

The Crystal and Molecular Structure of 5-Hydroxydibenzo-5-*H*-phosphole-5-oxide, C₁₂H₉O₂P

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The crystal structure has been determined and refined by least-squares calculations to a final *R* value of 3.2% for 773 independent reflexions. The material crystallizes in the orthorhombic system, space group *P*2₁2₁2₁ (*D*₂^h), with cell parameters *a* = 13.76 (1), *b* = 12.07 (1), *c* = 6.27 (1) Å, *Z* = 4. The structure consists of helices of hydrogen-bonded molecules along [001].

Introduction

5-Hydroxydibenzo-5-*H*-phosphole-5-oxide, C₁₂H₉O₂P, was prepared by J. W. Cornforth and coworkers (Milestone Research Laboratory of Shell Research Ltd.). It was of interest to know the precise stereochemistry of the molecule and in particular the shape and dimensions of the five-membered phosphole ring. To our knowledge, only two structures of phosphole compounds have been published (Coggon, Engel, McPhail & Guin, 1970; Ozbirn, Jacobson & Clardy, 1971). As the dimensions of the phosphole rings of these two structures are different, it was impossible to predict the shape of the phosphole ring of our compound. Therefore we have determined its structure by single-crystal X-ray analysis.

Experimental

Crystals suitable for X-ray work were supplied by J. W. Cornforth. The material crystallizes from ethanol in the orthorhombic system as white needles of square cross-section, elongated along [001] and bounded by (110) and (1 $\bar{1}$ 0). Precession photographs showed the extinctions *h*00: *h* = 2*n*, 0*k*0: *k* = 2*n*, 00*l*: *l* = 2*n*, denoting space group *P*2₁2₁2₁ (*D*₂^h).

A crystal with dimensions 0.2 × 0.2 × 0.5 mm was mounted with the *a* axis parallel to the ϕ axis on a Nonius automatic three-circle diffractometer. A least-squares fit on θ and $-\theta$ values measured for 15 reflexions with Mo *K* α radiation (λ = 0.7107 Å) gave the following lattice constants: *a* = 13.76 (1), *b* = 12.07 (1), *c* = 6.27 (1) Å, *V* = 1042 Å³, *Z* = 4, μ (Mo *K* α) = 0.238 mm⁻¹. On the diffractometer, equipped with scintillation counter and pulse-height discriminator, 773 reflexions with intensities significantly above background and with $\theta \leq 25^\circ$ ($\sin \theta/\lambda \leq 0.595$ Å⁻¹) were measured using a θ -2 θ scan and Zr-filtered Mo *K* radiation.

The normal Lorentz and polarization corrections were applied; no correction was made for absorption (transmission range 89–95%). The structure amplitudes were obtained on a common arbitrary scale.

Solution and refinement of the structure

The structure was solved by means of the Fourier method described by Tollin (1970) and with the aid of our computer programs *PATTOR* and *QFUNC*,* which are applicable to any space group. In the absence of sufficient data to derive the shape of the five-membered phosphole ring, we assumed for the starting model normal bond lengths and C–C–C angles in the 5-ring of 114° (C–P–C: 86°). The orientation of the molecule was readily determined with the program *PATTOR*. Runs of the translation seeking program, *QFUNC*, for the three 2₁ symmetry axes gave the following figures for the origin of the starting model which was arbitrarily chosen at the phosphorus atom:

$$\begin{array}{lll} 2_1(z): & x=0.35 & y=0.425 & z=0.425 \\ 2_1(y): & x=0.35 & & z=0.425 \\ 2_1(x): & & y=0.425 & z=0.425 \end{array}$$

The molecular origin was thus clearly established at 0.35, 0.425, 0.425. Full-matrix rigid-group least-squares refinement of this model resulted in *R* = 100% × $\sum ||F_o| - |F_c|| / \sum |F_o| = 14.2\%$ (*F*_o and *F*_c: observed and calculated structure factors). Full-matrix refinement of individual isotropic atoms gave *R* = 7.3%. Inclusion of the hydrogen atoms in calculated positions together with refinement of anisotropic temperature factors for the non-hydrogen atoms reduced *R* to a final value of 3.2%.

