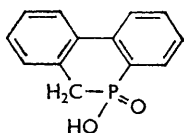


724. *9,10-Dihydro-9-hydroxy-9-phosphaphenanthrene 9-Oxide. X-Ray Determination of the Crystal and Molecular Structure.*

By P. J. WHEATLEY.

The crystal and molecular structure of what was presumed to be 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide has been determined by X-ray-diffraction methods. The formulation is confirmed and the exact molecular geometry established. Bond lengths agree well with standard values and with those found in dibenzylphosphinic acid. Molecules are linked together across a glide plane by O-H...O hydrogen bonds of length 2.533 Å.



(I) THE preceding paper describes the preparation and properties of 9,10-dihydro-9-hydroxy-9-phosphaphenanthrene 9-oxide (I). The present paper gives an account of the crystal and molecular structure determined by two-dimensional X-ray diffraction techniques.

Experimental.— $C_{13}H_{11}PO_2$. $M = 230.2$. Monoclinic. $a = 7.52_3$, $b = 18.88_6$, $c = 15.29_0$ Å, $\beta = 92^\circ 5'$. $U = 2171$ Å³. $D_m = 1.41$ (by flotation), $Z = 8$, $D_c = 1.408$, $F(000) = 960$. Space group, $B2_1/c$ (C_{2h}^5 , No. 14). Cu- K_α radiation ($\lambda = 1.542$ Å), single-crystal rotation and Weissenberg photographs.

The choice of space group was dictated by the morphology of the crystals and by convenience. The equivalent positions are those given in International Tables for space group No. 14, plus another four to which have been added ($\frac{1}{2}$, 0, $\frac{1}{2}$). Multiple-film Weissenberg photographs were taken round $[b]$ and $[c]$. Relative intensities were estimated visually by comparison with standard strips prepared from the same crystals. No correction was made for

absorption ($\mu = 21.6 \text{ cm.}^{-1}$). 149 $0kl$ and 69 $hk0$ reflexions were observed to be non-zero. Each projection was solved from a sharpened Patterson synthesis which served to locate the phosphorus atom and to determine the approximate orientation of the molecule. Successive Fourier syntheses gave the positions of the lighter atoms, and each projection was then refined by means of difference syntheses. The scattering factors used were those of Berghuis *et al.*¹ for the carbon and oxygen atoms, and that of Tomiie and Stam² for the phosphorus atom. Hydrogen atoms were ignored. Isotropic temperature factors $B = 3.8 \text{ \AA}^2$ and 2.0 \AA^2 were required for the $0kl$ and $hk0$ projections, respectively. Corrections for secondary extinction³ were applied to the eleven strongest $0kl$ and the three strongest $hk0$ reflexions. The final agreement index was $R = 11.0\%$ for the $0kl$ and $R = 12.6\%$ for the $hk0$ projection.

TABLE 1.

Fractional co-ordinates.

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
P	0.563	0.190	0.581	C ₄	0.446	-0.068	0.620	C ₉	0.551	0.080	0.349
O ₁	0.514	0.265	0.591	C ₅	0.504	-0.086	0.538	C ₁₀	0.594	0.134	0.291
O ₂	0.739	0.167	0.632	C ₆	0.544	-0.032	0.480	C ₁₁	0.628	0.203	0.319
C ₁	0.395	0.131	0.617	C ₇	0.500	0.036	0.506	C ₁₂	0.615	0.217	0.408
C ₂	0.442	0.054	0.589	C ₈	0.538	0.096	0.438	C ₁₃	0.572	0.165	0.468
C ₃	0.402	0.000	0.647								

TABLE 2.

Observed and calculated structure factors for one asymmetric unit.

