

The Crystal Structure of Dibenzyl Phosphoric Acid.*

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Dibenzyl-phosphoric acid, $(C_6H_5CH_2)_2PO_4H$, forms crystals of symmetry $P2_1/a$ with $a = 20.29$, $b = 5.71$, $c = 12.65$ Å, $\beta = 103^\circ 13'$. The crystal structure has been determined, and refined by Fourier and least-squares analysis of 2951 general (hkl) data. The dimensions and form of the diesterified phosphate group in this structure are compared with those used by Crick & Watson in the corresponding part of their model for deoxyribonucleic acid. There is a striking similarity between the two groups, although some of the precise dimensions given by this analysis are significantly different from those which had been assumed.

1. Introduction

All forms of nucleic acid which have so far been investigated have been found to be chains of alternating diesterified phosphate and ribose, or 2-deoxyribose, groups with a purine or a pyrimidine base attached to each sugar residue. The base is linked to the C_1 atom of the sugar and the phosphate groups to the C_3 and C_5 atoms (Brown & Todd, 1952). There are at least five different frequently occurring bases and two forms of sugar, but the evidence suggests strongly that most of the phosphate groups in all nucleic acids are diesterified. Accurate knowledge of the dimensions of this group is therefore essential for the construction of a precise model of any nucleic acid, and may provide a means of discrimination between suggested structures.

Hitherto no crystal structure containing a diesterified phosphate group has been determined. It was consequently necessary for Pauling & Corey (1953) and Crick & Watson (1954) to assume dimensions for this group in constructing their models for deoxyribonucleic acid. This paper describes the precise determination of the crystal structure of dibenzyl phosphoric acid, $(C_6H_5CH_2)_2PO_4H$, and gives a comparison between the dimensions found in this structure and those assumed in earlier work.

2. Experimental

A sample of dibenzyl phosphoric acid was very kindly made available to us by Prof. A. R. Todd and Dr D. McG. Brown of the Organic Chemistry Laboratories in the University of Cambridge. Monoclinic crystals were grown from solutions in ether and crystallo-

graphic data were obtained from oscillation and Weissenberg photographs.

Space group: $P2_1/a$.

$a = 20.287 \pm 0.040$, $b = 5.709 \pm 0.010$, $c = 12.648 \pm 0.020$ Å,
 $\beta = 103^\circ 13' \pm 0^\circ 10'$.

Number of molecules per unit cell: 4.

Calculated density: 1.29_6 g.cm.⁻³.

The indicated errors are estimates of standard deviations.

The unit-cell dimensions were determined from the spacings of high-order reflections on $(h0l)$ and $(hk0)$ Weissenberg photographs calibrated with NaCl powder lines. All the reflections measured were produced by Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations of wavelengths taken to be 1.5405 Å and 1.5443 Å, respectively.

Intensities were determined for 2951 Cu $K\alpha$ X-ray reflections by visual comparison between equi-inclination multiple-film Weissenberg photographs and an intensity scale. The layer-lines surveyed were $(h0l)$, ..., $(h5l)$ and $(hk0)$, ..., $(hk3)$. The intensities obtained from the various exposures of each single layer were placed on a common scale before being recorded on punched cards, so that they could be converted to F_o^2 , the various layers brought to the same absolute scale, multiple observations averaged, and the F_o^2 reduced to F_o values by means of IBM equipment. This procedure was found to be both fast and reliable. No gross errors in the F_o values were later discovered.

The intersecting layers were correlated by least squares; the residuals indicated a standard deviation of 12% for an F_o derived from one layer only. The intensities were placed on absolute scale by Wilson's method, which indicated a temperature factor of $\exp \{4.0 \sin^2 \theta / \lambda^2\}$.

3. Determination of the structure

Because of the short b axis of 5.7 Å it was expected that at least the x and z coordinates of the phosphorus

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atom could be found from the ($h0l$) Patterson projection. It was found that this projection indicated clearly the P-P and P-O interactions, and by superposing two copies of the map with the origin of one at the P-P interaction on the other it was possible to locate the two non-equivalent benzyl groups approximately. Chemical considerations then led to the positions of all atoms.

The trial structure set up on the basis of the Patterson synthesis was such that no two atoms were separated by less than 0.7 Å in projection. It was consequently efficient to refine this projection by least squares, using no off-diagonal terms save those for the x and z parameters of the same atom. Five stages of least-squares refinement were calculated in this way, by means of the programme for automatic least-squares iteration of structures of class $2/m$ by the ElectroData computer which has been described by Lavine & Rollett (see § 4, para. 2). The reliability factor $R = \Sigma|\Delta F| \div \Sigma|F_o|$ fell from 0.34 for the first set of structure factors to 0.21 for the fifth and last. The whole refinement of this projection occupied 10 hr. of machine time.