No shift in the final cycle of least-squares refinement exceeded 0.1 × the corresponding standard deviation. A difference electron density synthesis at the final stage gave no clear indication of the position of the hydrogen atom of the hydroxy group.

The final values of $|F_o|$ and $|F_c|$ are given in Table 1; the final atomic parameters and their standard deviations are given in Table 2.

For the refinement we used the program *NUCLS* [J. A. Ibers's version of *ORFLS* (Busing, Martin & Levy,

* Programs written by D. Bright.

1962)]. Throughout the refinement neutral atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were employed. The function min-

imized was $\sum w(|F_o| - |F_c|)^2$. The weight, w , was taken to be $1/\sigma^2(F_o)$, assuming that $\sigma(F_o)/F_o = \sigma(I)/(2I)$. The standard deviation of an observed intensity, $\sigma(I)$, was

Table 1. Observed and calculated structure amplitudes (electrons $\times 10$) for 5-hydroxydibenzo-5-H-phosphole-5-oxide

K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c	K	L	F _o	F _c
0	2	271	273	5	0	81	82	10	3	68	67	1	4	35	32	5	2	192	152	8	0	170	169
0	4	108	105	5	1	150	151	7	5	137	139	11	0	45	44	1	2	493	473	5	3	92	90
0	6	158	157	5	2	239	230	8	0	71	76	11	0	218	216	1	3	223	216	5	4	127	132
1	1	229	218	5	3	320	293	11	1	50	46	1	1	83	88	5	5	57	61	8	2	161	189
1	2	38	36	5	4	437	436	11	2	105	123	1	1	154	156	6	0	156	159	2	3	66	67
1	3	222	215	5	5	512	511	11	3	194	188	1	2	224	219	6	1	138	119	2	1	226	238
1	4	145	151	5	6	607	606	11	4	277	273	1	3	353	351	6	2	121	99	3	0	134	140
1	5	282	291	5	7	702	701	11	5	362	358	1	4	442	438	6	3	136	101	3	1	226	238
1	6	152	159	5	8	807	806	11	6	451	447	1	5	531	527	6	4	172	169	3	0	172	169
2	1	342	331	5	9	912	911	11	7	540	536	1	6	620	616	7	0	15	26	3	3	16	15
2	2	215	212	5	10	1017	1016	11	8	629	625	1	7	709	705	7	1	89	92	3	3	16	15
2	3	152	149	5	11	1122	1121	11	9	718	714	1	8	808	804	7	2	146	156	3	5	73	70
2	4	102	99	5	12	1227	1226	11	10	807	803	1	9	897	893	7	3	137	146	3	6	71	68
2	5	258	255	5	13	1332	1331	11	11	896	892	1	10	986	982	7	4	128	132	3	7	69	66
2	6	152	149	5	14	1437	1436	11	12	985	981	1	11	1075	1071	7	5	119	122	3	8	67	64
2	7	302	299	5	15	1542	1541	11	13	1074	1070	1	12	1164	1160	7	6	110	112	3	9	65	62
2	8	182	179	5	16	1647	1646	11	14	1163	1159	1	13	1253	1249	7	7	101	103	3	10	63	60
2	9	332	329	5	17	1752	1751	11	15	1252	1248	1	14	1342	1338	7	8	92	94	3	11	61	58
2	10	192	189	5	18	1857	1856	11	16	1341	1337	1	15	1431	1427	7	9	83	85	3	12	59	56
2	11	342	339	5	19	1962	1961	11	17	1430	1426	1	16	1520	1516	7	10	74	76	3	13	57	54
2	12	202	199	5	20	2067	2066	11	18	1519	1515	1	17	1609	1605	7	11	65	67	3	14	55	52
2	13	352	349	5	21	2172	2171	11	19	1608	1604	1	18	1698	1694	7	12	56	58	3	15	53	50
2	14	212	209	5	22	2277	2276	11	20	1697	1693	1	19	1787	1783	7	13	47	49	3	16	51	48
2	15	362	359	5	23	2382	2381	11	21	1786	1782	1	20	1876	1872	7	14	38	40	3	17	49	46
2	16	222	219	5	24	2487	2486	11	22	1875	1871	1	21	1965	1961	7	15	29	31	3	18	47	44
2	17	372	369	5	25	2592	2591	11	23	1964	1960	1	22	2054	2050	7	16	20	22	3	19	45	42
2	18	232	229	5	26	2697	2696	11	24	2053	2049	1	23	2143	2139	7	17	11	13	3	20	43	40
