is a modified uracil in which the H atom at position C(5) is replaced by a diphenylphosphine group. The uracil ring has expected bond lengths and angles but deviates from planarity more than usual. The P atom shows normal pyramidal coordination geometry. Hydrogen bonds connect the molecules to form (100) layers in the crystal. These layers are held together by van der Waals forces.

**Introduction.** The title compound was synthesized in order to study the coordination properties of a diphenylphosphine-substituted uracil molecule. In chemotherapy, C(5)-substituted pyrimidine nucleosides are used as cytostatic drugs, hence it was of interest to test this substance for possible anticancer effects. Experiments showed only a very small antitumour activity (Ellermann & Demuth, 1983), and for this reason the X-ray structure of 5-(diphenylphosphino)-uracil is of great interest to our continuing investigations.

**Experimental.** The compound was prepared using the procedure reported by Ellermann & Demuth (1983). Recrystallization from a mixture of dimethyl sulfoxide and water gave transparent plates of dimensions $0{\cdot}56 \times 0{\cdot}56 \times 0{\cdot}28$ mm. Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); $\omega$–$2\theta$ scan mode, scan width $(0{\cdot}900 + 0{\cdot}345\ \tan\theta)^\circ$, profile analysis with a modified Lehmann & Larsen (1974) procedure; lattice parameters refined by least-squares procedure *GIVER* (Krogmann, 1966) on the basis of 47 reflections with $17{\cdot}3 \le 2\theta \le 22{\cdot}6^\circ$; no absorption correction was applied; $(\sin\theta_{\text{max}})/\lambda = 0{\cdot}65$ Å$^{-1}$, index range $-15 \le h \le 15$, $k$ 0–12, $l$ 0–16; eight standard reflections (intensity variation 0·4%); 13 208 reflections ($2 \le \theta \le 27{\cdot}5^\circ$) were measured, after averaging symmetrical equivalents, 3300 reflections [12 unobserveds included, $I < 3\sigma(I)$] remained; $R_{\text{int}} = 0{\cdot}012$. Structure solved by direct methods, subsequent Fourier map revealed all non-H atoms and all H atoms could be located from a difference Fourier map; final refinement by blocked least-squares methods (based on $|F|$) of scale factor, coordinates and anisotropic temperature parameters (H atoms isotropic). Reflections with strong extinction effects were omitted. Refinement was concluded with 3294 reflections after omission of $\bar{3}11$, 111, 012, $\bar{1}13$, 013 and 113. $R = 0{\cdot}042$,† $wR = 0{\cdot}036$, $S = 6{\cdot}93$, $w = 1/\sigma^2(|F_o|)$, max. $\Delta/\sigma = 0{\cdot}16$; $\Delta\rho$ in the final difference Fourier synthesis $+0{\cdot}34$ and $-0{\cdot}23$ e Å$^{-3}$; scattering factors from *International Tables for X-ray Crystallography* (1974). Computations employed the *CRYSTAN* system (Burzlaff, Böhme & Gomm, 1977) and *ORTEP*II (Johnson, 1977) for plotting purposes.

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43978 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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**Discussion.** Atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Bond lengths and angles are listed in Table 2.

Fig. 1 shows a perspective view of the molecule with the atomic numbering scheme. The title substance is a 2,4(1*H*,3*H*)-pyrimidinedione molecule, in which the H atom at C(5) is replaced by a diphenylphosphine group. The P—C bonds form a pyramidal arrangement and there is no important difference in the geometry around the P atom compared with other phosphines, *e.g.* $P(C_6H_5)_3$ (Daly, 1964) and $P(C_6H_4OCH_3)_3$ (Allman, Goel & Beauchamp, 1986). Least-squares-planes calculations show that the phenyl rings are planar (maximum deviation 0·02 Å) and the uracil ring is planar within 0·07 Å. The uracil ring deviates from planarity more than usually expected. In comparable structures such as thymine monohydrate (Gerdil, 1961), the maximum deviation is only 0·008 Å. The dihedral angle between a plane through C(5), C(11), C(21) and the uracil ring is 46·5°. The plane of these three C atoms is inclined at an angle of 27·7° and 82·2° to the two phenyl rings, hence the molecule only possesses $C_1 \equiv 1$ symmetry.