The ($hk0$) Patterson synthesis was next calculated. Because the x coordinate of the phosphorus atom was known it was possible to locate the P-P interactions with reasonable certainty. A fourfold superposition of this map then gave the y coordinates of the oxygen atoms and all atoms of one benzyl group. The other benzyl group was not resolved from the phosphate group and it was necessary to derive its position from chemical considerations. A trial structure based on these deductions gave good qualitative agreement with $R = 0.54$. This trial was refined by two F_o and two

($F_o - F_c$) syntheses, after which R had fallen to 0.30. It was decided that there was no likelihood that the resulting atomic positions were seriously wrong, and that accurate parameters would be obtained most rapidly by use of general (hkl) data to resolve the atoms which overlap in projection. The structure so found is shown, as viewed down the b -axis, in Fig. 1. The molecule M is related to S , C , and G by the screw axis, the centre, and the glide plane respectively.

4. Three-dimensional refinement

The first part of the refinement was carried out with 1143 selected hkl data. All planes with $\sin \theta < 0.6$ were used and also those planes with $0.6 \leq \sin \theta < 0.7$ and $F_o \geq 16$ electrons/unit cell. Structure factors were computed by IBM equipment for 15 of the 19 P, O and C atoms of the molecule with the form factors given by McWeeny (1951) for O and C and the form factor in *Internationale Tabellen* (1935) for P. The signs given by these were used for F_o line syntheses at the x and z coordinates of the 4 C atoms omitted. The contributions of these atoms were then added to the structure factors and the totals used for least-squares refinement of the positions. The weighting system used in this and the succeeding five stages of least-squares was that adopted by Hughes (1941), namely

$$\begin{aligned} \sqrt{w} &= 1/|F_o| \quad \text{when } |F_o| > 4F_{\text{min.}}, \\ \sqrt{w} &= 1/|4F_{\text{min.}}| \quad \text{when } |F_o| \leq 4F_{\text{min.}}; \end{aligned}$$

$4F_{\text{min.}} = 6.4$ electrons/unit cell was used throughout. Two further stages of least-squares were calculated with these 1143 data.

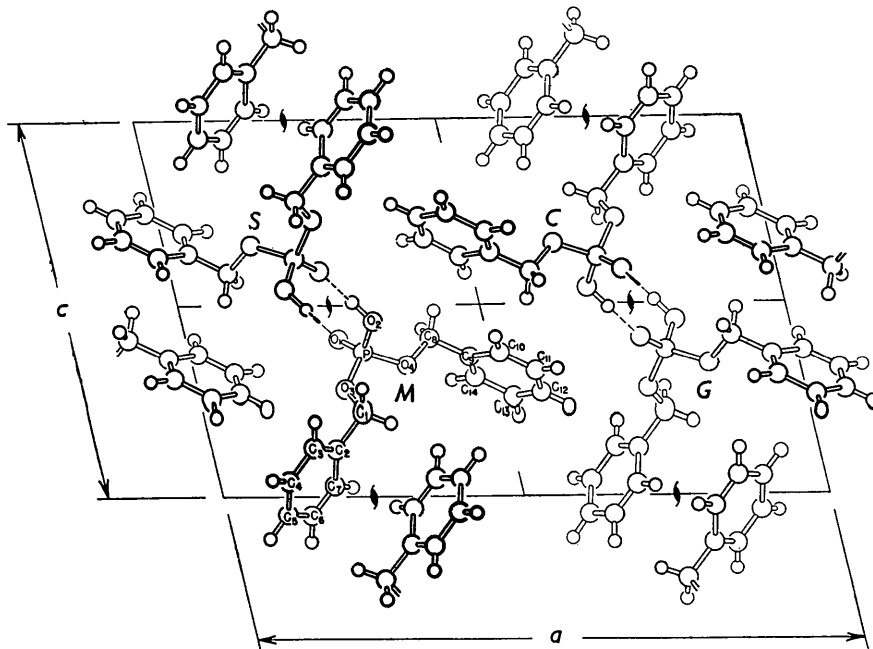


Fig. 1. Projection of the structure viewed down the b axis. Molecules S , C and G are related to molecule M by the screw axis, the centre of symmetry and the glide-plane respectively.