2	19	382	379	5	27	2802	2801	11	25	2142	2138	1	24	2232	2228	7	18	2	4	3	21	41	38
2	20	242	239	5	28	2907	2906	11	26	2231	2227	1	25	2321	2317	7	19	1	5	3	22	39	36
2	21	392	389	5	29	3012	3011	11	27	2320	2316	1	26	2410	2406	7	20	1	6	3	23	37	34
2	22	252	249	5	30	3117	3116	11	28	2409	2405	1	27	2499	2495	7	21	1	7	3	24	35	32
2	23	402	399	5	31	3222	3221	11	29	2498	2494	1	28	2588	2584	7	22	1	8	3	25	33	30
2	24	262	259	5	32	3327	3326	11	30	2587	2583	1	29	2677	2673	7	23	1	9	3	26	31	28
2	25	412	409	5	33	3432	3431	11	31	2676	2672	1	30	2766	2762	7	24	1	10	3	27	29	26
2	26	272	269	5	34	3537	3536	11	32	2765	2761	1	31	2855	2851	7	25	1	11	3	28	27	24
2	27	422	419	5	35	3642	3641	11	33	2854	2850	1	32	2944	2940	7	26	1	12	3	29	25	22
2	28	282	279	5	36	3747	3746	11	34	2943	2939	1	33	3033	3029	7	27	1	13	3	30	23	20
2	29	432	429	5	37	3852	3851	11	35	3032	3028	1	34	3122	3118	7	28	1	14	3	31	21	18
2	30	292	289	5	38	3957	3956	11	36	3121	3117	1	35	3211	3207	7	29	1	15	3	32	19	16
2	31	442	439	5	39	4062	4061	11	37	3210	3206	1	36	3300	3296	7	30	1	16	3	33	17	14
2	32	302	299	5	40	4167	4166	11	38	3300	3296	1	37	3389	3385	7	31	1	17	3	34	15	12
2	33	452	449	5	41	4272	4271	11	39	3389	3385	1	38	3478	3474	7	32	1	18	3	35	13	10
2	34	312	309	5	42	4377	4376	11	40	3478	3474	1	39	3567	3563	7	33	1	19	3	36	11	8
2	35	462	459	5	43	4482	4481	11	41	3567	3563	1	40	3656	3652	7	34	1	20	3	37	9	6
2	36	322	319	5	44	4587	4586	11	42	3656	3652	1	41	3745	3741	7	35	1	21	3	38	7	4
2	37	472	469	5	45	4692	4691	11	43	3745	3741	1	42	3834	3830	7	36	1	22	3	39	5	2
2	38	332	329	5	46	4797	4796	11	44	3834	3830	1	43	3923	3919	7	37	1	23	3	40	3	0
2	39	482	479	5	47	4902	4901	11	45	3923	3919	1	44	4012	4008	7	38	1	24	3	41	1	0
2	40	342	339	5	48	5007	5006	11	46	4012	4008	1	45	4101	4097	7	39	1	25	3	42	0	0
2	41	492	489	5	49	5112	5111	11	47	4101	4097	1	46	4190	4186	7	40	1	26	3	43	0	0
2	42	352	349	5	50	5217	5216	11	48	4190	4186	1	47	4279	4275	7	41	1	27	3	44	0	0
2	43	502	499	5	51	5322	5321	11	49	4279	4275	1	48	4368	4364	7	42	1	28	3	45	0	0
2	44	362	359	5	52	5427	5426	11	50	4368	4364	1	49	4457	4453	7	43	1	29	3	46	0	0
2	45	512	509	5	53	5532	5531	11	51	4457	4453	1	50	4546	4542	7	44	1	30	3	47	0	0
2	46	372	369	5	54	5637	5636	11	52	4546	4542	1	51	4635	4631	7	45	1	31	3	48	0	0
2	47	522	519	5	55	5742	5741	11	53	4635	4631	1	52	4724	4720	7	46	1	32	3	49	0	0
2	48	382	379	5	56	5847	5846	11	54	4724	4720	1	53	4813	4809	7	47	1	33	3	50	0	0
2	49	532	529	5	57	5952	5951	11	55	4813	4809	1	54	4902	4898	7	48	1	34	3	51	0	0
2	50	392	389	5	58	6057	6056	11	56	4902	4898	1	55	4991	4987	7	49	1	35	3	52	0	0
2	51	542	539	5	59	6162	6161	11	57	4991	4987	1	56	5080	5076	7	50	1	36	3	53	0	0
2	52	402	399	5	60	6267	6266	11	58	5080	5076	1	57	5169	5165	7	51	1	37	3	54	0	0
2	53	552	549	5	61	6372	6371	11	59	5169	5165	1	58	5258	5254	7	52	1	38	3	55	0	0
2	54	412	409	5	62	6477	6476	11	60	5258	5254	1	59	5347	5343	7	53	1	39	3	56	0	0
2	55	562	559	5	63	6582	6581	11	61	5347	5343	1	60	5436	5432	7	54	1	40	3	57	0	0
2	56	422	419	5	64	6687	6686	11	62	5436	5432	1	61	5525	5521	7	55	1	41	3	58	0	0
2	57	572	569	5	65	6792	6791	11	63	5525	5521	1	62	5614	5610	7	56	1	42	3	59	0	0</