Table 1. *Atom coordinates* (×10⁴) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$)

$$U_{eq} = (1/6\pi^2)\textstyle\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| P(1) | 2697 (1) | 4767 (1) | 8338 (1) | 3·6 |
| O(2) | 4725 (1) | 10262 (1) | 8567 (1) | 4·7 |
| O(4) | 3691 (1) | 6612 (1) | 10296 (1) | 5·5 |
| N(1) | 3965 (1) | 8402 (1) | 7557 (1) | 3·6 |
| N(3) | 4195 (1) | 8416 (1) | 9419 (1) | 4·0 |
| C(2) | 4323 (1) | 9110 (1) | 8518 (1) | 3·6 |
| C(4) | 3736 (1) | 7123 (1) | 9428 (1) | 3·8 |
| C(5) | 3306 (1) | 6479 (1) | 8359 (1) | 3·3 |
| C(6) | 3478 (1) | 7136 (1) | 7488 (1) | 3·4 |
| C(11) | 1216 (1) | 5109 (1) | 8410 (1) | 3·6 |
| C(12) | 872 (1) | 6272 (1) | 8860 (1) | 4·6 |
| C(13) | −249 (1) | 6389 (1) | 8953 (1) | 5·4 |
| C(14) | −1042 (1) | 5364 (2) | 8596 (1) | 5·6 |
| C(15) | −709 (1) | 4203 (2) | 8148 (1) | 5·8 |
| C(16) | 409 (1) | 4069 (1) | 8065 (1) | 4·8 |
| C(21) | 2433 (1) | 4339 (1) | 6879 (1) | 4·0 |
| C(22) | 3055 (1) | 3251 (1) | 6627 (1) | 5·4 |
| C(23) | 2954 (1) | 2905 (2) | 5542 (1) | 7·5 |
| C(24) | 2236 (2) | 3645 (2) | 4708 (1) | 8·0 |
| C(25) | 1592 (1) | 4703 (2) | 4937 (1) | 6·7 |
| C(26) | 1675 (1) | 5046 (1) | 6023 (1) | 5·0 |

Table 2. *Selected bond distances* (Å) *and angles* (°)

E.s.d.'s are given in parentheses.

| | | | |
|---|---|---|---|
| N(1)—H(1) | 0·87 (1) | Phenyl rings | |
| N(1)—C(2) | 1·361 (1) | | |
| C(2)—O(2) | 1·223 (1) | C—P | 1·829 (1)–1·837 (1) |
| C(2)—N(3) | 1·370 (2) | C—C | 1·370 (2)–1·391 (2) |
| N(3)—H(3) | 0·91 (1) | C—C(mean) | 1·383 |
| N(3)—C(4) | 1·383 (2) | | |
| C(4)—O(4) | 1·221 (1) | | |
| C(4)—C(5) | 1·450 (1) | | |
| C(5)—P | 1·828 (1) | | |
| C(5)—C(6) | 1·340 (2) | N(1)—H···O(4$^{ii}$) | 2·782 (1) |
| C(6)—H(6) | 0·93 (1) | N(3)—H···O(2$^{i}$) | 2·830 (1) |
| C(6)—N(1) | 1·364 (1) | | |
| C(5)—P—C(11) | 102·71 (5) | P—C(5)—C(6) | 125·5 (1) |
| C(11)—P—C(21) | 101·02 (5) | C(4)—C(5)—C(6) | 117·3 (1) |
| C(21)—P—C(5) | 100·54 (5) | H(6)—C(6)—C(5) | 124·1 (6) |
| H(1)—N(1)—C(2) | 120·9 (6) | N(1)—C(6)—C(5) | 123·1 (1) |
| C(6)—N(1)—C(2) | 123·1 (1) | | |
| O(2)—C(2)—N(3) | 123·3 (1) | | |
| N(1)—C(2)—N(3) | 114·0 (1) | Phenyl rings | |
| H(3)—N(3)—C(4) | 117·1 (6) | | |
| C(2)—N(3)—C(4) | 126·7 (1) | C—C—C | 118·1 (1)–120·9 (1) |
| O(4)—C(4)—C(5) | 124·4 (1) | C—C—C(mean) | 120·0 |
| N(3)—C(4)—C(5) | 115·6 (1) | | |
| | | N(1)—H(1)···O(4$^{ii}$) | 143 (2) |
| | | N(3)—H(3)···O(2$^{i}$) | 171 (5) |

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

The bond distances of the uracil moiety are as expected (*cf.* Kovács & Párkányi, 1982). Small deviations of the bond angles are due to the slight non-planarity. The diphenylphosphino unit is closely comparable to triphenylphosphorus (Daly, 1964).

The molecular packing is illustrated in Fig. 2. The molecules are held together by asymmetrical hydrogen bonds, as assumed earlier (Ellermann & Demuth, 1983). The uracil moieties are linked by N(1)—H···O(4) hydrogen bonds [2·782 (1) Å] to form one-dimensional chains along **c**. These bonds have a rather small angle at H(1) of 143 (2)°. These chains are linked across the inversion centres ($\frac{1}{2}$00) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) by a pair of N(3)—H···O(2) hydrogen bonds [2·830 (1) Å]. These bonds are almost linear, the angle at H(3) being 171 (5)°. In the third direction these layers are connected by van der Waals forces.