All the data were then used for three further stages of least-squares refinement by the Datatron computer, which was very kindly made available to us by the ElectroData company of Pasadena, California. Each of the first two of these stages occupied nearly 12 hr. of computer time and the third stage (in which hydrogen contributions were included) required 20 hr. The computer programme employed has been described by Lavine & Rollett (1956). The positional parameters only were refined in the first stage, but the results of the second stage were used to assign individual isotropic temperature factors to the atoms. Two different kinds of O atom and five kinds of C atom were employed for the third stage. This, together with the positional shifts and the contributions of the hydrogen atoms, reduced R from 0.207 to 0.158 for the structure factors of the third stage. The r.m.s. positional shift in this stage was 0.014 Å. An $(F_o - F_c)$ synthesis was calculated with the structure factors used for the least squares and this synthesis showed relatively flat background in regions far from atomic centres, but features up to $\pm 1.2 \text{ e.Å}^{-3}$ in height near the atoms, corresponding to anisotropic thermal vibration.

The anisotropies of the individual atoms were determined from the $(F_o - F_c)$ synthesis by a method formally similar to that given by Cochran (1951). The values of α, \dots, η in the expression

$$-\ln T = \alpha h^2 + \beta k^2 + \gamma l^2 + \delta hk + \epsilon kl + \eta lh$$

(see Rollett & Davies, 1955) were, however, evaluated directly from $(\partial^2 D / \partial x^2), \dots, (\partial^2 D / \partial z \partial x)$ without determination of the principal vibration directions. We are indebted to Dr D. W. J. Cruickshank for suggesting this simplification (private communication). The approximations for α, \dots, η which we derived and used were:

$$\Delta\alpha = \frac{3V \left\{ \left(\frac{4}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial x^2} \right) - \left(\frac{\partial^2 D}{\partial y^2} \right) - \left(\frac{1 - 4 \cos^2 \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z^2} \right) - \left(\frac{8 \cos \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z \partial x} \right) \right\}}{40\pi^2 a^2 \sum_h fT \left(\frac{h}{a} \right)^4}$$

$$\Delta\beta = \frac{3V \left\{ \left(\frac{-1}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial x^2} \right) + 4 \left(\frac{\partial^2 D}{\partial y^2} \right) - \left(\frac{1}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z^2} \right) + \left(\frac{2 \cos \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z \partial x} \right) \right\}}{40\pi^2 b^2 \sum_k fT \left(\frac{k}{b} \right)^4}$$

$\Delta\gamma$ similar to $\Delta\alpha$ with interchange of $h, l; x, z; a, c$.

$$\Delta\delta = \frac{10V \left(\frac{\partial^2 D}{\partial x \partial y} \right)}{40\pi^2 ab \sum_{hk} fT \left(\frac{h^2 k^2}{a^2 b^2} \right)}$$

$\Delta\epsilon$ similar to $\Delta\delta$ with interchange of $h, l; x, z; a, c$.

$$\Delta\eta = \frac{V \left\{ \left(\frac{-8 \cos \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial x^2} \right) + 2 \cos \beta_0 \left(\frac{\partial^2 D}{\partial y^2} \right) - \left(\frac{8 \cos \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z^2} \right) + \left(\frac{10 + 6 \cos^2 \beta_0}{\sin^2 \beta_0} \right) \left(\frac{\partial^2 D}{\partial z \partial x} \right) \right\}}{40\pi^2 ac \sum_{hl} fT \left(\frac{h^2 l^2}{a^2 c^2} \right)}$$

These expressions ignore the possibility of an error in scale factor. In this application the scale factor was, in fact, correct within 2%. Note that $\cos \beta_0$ and $\sin \beta_0$ are functions of the angle between a and c , not of the coefficient of k^2 .

The positions and vibrations obtained from the $(F_o - F_c)$ synthesis were used in the calculation of a set of 2471 structure factors, accompanied by least-squares refinement of all parameters except those for hydrogen atoms, by the SWAC.

The weighting system used in this stage of least squares was

$$\begin{aligned} \sqrt{w} &= 4F_{\min.}/|F_o| \quad \text{when } |F_o| > 4F_{\min.}, \\ \sqrt{w} &= |F_o|/4F_{\min.} \quad \text{when } |F_o| < 4F_{\min.}, \end{aligned}$$

and $4F_{\min.}$ was taken to be 6.4 electrons/unit cell. The computer programme used is described by Sparks, Prosen, Kruse & Trueblood (1956). The structure factors gave an R factor of 0.120, and this fell to 0.110 when fifteen strong low-order planes were omitted on the ground that their F_o were inaccurate because of extinction. The accidental absences were left out of these calculations altogether because in the previous stage only 142 out of 474 of these planes gave F_c above the limit of observation for F_o .