estimated from counting statistics. Weight analyses based on $\sin \theta/\lambda$ and F_o ranges indicated that this scheme was satisfactory.

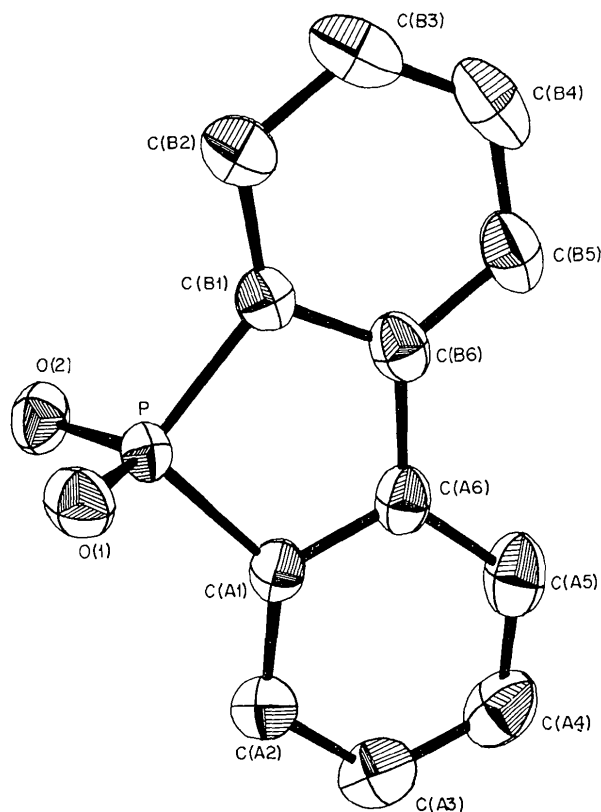


Fig. 1. The 5-hydroxydibenzo-5-*H*-phosphole-5-oxide molecule (vibration ellipsoids are at 40% probability).