$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	
0.2,0	4.1	-3.8	0.1,4	12.9	13.2	0.1,8	9.5	-9.3	3	4.1	3.6	4	0.7	-0.9	4.1,0	12.5	12.4	
4	0.6	-0.1	2	9.6	10.8	2	7.7	7.8	4	6.4	6.6	5	1.0	-1.0	2	2.5	3.1	
6	2.7	2.9	3	6.3	-7.0	3	0.9	0.9	5	3.3	3.2	6	1.6	-1.5	3	1.6	-1.6	
8	10.7	-11.5	4	1.0	-1.1	5	1.3	-1.6	7	2.8	-2.3	8	1.5	1.5	5	3.9	-3.1	
10	2.9	2.7	5	3.6	3.5	6	2.0	2.5	8	3.8	-3.5				6	4.6	-5.5	
12	1.5	1.5	6	0.7	0.9	7	1.9	-0.8	9	2.1	2.3				7	1.6	1.1	
14	1.5	-0.5	7	8.3	7.9	8	2.2	2.4	10	2.5	2.7	0.2,0	4.4	-4.0	8	3.2	-3.7	
16	2.5	1.7	8	3.4	3.6	9	6.0	6.7	12	2.8	-2.6	4	0.7	-0.1	9	9.4	-9.9	
18	2.2	-2.6	10	3.1	-2.5	10	6.1	-6.3	14	1.7	-1.8	6	3.2	3.1	10	3.2	-4.2	
22	2.1	1.6	11	3.7	3.8	11	1.5	2.2	16	1.4	1.1	8	12.1	-12.4	11	1.4	-0.3	
			12	3.2	-3.5	12	0.8	1.4	18	1.0	-0.9	10	3.5	3.2	12	3.6	6.0	
			13	2.9	-3.4	13	2.0	-2.0				12	2.0	1.8	13	2.8	2.3	
0.0,2	26.7	28.3	14	3.5	-3.5	14	0.8	0.5	0.1,14	2.9	2.6	14	2.0	-0.6	14	4.8	-6.2	
4	23.3	-21.7	15	4.8	-4.8	15	6.8	-7.4	2	0.8	0.6	16	3.1	2.4	16	3.9	-3.9	
6	7.7	-7.5	16	4.1	-4.8	16	1.1	-1.0	3	1.0	0.5	18	2.8	-3.9	17	3.8	4.8	
10	5.0	4.7	17	4.1	5.1	17	1.9	-2.2	5	2.2	3.0	22	2.7	2.9	18	1.3	-0.6	
12	3.6	3.2	18	1.0	-1.5	18	1.5	1.5	6	1.4	2.0	2.0,0	43.3	42.9	19	1.6	-1.3	
14	3.6	2.5	19	1.9	-2.0	19	0.8	1.0	7	1.9	1.7	4	5.9	5.2				
16	1.4	-1.9	23	1.4	0.8	20	1.5	-1.8	8	1.5	-0.6	4	6.9	-8.3	6.1,0	6.6	4.9	
18	2.4	-2.7							9	1.8	-0.9	8	1.7	-1.7	2	3.0	2.6	
						0.1,10	3.8	-3.3	10	1.3	1.2	3	1.3	1.0	2.1,0	22.5	23.0	4
0.1,2	9.4	9.2				2	4.7	-4.8	11	1.3	1.0	2.1,0	22.5	23.0	4	3.6	3.7	
2	2.7	3.8	0.1,6	12.7	-12.7	3	1.6	1.3	14	1.1	-0.9	2	7.8	7.9	5	3.4	-2.9	
3	12.9	-13.3	2	14.5	15.2	4	3.6	3.7	15	1.5	-1.6	3	8.3	-7.4	6	7.4	-8.2	
4	5.1	5.3	3	1.6	-1.8	5	0.8	-0.7	16	1.3	1.0	4	3.4	5.3	8	4.3	3.7	
5	7.6	-7.5	4	1.2	-0.7	6	0.7	-0.1				5	2.0	-3.0	9	4.6	-4.5	
6	1.9	-1.9	5	12.0	11.7	7	2.6	-1.6	0.1,16	2.7	2.8	6	10.9	-11.4	10	1.5	-1.4	
7	11.0	11.0	6	4.8	4.5	8	0.9	-0.5	2	1.0	0.9	7	3.9	4.3	13	2.4	3.4	
8	7.9	-7.4	7	1.7	2.0	9	4.0	4.2	3	1.1	-0.8	8	5.6	-5.2	15	1.3	-1.5	
9	5.7	6.2	8	3.7	3.5	10	2.5	-2.8	4	0.9	-1.3	9	12.3	-11.8	16	4.3	-4.3	
10	0.9	-0.3	9	1.4	-1.6	11	1.0	2.0	7	2.6	3.1	10	3.2	2.5	17	2.8	3.0	
13	1.5	2.4	10	2.7	-2.1	12	4.8	-6.0	9	2.0	-2.0	11	1.3	1.5				
14	4.4	-5.4	11	2.2	1.8	15	1.9	2.2	11	1.4	0.7	12	2.0	-0.8	8.2,0	1.3	-0.7	
15	6.8	-7.4	12	1.5	1.7	16	1.2	1.2	12	0.6	-0.6	13	2.1	0.4	4	1.3	1.3	
16	1.3	-2.2	13	1.9	-1.6	17	2.5	-2.6	13	1.0	1.0	14	1.8	-1.6	6	2.1	-1.4	
17	2.4	1.6	16	3.7	-3.8	18	0.9	-0.9				16	1.9	1.8	7	3.2	-2.8	
18	1.6	-1.2	17	1.2	0.9				0.1,18	1.1	1.0	17	2.0	2.7	8	3.9	4.9	
22	1.2	0.7	18	1.5	0.5	0.1,12	0.8	-0.9	2	1.7	1.7	18	4.7	-5.6	9	1.5	-1.3	
23	1.7	1.5	22	1.3	-1.3	2	3.3	-3.4	3	0.7	0.8	22	2.5	2.9	10	1.6	-1.1	