The biggest positional shift given by this least-squares calculation was about one-third as large as that for the stage before. Since in this latest stage no positional shift was more than 1.5 times the corresponding standard deviation it was concluded that no significant improvement of accuracy would be secured by further stages of refinement. This conclusion was confirmed by the quality of structure factor agreement, which was uniformly good and approximately as close as the correlations between F_o values derived from

Table 1. Atomic positional coordinates

	x/a	y/b	z/c
P	0.28960	0.35596	0.37389
O ₁	0.25171	0.16530	0.41083
O ₂	0.31645	0.55349	0.45595
O ₃	0.24488	0.46202	0.26947
O ₄	0.35393	0.26739	0.33705
C ₁	0.26457	0.67249	0.21802
C ₂	0.20720	0.73566	0.12482
C ₃	0.17015	0.93559	0.12975
C ₄	0.11644	0.98970	0.04116
C ₅	0.10058	0.84361	-0.04865
C ₆	0.13916	0.65434	-0.05163
C ₇	0.19080	0.59529	0.03294
C ₈	0.40400	0.12742	0.41283
C ₉	0.46199	0.08141	0.36097
C ₁₀	0.51478	0.24203	0.36967
C ₁₁	0.56709	0.19780	0.31800
C ₁₂	0.56888	-0.00201	0.26249
C ₁₃	0.51719	-0.16333	0.25423
C ₁₄	0.46405	-0.12272	0.30425

Table 2. Assumed hydrogen coordinates

	x/a	y/b	z/c
H ₁	0.1830	0.0316	0.2003
H ₂	0.0891	0.1208	0.0454
H ₃	0.0587	0.8962	0.8945
H ₄	0.1235	0.5674	0.8792
H ₅	0.2173	0.4698	0.0272
H ₆	0.5134	0.3916	0.4124
H ₇	0.6017	0.3186	0.3306
H ₈	0.6078	0.9657	0.2290
H ₉	0.5224	0.6865	0.2093
H ₁₀	0.4237	0.7540	0.2947
H ₁₁	0.3070	0.6412	0.1979
H ₁₂	0.2710	0.8008	0.2774
H ₁₃	0.4210	0.2202	0.4829
H ₁₄	0.3850	0.9767	0.4330
H ₁₅	0.2890	0.6000	0.5094

Table 3. Atomic vibration parameters

	α	β	γ	δ	ϵ	η
P	196	2978	535	62	18	244
O ₁	354	3878	734	-176	277	432
O ₂	290	4280	750	-129	-620	350
O ₃	219	3163	746	-69	356	169
O ₄	264	4228	530	393	313	277
C ₁	275	4012	913	-301	774	109
C ₂	253	3293	622	-115	236	244
C ₃	381	3752	955	-75	-257	312
C ₄	384	4645	1750	353	836	200
C ₅	496	6720	1033	-174	1201	-306
C ₆	653	6814	674	-322	-304	-118
C ₇	539	4729	746	176	-381	313
C ₈	275	5079	672	542	775	259
C ₉	210	3600	560	217	282	109
C ₁₀	328	3757	855	-140	90	260
C ₁₁	278	6353	998	-303	632	274
C ₁₂	287	6027	1157	282	-98	544
C ₁₃	421	4466	1263	486	-810	493
C ₁₄	297	4155	993	-123	-114	188

H atoms are given the same vibrations as the adjacent heavier atom.

The temperature factor is

$$T = \exp [-10^{-5} \{ \alpha h^2 + \beta k^2 + \gamma l^2 + \delta hk + \epsilon kl + \eta lh \}].$$

photographs obtained by rotation about different axes (see § 2).

The final values of all the atomic parameters are given in Tables 1, 2 and 3. It should be noted that the positions of the hydrogen atoms were calculated by assuming reasonable bond lengths and angles. These positions have not been checked by estimation of the electron density in the structure, but the form of the molecule is quite unambiguous. The 2471 values of hkl , $|F_o|$, F_c and $(F_o - F_c)$ are recorded in Table 8.*

5. Accuracy

The standard deviations of the positional parameters were determined without allowance for the effects of off-diagonal terms in the matrix of the least-squares normal equations, except for multiplication of the results for x and z by 1.05 because of the β angle of $103^\circ 13'$. The expression used was therefore:

$$\sigma^2(x) = (\Sigma w \Delta^2) / (n-s) [\Sigma w (\partial F / \partial x)^2],$$

where $(n-s)$ is the number of degrees of freedom.

