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The Crystal and Molecular Structure of 5-Hydroxydibenzo-5-*H*-phosphole-5-oxide, $C_{12}H_9O_2P$

BY J. J. DE BOER AND D. BRIGHT

Koninklijke/Shell-Laboratorium, Amsterdam, (Shell Research B.V.), The Netherlands

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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 $P2_12_12_1$ (D_2^4), with cell parameters $a=13{\cdot}76$ (1), $b=12{\cdot}07$ (1), $c=6{\cdot}27$ (1) Å, $Z=4$. The structure consists of helices of hydrogen-bonded molecules along [001].

Introduction

5-Hydroxydibenzo-5-*H*-phosphole-5-oxide, $C_{12}H_9O_2P$, was prepared by J. W. Cornforth and coworkers (Milstead 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 $h00$: $h=2n$, $0k0$: $k=2n$, $00l$: $l=2n$, denoting space group $P2_12_12_1$ (D_2^4).

A crystal with dimensions $0{\cdot}2\times0{\cdot}2\times0{\cdot}5$ 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 $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) gave the following lattice constants: $a=13{\cdot}76$ (1), $b=12{\cdot}07$ (1), $c=6{\cdot}27$ (1) Å, $V=1042$ Å^3, $Z=4$, μ(Mo $K\alpha$)$=0{\cdot}238$ mm^{-1}. On the diffractometer, equipped with scintillation counter and pulse-height discriminator, 773 reflexions with intensities significantly above background and with $\theta\leq25°$ ($\sin\theta/\lambda\leq0{\cdot}595$ Å^{-1}) were measured using a θ–2θ 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 2_1 symmetry axes gave the following figures for the origin of the starting model which was arbitrarily chosen at the phosphorus atom:

$2_1(z)$: $x=0{\cdot}35$	$y=0{\cdot}425$	
$2_1(y)$: $x=0{\cdot}35$		$z=0{\cdot}425$
$2_1(x)$:	$y=0{\cdot}425$	$z=0{\cdot}425$.

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 $R=100\%\times\sum||F_o|-|F_c||/\sum|F_o|=14{\cdot}2\%$ (F_o and F_c: observed and calculated structure factors). Full-matrix refinement of individual isotropic atoms gave $R=7{\cdot}3\%$. 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 minimized 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* × 10) *for 5-hydroxydibenzo-5-H-phosphole-5-oxide*

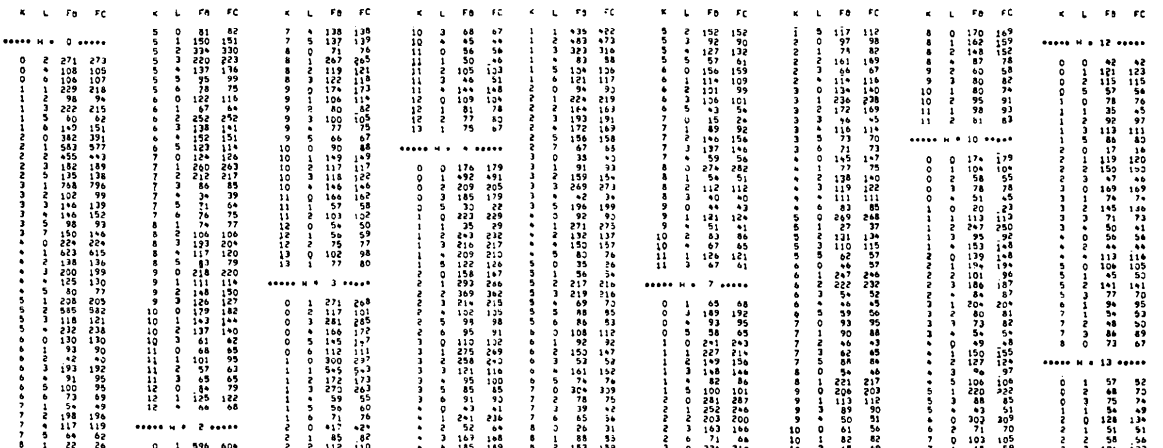

Table 2. *5-Hydroxydibenzo-5-H-phosphole-5-oxide final least-squares parameters*

The form of the anisotropic thermal ellipsoid is given by $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Numbers in parentheses here and elsewhere are estimated standard deviations in the least significant digits.