TABLE 3.

Bond angles.

O ₁ PO ₂	115°	PC ₁ C ₂	109°	C ₂ C ₃ C ₄	115°	C ₁ C ₂ C ₃	117°	C ₁₀ C ₁₁ C ₁₂	117°
O ₁ PC ₁	113	PC ₁₃ C ₈	123	C ₃ C ₄ C ₅	125	C ₆ C ₇ C ₈	115	C ₁₁ C ₁₂ C ₁₃	123
O ₁ PC ₁₃	115	C ₁ C ₂ C ₇	124	C ₄ C ₅ C ₆	119	C ₇ C ₈ C ₉	120	C ₁₂ C ₁₃ C ₈	119
O ₂ PC ₁₃	110	C ₂ C ₇ C ₈	120	C ₅ C ₆ C ₇	116	C ₈ C ₉ C ₁₀	119	C ₁₃ C ₈ C ₉	120
O ₂ PC ₁	105	C ₇ C ₈ C ₁₃	119	C ₆ C ₇ C ₂	125	C ₉ C ₁₀ C ₁₁	122	PC ₁₃ C ₁₂	118
C ₁ PC ₁₃	101	C ₇ C ₂ C ₃	119						

¹ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

² Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

³ James, "The Optical Principle of the Diffraction of X-rays," G. Bell & Sons, Ltd., p. 292.

Results.—The co-ordinates of the atoms are given in Table 1, and the observed and calculated structure factors in Table 2. Figs. 1(a) and (b) show the final Fourier maps of the $0kl$ and $hk0$ projections, respectively. The molecule which is drawn in corresponds to the co-ordinates listed in Table 1. Fig. 2 shows the bond lengths and the numbering of the atoms. The bond angles are given in Table 3. Formal standard deviations are not given, since they are well known to be unreliable or misleading when applied to an analysis based merely on two projections, especially when one of the projections is badly

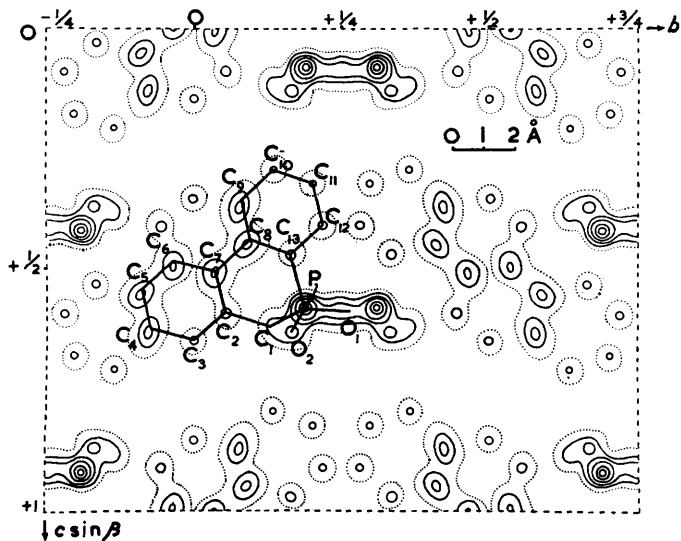


FIG. 1. (a) Projection of the contents of the unit cell down $[a]$.