The results of these calculations for all positional coordinates of P, O and C are given in Table 4. The

Table 4. Standard deviations of atomic positions

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
P	0.0013	0.0014	0.0013
O ₁	0.0042	0.0043	0.0039
O ₂	0.0039	0.0045	0.0037
O ₃	0.0035	0.0039	0.0037
O ₄	0.0036	0.0042	0.0034
C ₁	0.0063	0.0073	0.0074
C ₂	0.0056	0.0062	0.0055
C ₃	0.0075	0.0080	0.0077
C ₄	0.0090	0.0094	0.0114
C ₅	0.0096	0.0097	0.0095
C ₆	0.0109	0.0102	0.0084
C ₇	0.0095	0.0086	0.0070
C ₈	0.0062	0.0071	0.0060
C ₉	0.0056	0.0063	0.0052
C ₁₀	0.0069	0.0079	0.0072
C ₁₁	0.0068	0.0090	0.0076
C ₁₂	0.0066	0.0090	0.0080
C ₁₃	0.0085	0.0084	0.0097
C ₁₄	0.0075	0.0073	0.0075

standard deviations for bond lengths and angles were derived with the assumption that all positional parameters were independent. These standard deviations are given with the actual values in Table 5.

The vibrational parameters were not refined to such

* Table 8, recording 2471 values of F_o , F_c and $(F_o - F_c)$, has been deposited as Document No. 4720 with the ADI Auxiliary, Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the document number and by remitting \$7.50 for photoprints, or \$2.75 for 35 mm. microfilm. Advance payment is required. Make cheques or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 5. *Bond distances and angles*

Bond	Distances	
	Length (Å)	Standard deviation (Å)
P-O ₁	1.469	0.0045
P-O ₂	1.545	0.0044
P-O ₃	1.545	0.0041
P-O ₄	1.566	0.0039
O ₃ -C ₁	1.465	0.0084
O ₄ -C ₈	1.464	0.0076
C ₁ -C ₂	1.499	0.0090
C ₈ -C ₉	1.495	0.0084
C ₂ -C ₃	1.376	0.0101
C ₃ -C ₄	1.407	0.0127
C ₄ -C ₅	1.387	0.0147
C ₅ -C ₆	1.340	0.0145
C ₆ -C ₇	1.358	0.0131
C ₇ -C ₂	1.388	0.0112
C ₉ -C ₁₀	1.395	0.0096
C ₁₀ -C ₁₁	1.391	0.0099
C ₁₁ -C ₁₂	1.344	0.0127
C ₁₂ -C ₁₃	1.382	0.0119
C ₁₃ -C ₁₄	1.389	0.0117
C ₁₄ -C ₉	1.374	0.0098

Angle	Angles	
	Value (°)	Standard deviation (°)
O ₁ PO ₂	117.2	0.22
O ₁ PO ₃	108.3	0.22
O ₁ PO ₄	112.8	0.22
O ₂ PO ₃	109.6	0.24
O ₃ PO ₄	103.8	0.21
O ₄ PO ₂	104.2	0.22
PO ₃ C ₁	122.3	0.34
PO ₄ C ₈	118.8	0.32
O ₃ C ₁ C ₂	107.8	0.49
O ₄ C ₈ C ₉	107.8	0.46
C ₁ C ₂ C ₃	119.9	0.58
C ₁ C ₂ C ₇	120.9	0.60
C ₇ C ₂ C ₃	119.2	0.57
C ₉ C ₃ C ₄	118.5	0.68
C ₃ C ₄ C ₅	120.8	0.79
C ₄ C ₅ C ₆	118.7	0.83
C ₅ C ₆ C ₇	121.9	0.84
C ₆ C ₇ C ₂	120.7	0.73
C ₉ C ₃ C ₁₀	121.1	0.58
C ₈ C ₉ C ₁₄	119.9	0.57
C ₁₄ C ₉ C ₁₀	119.0	0.54
C ₉ C ₁₀ C ₁₁	119.9	0.67
C ₁₀ C ₁₁ C ₁₂	120.9	0.75
C ₁₁ C ₁₂ C ₁₃	119.7	0.60
C ₁₂ C ₁₃ C ₁₄	120.6	0.71
C ₁₃ C ₁₄ C ₉	119.9	0.63

complete convergence as the positions, and standard deviations for vibrations have not been computed.

6. Discussion

All intramolecular bond distances and angles are given in Table 5 and shown in Fig. 2. There are no previous determinations whatever of dimensions in diesterified phosphate groups and for comparison with the P-O distances of 1.469, 1.545, 1.545 and 1.566 Å obtained here we have only work on phosphoric acid, its mono-potassium salt, and diphosphorus pentoxide.

Smith, Brown & Lehr (1955) have carried out a crystal-structure analysis of H₃PO₄ by Fourier projections and found P-O distances ranging from 1.52 to 1.59 Å. Within the limits of error of their results, there is no conflict with those obtained here. West (1930) obtained 1.56 Å for the mean P-O distance in KH₂PO₄, which again is in substantial agreement with our results. The difference between the Schomaker-Stevenson value of 1.10+0.74-0.14 = 1.70 Å and the experimental 1.55 Å for P-O has been discussed by Pauling (1952).