	Fractional coordinates			Anisotropic vibration parameters					
	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0·34947 (7)	0·43136 (8)	0·43602 (16)	0·00354 (4)	0·00551 (6)	0·01910 (24)	0·00043 (5)	−0·00025 (11)	0·0010 (3)
O(1)	0·31081 (16)	0·53943 (18)	0·5085 (4)	0·00590 (14)	0·00688 (19)	0·0274 (8)	0·00141 (14)	0·0019 (3)	−0·0000 (3)
O(2)	0·27482 (17)	0·36284 (21)	0·3054 (4)	0·00485 (15)	0·00779 (20)	0·0281 (8)	−0·00085 (15)	−0·0022 (3)	0·0017 (4)
C(*A*1)	0·3984 (3)	0·3406 (3)	0·6325 (6)	0·0046 (2)	0·0059 (3)	0·0195 (11)	0·0006 (2)	−0·0011 (4)	−0·0016 (5)
C(*A*2)	0·3515 (3)	0·2902 (3)	0·8028 (6)	0·0063 (2)	0·0059 (3)	0·0241 (11)	0·0003 (3)	0·0005 (6)	0·0003 (5)
C(*A*3)	0·4058 (3)	0·2243 (3)	0·9411 (8)	0·0097 (3)	0·0066 (3)	0·0275 (13)	0·0017 (3)	−0·0000 (7)	−0·0005 (7)
C(*A*4)	0·5058 (4)	0·2123 (3)	0·9104 (8)	0·0094 (3)	0·0076 (4)	0·0303 (15)	0·0027 (3)	−0·0033 (7)	0·0019 (6)
C(*A*5)	0·5515 (3)	0·2625 (3)	0·7416 (8)	0·0063 (3)	0·0077 (3)	0·0374 (16)	0·0025 (3)	−0·0031 (6)	−0·0013 (7)
C(*A*6)	0·4984 (3)	0·3277 (3)	0·5985 (6)	0·0048 (2)	0·0059 (3)	0·0245 (12)	0·0010 (2)	−0·0019 (5)	−0·0024 (5)
C(*B*1)	0·4639 (2)	0·4463 (3)	0·2999 (6)	0·0043 (2)	0·0057 (3)	0·0219 (11)	−0·0001 (2)	−0·0001 (4)	−0·0013 (5)
C(*B*2)	0·4857 (3)	0·5083 (3)	0·1203 (6)	0·0061 (3)	0·0076 (3)	0·0272 (15)	−0·0007 (2)	0·0023 (5)	−0·0005 (6)
C(*B*3)	0·5825 (3)	0·5122 (4)	0·0532 (8)	0·0079 (3)	0·0104 (4)	0·0361 (15)	−0·0016 (3)	0·0066 (7)	−0·0004 (9)
C(*B*4)	0·6538 (3)	0·4548 (4)	0·1616 (9)	0·0047 (2)	0·0132 (5)	0·0492 (18)	−0·0013 (3)	0·0047 (7)	−0·0044 (9)
C(*B*5)	0·6313 (3)	0·3921 (4)	0·3411 (8)	0·0042 (2)	0·0109 (4)	0·0379 (16)	0·0006 (3)	0·0006 (5)	−0·0024 (7)
C(*B*6)	0·5357 (2)	0·3881 (3)	0·4104 (6)	0·0044 (2)	0·0068 (3)	0·0257 (12)	0·0003 (2)	0·0004 (5)	−0·0034 (5)

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

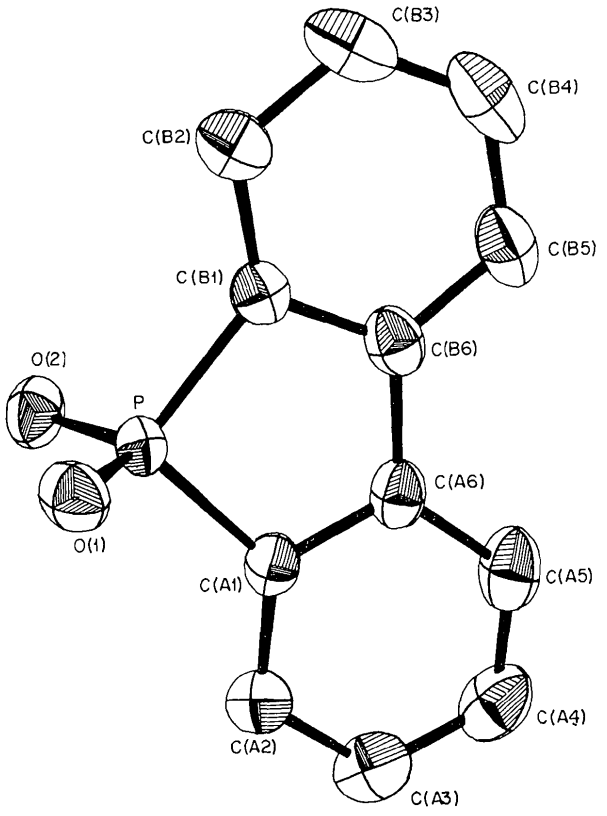

Fig. 1. The 5-hydroxydibenzo-5-*H*-phosphole-5-oxide molecule (vibration ellipsoids are at 40% probability).