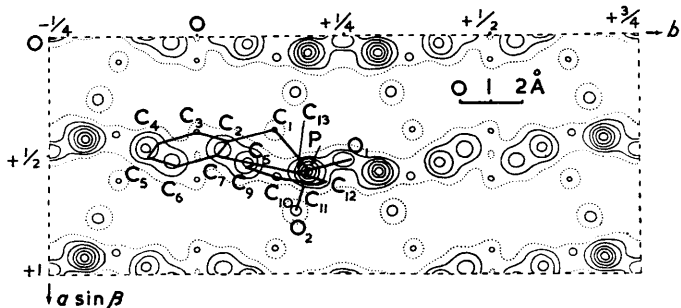


FIG. 1. (b) Projection of the contents of the unit cell down $[c]$.

(The contours are drawn at equal arbitrary intervals.)

resolved. The bond lengths given in Table 2 must be liable to errors which in some cases may amount to ± 0.05 Å, though, as is often the case, the agreement between chemical equivalent bonds suggests that the errors can frequently be less than this. The bond lengths agree well with the standard values⁴ and with those found in dibenzylphosphinic acid $(C_6H_5 \cdot CH_2)_2PO \cdot OH$.⁵ The mean C-C distance in the benzene rings is 1.394 Å. The length of the bond C_7-C_8 (1.57 Å) indicates that there is no conjugation between the benzene rings. The equality in length of the bonds $P-C_1$ (1.79 Å) and $P-C_{13}$ (1.80 Å)

⁴ Sutton *et al.*, "Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, No. 11.

⁵ Dunitz and Rollett, *Acta Cryst.*, 1956, **9**, 327.

suggests that there is little conjugation between the phosphorus atom and the adjacent benzene ring, though the P-C₁₃ distance is considerably shorter than that found between a phosphorus atom and an unconstrained benzene ring in 1,2-dimethyl-1,2-diphenyldi-phosphine disulphide (1.88 Å).⁶

One aspect of the molecule is shown in Fig. 2, and another in Fig. 1(b). It will be seen that, except for the two oxygen atoms, the atoms lie approximately in two planes with the atoms C₇ and C₈ common to both planes. One plane (A) contains the atoms C₁ to C₈; the other plane (B) contains the atoms C₇ to C₁₃ and the phosphorus atom. These planes are described by the equations:

$$(A) \quad 4.6848x' + 0.4194y' + 1.7180z' - 31.1071 = 0;$$

$$(B) \quad 4.9053x' - 1.1168y' + 0.5547z' - 21.4785 = 0.$$

These are the best planes through the six atoms of each benzene ring. They are obtained in terms of an orthogonal cell in which [b'] and [c'] correspond to the original [b] and [c],

TABLE 4.
Departures from planarity.

Distance (Å) of atom from Plane A		Distance (Å) of atom from Plane B		Distance (Å) of atom from Plane A		Distance (Å) of atom from Plane B	
C ₁	-0.03	C ₇	+0.08	C ₅	-0.03	C ₁₁	0
C ₂	+0.03	C ₈	-0.01	C ₆	+0.03	C ₁₂	0
C ₃	-0.03	C ₉	+0.01	C ₇	-0.03	C ₁₃	0
C ₄	+0.03	C ₁₀	0	C ₈	-0.03	P	+0.02

and in which [a'] is perpendicular to [b'] and [c']. The perpendicular distances of the various atoms from these planes are shown in Table 4. The angle between the two planes is 22°.

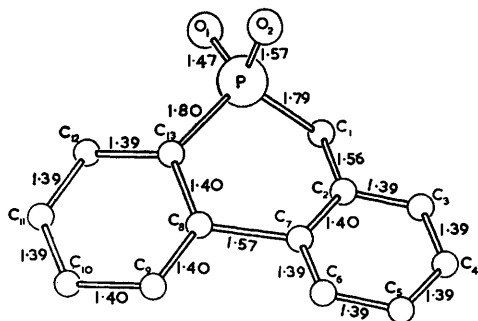


FIG. 2. The numbering of the atoms and the bond lengths.

Molecules are linked across a glide plane by means of hydrogen bonds O₂-H...O₁ of length 2.533 Å to form infinite zig-zags parallel to [a]. Other intermolecular distances are normal.

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⁶ Wheatley, *J.*, 1960, 523.