The electron diffraction work of Hampson & Stosick (1938) on P₄O₁₀, in the gas phase gave P=O 1.39 Å and P-OP 1.62 Å. It would appear that an oxygen atom between two phosphorus atoms is not able to form such strong π bonds with either as the bond between phosphorus and an oxygen attached to carbon. It is somewhat surprising, however, that the effect of this upon the net charge on the P atoms in P₄O₁₀ should be to reduce the P=O length by 0.08 Å. These electron diffraction results may be compared with the crystal structure of (NH₄)₄P₄O₁₂ determined by Romers, Ketelaar & MacGillavry (1949) in which P-O 1.46 Å for unshared oxygen atoms and P-O 1.62 Å for shared oxygen atoms were obtained.

The O-C distances of 1.465 and 1.464 Å in dibenzyl phosphoric acid are somewhat longer than the value of 1.42 Å given by the Schomaker-Stevenson rule. It should be noted that similarly long methoxyl bonds were found by O'Gorman, Shand & Schomaker (1950) in methyl chloroformate (1.46 Å), methyl formate (1.47 Å), and methyl acetate (1.46 Å). The O-C lengths in methyl hydroxylamine, methyl alcohol and dimethyl ether are given as 1.44 Å, 1.44 Å and 1.43 Å, respectively. The three last values are taken from the compilation of electron diffraction results by Allen & Sutton (1950).

The probability of obtaining the methylene-to-benzene mean single bond length as short as 1.497 Å with standard deviation 0.0062 Å from a structure in which the true length is as great as 1.542 Å is given as less than 1×10^{-11} by the normal law of error. All probabilities given in this discussion are evaluated from

$$P = 1 - \operatorname{erf} \{ \Delta l / [\sqrt{2} \cdot \sigma(\Delta l)] \}.$$

This result must be regarded as clear evidence of shortening of this bond below the single-bond length found in diamond. The actual value obtained is, moreover, in close agreement with the results of McHugh & Schomaker (1955) for propylene and isobutene (about 1.50 Å in both).

The high temperature factors of the carbon atoms in the benzene rings most remote from the phosphate group are reflected in their greater positional standard deviations (see Table 4). It must also be borne in mind that the time-averaged electron densities of these atoms overlap seriously. In these circumstances the off diagonal terms in the least-squares normal matrix

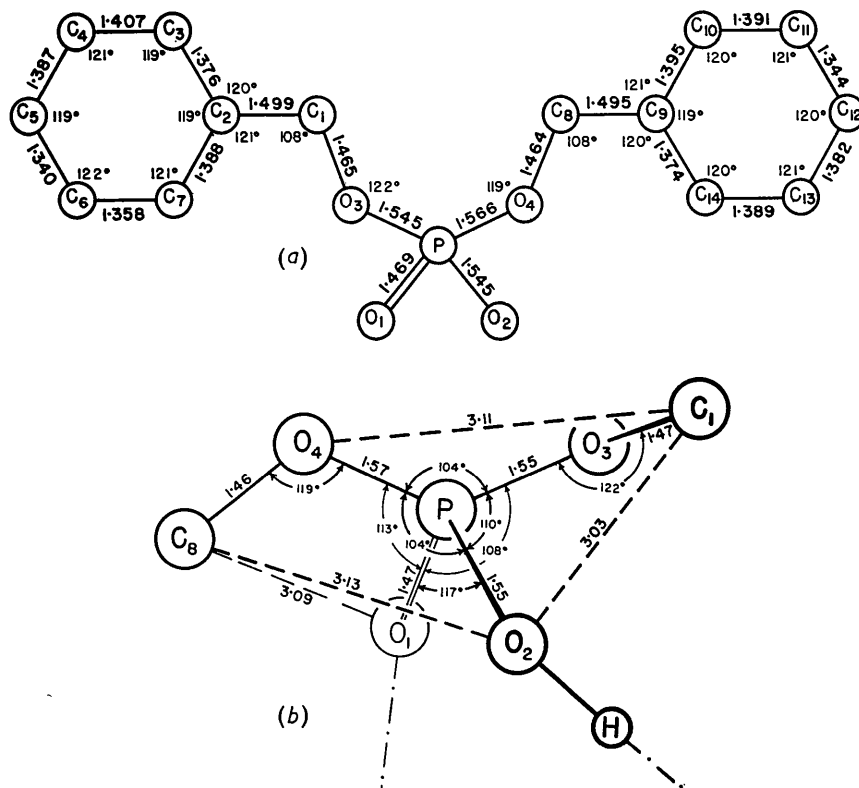


Fig. 2. (a) Bond lengths and angles in the molecule of dibenzyl phosphoric acid. All dimensions are shown except the angles at the phosphorus atom, for which see (b). (b) Diagrammatic representation of the configuration and dimensions of the diesterified phosphate group in dibenzyl phosphoric acid. The planes PO_3C_1 and PO_4C_8 make an angle of 88° .