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

P——O(1)	1·481 (2)	P——O(2)	1·553 (3)
P——C(*A*1)	1·781 (4)	P——C(*B*1)	1·800 (4)
C(*A*6)–C(*B*6)	1·479 (5)		
C(*A*1)–C(*A*2)	1·388 (5)	C(*B*1)–C(*B*2)	1·386 (5)
C(*A*2)–C(*A*3)	1·394 (5)	C(*B*2)–C(*B*3)	1·397 (5)
C(*A*3)–C(*A*4)	1·397 (6)	C(*B*3)–C(*B*4)	1·380 (6)
C(*A*4)–C(*A*5)	1·372 (6)	C(*B*4)–C(*B*5)	1·392 (7)
C(*A*5)–C(*A*6)	1·399 (5)	C(*B*5)–C(*B*6)	1·386 (5)
C(*A*6)–C(*A*1)	1·401 (5)	C(*B*6)–C(*B*1)	1·396 (5)

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(*A*1): 1·781 (4) Å, P–C(*B*1): 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 (Ozbirn, Jacobson & Clardy, 1971), but agree reasonably well with those in 1-benzylphosphole, 1·783 Å (Coggon, Engel, McPhail & Quin, 1970). We do not

Table 3 (*cont.*)

O(1)—P——O(2)	113·2 (1)	C(A1)–P——C(*B*1)	93·4 (2)
O(1)—P——C(*A*1)	117·7 (2)	O(1)—P——C(*B*1)	111·8 (2)
O(2)—P——C(*A*1)	106·7 (2)	O(2)—P——C(*B*2)	112·4 (2)
P——C(*A*1)–C(*A*2)	128·8 (3)	P——C(*B*1)–C(*B*2)	129·0 (3)
P——C(*A*1)–C(*A*6)	109·5 (3)	P——C(*B*1)–C(*B*6)	109·4 (3)
C(*A*5)–C(*A*6)–C(*B*6)	127·5 (3)	C(*B*5)–C(*B*6)–C(*A*6)	126·6 (4)
C(*A*1)–C(*A*6)–C(*B*6)	114·0 (3)	C(*B*1)–C(*B*6)–C(*A*6)	113·6 (3)
C(*A*6)–C(*A*1)–C(*A*2)	121·7 (3)	C(*B*6)–C(*B*1)–C(*B*2)	121·5 (3)
C(*A*1)–C(*A*2)–C(*A*3)	118·7 (4)	C(*B*1)–C(*B*2)–C(*B*3)	118·0 (4)
C(*A*2)–C(*A*3)–C(*A*4)	120·0 (4)	C(*B*2)–C(*B*3)–C(*B*4)	120·8 (4)
C(*A*3)–C(*A*4)–C(*A*5)	120·8 (4)	C(*B*3)–C(*B*4)–C(*B*5)	120·8 (4)
C(*A*4)–C(*A*5)–C(*A*6)	120·3 (4)	C(*B*4)–C(*B*5)–C(*B*6)	118·9 (4)
C(*A*5)–C(*A*6)–C(*A*1)	118·5 (4)	C(*B*5)–C(*B*6)–C(*B*1)	119·9 (4)

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(*A*2′) and O(1)–C(*A*4′), 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(*A*3)–C(*B*1′), 3·590 (6) Å, and between C(5*A*)–C(*B*3′), 3·618 (6) Å, [C(*B*1′) and C(*B*3′) 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.

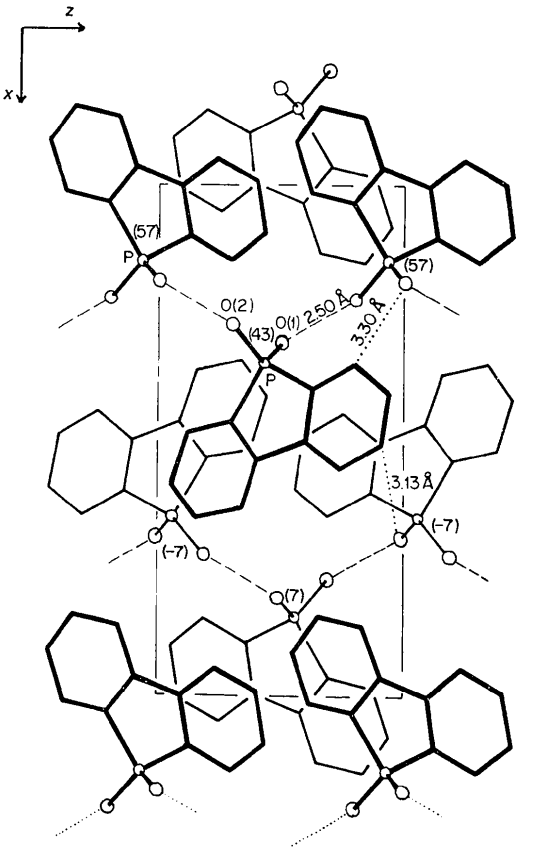

Fig. 2. 5-Hydroxydibenzo-5-*H*-phosphole-5-oxide projected on (101). Hydrogen-bonding scheme and shortest C–O distances are shown (*Y* values of phosphorus atoms are given in parentheses).

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