Table 3. Bond lengths (Å) and angles (°)

P—O(1)	1.481 (2)	P—O(2)	1.553 (3)
P—C(A1)	1.781 (4)	P—C(B1)	1.800 (4)
C(A6)—C(B6)	1.479 (5)		
C(A1)—C(A2)	1.388 (5)	C(B1)—C(B2)	1.386 (5)
C(A2)—C(A3)	1.394 (5)	C(B2)—C(B3)	1.397 (5)
C(A3)—C(A4)	1.397 (6)	C(B3)—C(B4)	1.380 (6)
C(A4)—C(A5)	1.372 (6)	C(B4)—C(B5)	1.392 (7)
C(A5)—C(A6)	1.399 (5)	C(B5)—C(B6)	1.386 (5)
C(A6)—C(A1)	1.401 (5)	C(B6)—C(B1)	1.396 (5)

Table 3 (cont.)

O(1)—P—O(2)	113.2 (1)	C(A1)—P—C(B1)	93.4 (2)
O(1)—P—C(A1)	117.7 (2)	O(1)—P—C(B1)	111.8 (2)
O(2)—P—C(A1)	106.7 (2)	O(2)—P—C(B2)	112.4 (2)
P—C(A1)—C(A2)	128.8 (3)	P—C(B1)—C(B2)	129.0 (3)
P—C(A1)—C(A6)	109.5 (3)	P—C(B1)—C(B6)	109.4 (3)
C(A5)—C(A6)—C(B6)	127.5 (3)	C(B5)—C(B6)—C(A6)	126.6 (4)
C(A1)—C(A6)—C(B6)	114.0 (3)	C(B1)—C(B6)—C(A6)	113.6 (3)
C(A6)—C(A1)—C(A2)	121.7 (3)	C(B6)—C(B1)—C(B2)	121.5 (3)
C(A1)—C(A2)—C(A3)	118.7 (4)	C(B1)—C(B2)—C(B3)	118.0 (4)
C(A2)—C(A3)—C(A4)	120.0 (4)	C(B2)—C(B3)—C(B4)	120.8 (4)
C(A3)—C(A4)—C(A5)	120.8 (4)	C(B3)—C(B4)—C(B5)	120.8 (4)
C(A4)—C(A5)—C(A6)	120.3 (4)	C(B4)—C(B5)—C(B6)	118.9 (4)
C(A5)—C(A6)—C(A1)	118.5 (4)	C(B5)—C(B6)—C(B1)	119.9 (4)

Description of the structure and discussion

The molecule and the atomic numbering scheme are shown in Fig. 1 (Johnson, 1965); the bond distances and angles and their estimated standard deviations, calculated by ORFFE (Busing, Martin & Levy, 1964), are given in Table 3.

The two benzo rings are essentially equivalent; the corresponding bond lengths and angles are all equal within experimental error. The values of the distances and angles indicate electron delocalization in the benzo rings. These structural parameters compare well with the corresponding distances and angles in other heteroaromatics such as dibenzofuran (Dideberg, Dupont & André, 1972), carbazole (Kurahashi, Fukuyo, Shimada, Furusaki & Nitta, 1969), dibenzothiophene (Schaffrin & Trotter, 1970), dibenzoselenophene (Hope, Knobler & McCullough, 1970) and 9-fluorenone (Luss & Smith, 1972). In these compounds the dihedral angles between the five-membered heteroaromatic ring and the benzo rings are about 1°; we find 1.2 (2)° and 2.0 (2)° for the angles between the phosphole ring and ring A and ring B, respectively. Apparently, these dihedral angles are easily affected by packing forces.

Ignoring the difference between the oxo and the hydroxy group, the molecule has potential *mm*2 symmetry. This potential molecular symmetry is reduced, however, by the phosphorus atom, which deviates from the best least-squares plane through all carbon atoms by 0.064 (1) Å, while all carbon atoms lie within 0.018 (4) Å of that plane. The dihedral angle between the P—O(1)—O(2) plane and the plane through all carbon atoms is 85.5 (1)°.