connecting the position of one atom with the vibrations of its neighbours become significantly large. The effects of this are twofold. First, the rate of convergence decreases for a refinement in which these terms are ignored (as here). Second, the standard deviations for the positions of the overlapping atoms are underestimated by the diagonal approximation which we are forced to use when the off diagonal terms are unknown. In fact, we find two *meta-para* carbon-carbon bonds which are very short (1.340 and 1.344 Å) in this structure. The probability for observing a length shorter than 1.345 Å, given a true length equal to the mean of 1.378 Å for all twelve bonds in the rings, is about 0.01, according to the standard deviation for $C_{11}-C_{12}$, and a similar value is found for C_5-C_6 . For the reasons stated above, however, we prefer not to attach significance to these discrepancies.

For each benzyl group a plane was calculated by the method of least-squares to pass as nearly as possible through all seven atoms. Atoms C_1-C_7 all lie within 0.019 Å of one plane and atoms C_8-C_{14} all lie within 0.016 Å of the other. In neither case is there any significant departure from planarity.

A very interesting comparison may be made between the phosphate group and its neighbours in this structure and the corresponding part of the successful model for deoxyribonucleic acid described by Crick &

Table 6. Comparison between dibenzyl phosphoric acid and the assumptions of Crick & Watson

Dimension	Crick & Watson (1954)	Observed
P-O ₁	1.45 Å	1.469 Å
P-O ₂	1.49	1.545
P-O ₃	1.64	1.545
P-O ₄	1.65	1.566
O ₃ -C ₁	1.41	1.465
O ₄ -C ₈	1.38	1.464
O ₁ PO ₂	117.9°	117.2°
O ₁ PO ₃	107.9	108.3
O ₁ PO ₄	110.3	112.8
O ₂ PO ₃	108.7	109.6
O ₃ PO ₄	110.1	103.8
O ₄ PO ₂	108.7	104.2
C ₈ O ₄ P-PO ₃ C ₁ dihedral	63	88

All atom numbers refer to dibenzyl phosphoric acid.

Watson (1954). In Table 6 the corresponding dimensions of the two structures are listed. If the factors determining the length of the ester link between successive sugar residues are considered, we find that the errors of the assumed dimensions in the Crick-Watson structure are closely compensated. The assumed P-OC distances were too long by 0.09 Å, but the PO-C lengths were taken to be too short by 0.07 Å. The bond

angles at the oxygen atoms were made too small by 10° , but the angle between the esterified P–O bonds was given a value 6° greater than that observed here. In this connection it is noteworthy that the bond angles at the P atom appear to be deformed quite easily by as much as 3° by van der Waals forces. Fig. 2(b) shows that the equivalent angles O_1PO_3 and O_1PO_4 differ by 6° and the similarly equivalent angles O_2PO_3 and O_2PO_4 disagree by 5° . These effects are certainly not errors of the analysis and it may be seen that they are related in a simple way to the close approaches between O_2 and C_1 and between O_1 and C_8 .

A further point of great significance arises from comparison between Figs. 1 and 2(b) of this paper and Figs. 7 and 8 of the paper by Crick & Watson. From Fig. 2(b) it may be seen that all four atoms C_8 , O_4 , P and O_3 in dibenzyl phosphoric acid lie approximately in a plane, with C_1 emerging from this plane at a large angle. This configuration is reproduced in the Crick–Watson model by the planar arrangement of C'_5 , O_3 , P and O_4 , with C'_3 a long way out of the plane. The dihedral angle between the two POC planes is 88° in dibenzyl phosphoric acid, but only 63° in the Crick–Watson model. This difference of detail is, however, easily understood in terms of van der Waals repulsion between the phosphate group and the deoxyribose ring.*

This close correspondence suggests that the configuration of Fig. 2(b) is the most stable form of the diesterified phosphate group. If this could be demonstrated we should have a useful restriction on the possible forms of other kinds of nucleic acid.

A hypothesis to account for the apparent stability of the configuration with a POC–POC dihedral angle near to 90° is that this configuration allows the two oxygen atoms to form π bonds involving two different orbitals on the P atom. This idea is further supported by the fact that the dihedral angles $PO_3C_1-PO_2H$ and $PO_4C_8-PO_2H$ are also near to 90° , assuming the H atom (which was not directly located in the structure analysis) to lie between O_2 of molecule *M* and O_1 of molecule *S*, forming a strong hydrogen bond of length 2.494 \AA (see Fig. 1). If this explanation is correct it would be reasonable to expect longer P–O bonds in *cyclo*-ethylene-monophosphate than in dibenzyl phosphoric acid. The existence of a dependence of P–O length on spatial arrangement is suggested by the quite definite difference of 0.021 \AA between P– O_3 and P– O_4 . Each of these has a standard deviation of 0.0041 \AA , and the chance of a random difference as big as 0.021 \AA is 0.0003 .