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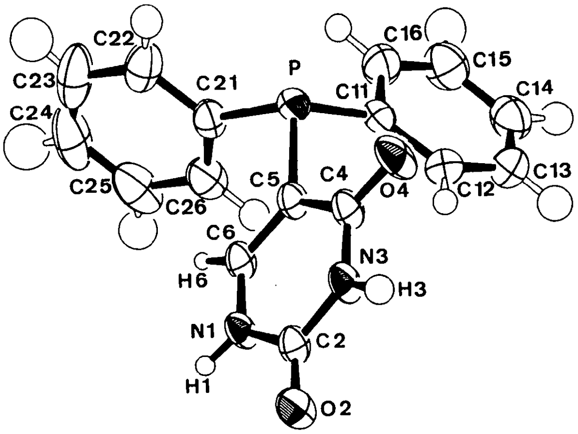

Fig. 1. Perspective view of the molecule with 50% probability thermal ellipsoids. The numbering of the H atoms is the same as that of the neighbouring C, N atoms. The first digit of the phenyl C symbol stands for the ring number.

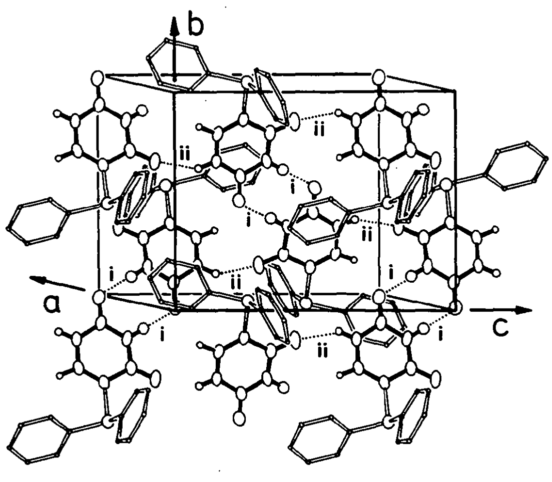

Fig. 2. Molecular packing in the crystal of 5-(diphenylphosphino)uracil; the phenyl rings are symbolized for clarity.

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# The Structure of a Five-Membered Cyclic Sultone

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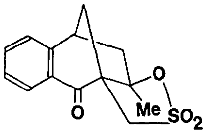
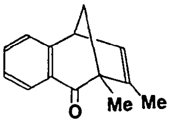
**Abstract.** 1,5-Dihydro-3a,5-dimethyl-1*H*-1,5-methanonaphtho[2,1-*c*][1,2]oxathiol-4(3a*H*)-one 3,3-dioxide, $C_{14}H_{14}O_4S$, $M_r = 278{\cdot}2$, monoclinic, *Cc*, $a = 7{\cdot}450\,(10)$, $b = 25{\cdot}246\,(10)$, $c = 6{\cdot}980\,(5)$ Å, $\beta = 104{\cdot}6\,(1)^\circ$, $U = 1270{\cdot}7$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}455$ g cm$^{-3}$, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}5$ cm$^{-1}$, $F(000) = 584$, $T = 293$ K, $R = 0{\cdot}062$ for 1012 reflexions with $I > 3\sigma(I)$. The structure contains a five- and a seven-membered saturated sultone ring. It is compared with known structures of saturated and partially unsaturated sultone rings. Bond lengths of interest are: mean acyclic S—O 1·415 (5), cyclic S—O 1·58 (1) and S—C 1·78 (1) Å.

**Introduction.** In our studies of the rearrangement reactions of 1-methoxy-2,6-dimethylbenzobarrelene derivatives in sulfuric acid we obtained the sultone (1) whose structure was established by X-ray diffraction (Brown, Heaney & Mason, 1984). The product was thought to arise by sulfonation of an olefin (Roberts & Williams, 1987) concurrently with a 1,2-acyl shift. Since the complex formed between dioxan and sulfur trioxide is known to have electrophilic properties (Wolinsky, Dimmel & Gibson, 1967; Dimmel & Fu, 1973) we have studied the reaction of the ketone (2) with that reagent. The sultone (1) was formed but in addition we isolated a second sultone (3) whose X-ray crystal structure is now reported.



(1)



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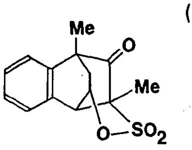

(3)

**Experimental.** Preparation by the method of Brown, Heaney, Ley, Mason & Singh (1978); colourless acicular crystals grown from ethanol, crystal (1·0 × 0·1 × 0·2 mm) mounted about **c**; Stoe Weissenberg diffractometer, $(\sin\theta)/\lambda < 0{\cdot}6$ Å$^{-1}$; lattice parameters from maximizing fit of axial row reflexions $10 < 2\theta < 30^\circ$; 1186 unique reflexions measured, 1012 with

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