The potential symmetry is further reduced by the asymmetry of the phosphorus-carbon bonds [P—C(A1): 1.781 (4) Å, P—C(B1): 1.800 (4) Å]. This effect is probably caused by crystal packing. A similar situation was found in phospholanic acid (Alver & Kjøge, 1969) [P—C=1.776 (16) and 1.797 (20) Å], which crystallizes with a similar packing system. The phosphorus-carbon bonds [1.781 (4), 1.800 (4) Å] are shorter than those found in triphenylphosphorus, 1.828 (3) Å (Daly, 1964), and in 1,2,5-triphenylphosphole, 1.822 Å (Ozbiir, Jacobson & Clardy, 1971), but agree reasonably well with those in 1-benzylphosphole, 1.783 Å (Coggon, Engel, McPhail & Quin, 1970). We do not

have a valid chemical explanation for these differences.

Although we were unable to locate the hydroxyl hydrogen atom, the oxo [O(1)] and hydroxyl [O(2)] groups are clearly distinguished by the P–O distances of 1.482 (2) Å for the 'double' bond (oxo) and 1.533 (3) Å for the 'single' bond (hydroxy). These distances are similar to those found in phosphoric acid (Furberg, 1955), in a number of phosphates (for references, see *Structure Reports*), and in phospholanic acid (Alver & Kjøge, 1969).

A projection of the unit cell on (101) is shown in Fig. 2. The molecules are linked by hydrogen bridges of 2.500 (6) Å between the oxygen of the hydroxyl group of one molecule and the oxo atom of the next to form infinite helices around the screw axes parallel to *c*. This arrangement is also found in phospholanic acid (Alver & Kjøge, 1969), in which the hydrogen bond is 2.48 Å. A similar short hydrogen bond occurs in phosphoric acid (Furberg, 1955) and in a number of phosphates (for references see *Structure Reports*).

Disregarding the intermolecular hydrogen bond, the molecules are well separated. The shortest intermolecular C–O distances are O(1)–C(A2') and O(1)–C(A4'), being 3.299 (6) and 3.313 (6) Å, respectively; all other intermolecular contacts between carbon and oxygen are above 3.40 Å. The shortest non-bonding C–C interactions are between C(A3)–C(B1'), 3.590 (6) Å, and between C(5A)–C(B3'), 3.618 (6) Å, [C(B1') and C(B3') at $x, y, 1+z$], but the corresponding H...H distances are longer than 3.70 Å. All other C...C distances are longer than 3.70 Å.

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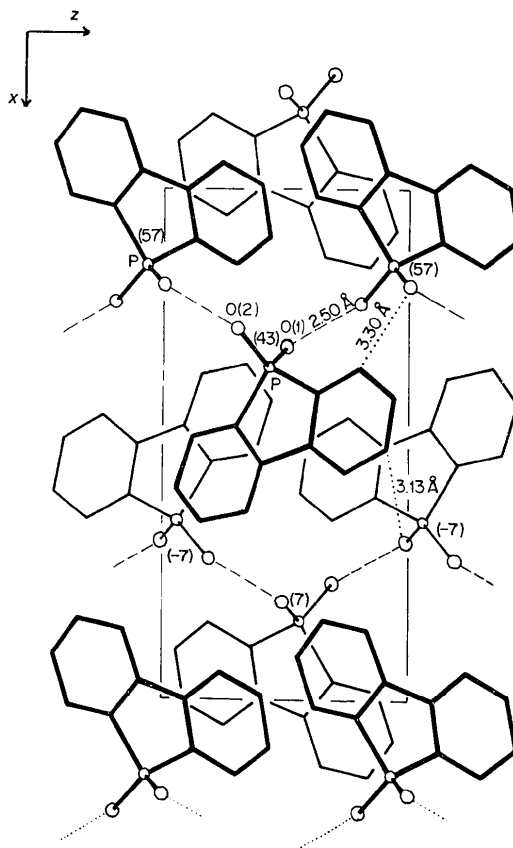


Fig. 2. 5-Hydroxydibenzo-5-*H*-phosphole-5-oxide projected on (101). Hydrogen-bonding scheme and shortest C–O distances are shown (*Y* values of phosphorus atoms are given in parentheses).