The short distances between oxygen and carbon atoms covalently linked by two intervening atoms are

given in Table 7. It is noteworthy that all eight of these distances are between 3.030 \AA and 3.393 \AA . The closest approaches between atoms in different

Table 7. *Close approaches between pairs of atoms indirectly covalently linked*

Distance	Intervening atoms	Length (Å)
O_2C_1	PO_3	3.030
O_4C_1	PO_3	3.107
O_1C_8	PO_4	3.092
O_2C_8	PO_4	3.132
O_3C_3	C_1C_2	3.393
O_3C_7	C_1C_2	3.038
O_4C_{10}	C_8C_9	3.197
O_4C_{14}	C_8C_9	3.248
O_1O_2	P	2.573
O_1O_3	P	2.444
O_1O_4	P	2.530
O_2O_3	P	2.526
O_2O_4	P	2.455
O_3O_4	P	2.448

molecules are 3.558 \AA between $C_8(M)$ and $C_{10}(C)$, 3.560 \AA between $O_3(M)$ and $C_{12}(G-a)$, 3.561 \AA between $C_{11}(M)$ and $O_2(C)$, and 3.662 \AA between $C_8(M)$ and $C_9(C)$.

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* Note added in proof, 19 January 1956.—Mrs Dorothy Crowfoot Hodgkin has kindly communicated to us preliminary positions for the atoms of the diesterified phosphate groups in the crystal structures of wet and air-dried vitamin B12. Our calculations from these positions give POC–POC dihedral angles of 83° for the wet form and 56° for the air-dried form.

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A Refinement of the Crystal Structure of Succinamide*

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The structure of succinamide has been refined to a high degree of precision by three-dimensional Fourier and least-squares methods. In this structure the molecules are planar and are tied into layers by a net of hydrogen bonds. The bond lengths in the amide group are C-N = 1.333 and C-O = 1.238 Å; the bond angles are C-C-N = 115° 36', C-C-O = 122° 23', and N-C-O = 122° 2'. The two non-equivalent C-C bonds have lengths of 1.512 and 1.501 Å, the central bond being slightly but significantly longer.

Introduction

When the crystal-structure determination of succinamide was initiated, the dimensions of the terminal amide group had been determined in only three compounds: acetamide (Senti & Harker, 1940), glutamine (Cochran & Penfold, 1952) and glycy lasparagine (Pasternak, Katz & Corey, 1954). Because the bond lengths and angles reported for this group in these three investigations differed significantly, a precise determination of the succinamide structure, which is simpler than any of the other three, was considered to be of value. Recently, the crystal structures of formamide (Ladell & Post, 1954) and oxamide (Ayerst & Duke, 1954) have also been published.

Experimental

Unit cell and space group

Crystals of succinamide grown from water solutions were monoclinic plates bounded by {001} faces and showing perfect cleavage along {100}. Unit-cell dimensions were derived from single-crystal rotation photographs obtained with a Straumanis-type camera; they are, with their limits of error,

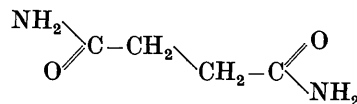
$$a_0 = 6.932 \pm 0.003, \quad b = 7.994 \pm 0.003, \quad c = 9.878 \pm 0.004 \text{ \AA}, \\ \beta = 102^\circ 28' \pm 5'.$$

The density observed by flotation is 1.442 ± 0.005 g.cm.⁻³, and the number of molecules per unit cell is 4 (calculated 3.998).

The observed systematic absences are hkl when $h+k$ is odd and $h0l$ when h or l are odd; they are characteristic of the space groups Cc (4 general positions) and $C2/c$ (centrosymmetric, 8 general positions).

Trial structure

A trial structure for succinamide



has been reported previously (Pasternak, 1953). The observations of (a) perfect cleavage of the crystals along {100}, (b) outstandingly strong ($h00$) reflections showing normal decline, (c) extremely weak ($hk0$) reflections when h and k are odd, (d) a very similar intensity distribution on layer lines with h even and with h odd, respectively, pointed to an almost perfect layer structure parallel to (100) with the layers of molecules at $x = \frac{1}{4}$ and $\frac{3}{4}$. By taking into account known bond lengths and bond angles, van der Waals distances, and the expectation of hydrogen bond formation, the configuration of the molecules and their

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