The Crystal and Molecular Structure of Methyl Pinacol Phosphate

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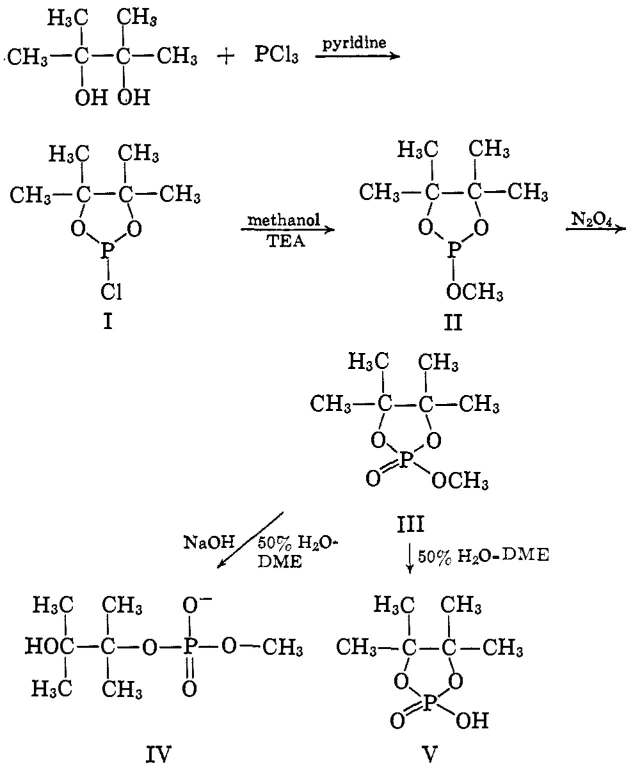
Abstract: Methyl pinacol phosphate crystallizes in the space group $P2_12_12_1$ with cell dimensions a = 9.48, b = 13.29, and c = 7.70 A. A three-dimensional, least-squares refinement with isotropic temperature factors resulted in an R factor of 9% for 729 X-ray intensities. The ring portion of the molecule is very similar to the ring portion of methyl ethylene phosphate, but the methyl ester group is rotated approximately 180° from its position in methyl ethylene phosphate. The position of the methyl ester group is discussed in terms of π bonding; the relationship between symmetry and π bonding in phosphate esters is also discussed.

Our interest in the cause of the rapid rates of hydrolysis of five-membered ring esters of phosphoric acid, which is presumably associated with the thermodynamic ring strain which has been reported to be an intrinsic property of these ring systems,[1] led us to undertake a determination of the structure of methyl pinacol phosphate by single crystal, X-ray diffraction analysis. Presumably, comparison of the structural parameters of the highly reactive esters with those of normal esters should give insight into the source of the observed strain in these systems.

Although the details of the synthesis of methyl pinacol phosphate will be presented in a separate paper,[2] the steps in the synthesis are given here. Pinacol with phosphorus trichloride in the presence of pyridine afforded the pinacol phosphorochloridite[3] (I). I further reacted with dry methanol with added triethylamine to give methyl pinacol phosphite[3] (II). Oxidation of II with dinitrogen tetroxide[4] produced III.

Although no quantitative estimate of reaction rate has been obtained, methyl pinacol phosphate reacts with 50% 1,2-dimethoxyethane–water solution, which is 0.1 N in sodium hydroxide, at a rate too fast to measure by titrimetric methods.[2] The principal product of the reaction is methyl O-pinacol phosphate monoanion (IV). The fast rate of hydrolysis and the product of hydrolysis in alkaline solution are consistent with the behavior of other observed five-membered ring esters of phosphoric acid, *e.g.*, methyl ethylene phosphate.[5–8]

When methyl pinacol phosphate is subjected to solvolysis in 50% 1,2-dimethoxyethane-water solution in the absence of base, the rate of hydrolysis becomes measurable by conductometric methods[2] and the only observed product is pinacol phosphoric acid (V). This appears to be the first example of predominant ring retention by a five-membered ring phosphate ester under solvolytic conditions, although small amounts of ring-retained solvolysis products have been identified.[5,9]



Collection and Reduction of X-Ray Data. Methyl pinacol phosphate crystallized from petroleum ether (bp 90–120°) in thin plates. The orthorhombic space group, as indicated by extinction of odd reflections along each of the three axes, is $P2_12_12_1$ with a = 9.48 ± 0.01 A, b = 13.29 ± 0.01 A, and c = 7.70 ± 0.01 A. The number of molecules per unit cell is four and the X-ray density is 1.329 g/cm^3. The plate obtained from petroleum ether is elongated along the b axis and the faces are perpendicular to the a and c axes. Crystals grown by sublimation of the ester are rectangular prisms with the long crystal axis along b; the faces of the crystal are, however, the diagonal 101 planes. The unit cell dimensions, number of molecules per unit cell, and the crystal system are the same for crystals grown by either method, but crystals obtained by

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[1] E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963); J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).

[2] J. R. Cox, Jr., and M. G. Newton, to be published.

[3] A. E. Arbuzov and M. M. Azanovskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 473 (1949).

[4] J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5441 (1958).

[5] F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

[6] J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *ibid.*, **78**, 4858 (1956).

[7] P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

[8] A. Eberhard and F. H. Westheimer, *ibid.*, **87**, 253 (1965).

[9] D. M. Brown, D. I. Magrath, and A. R. Todd, *J. Chem. Soc.*, 4396 (1955).

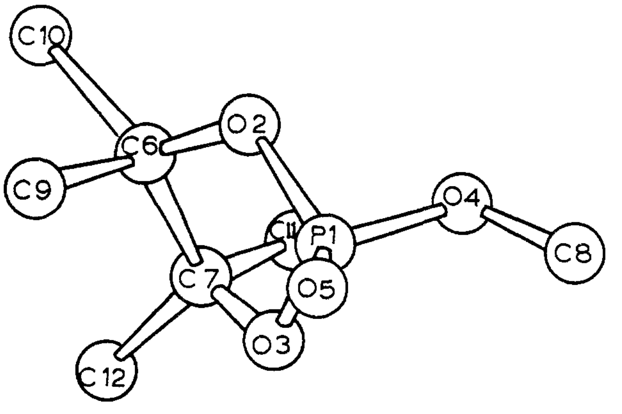

Figure 1. Perspective drawing of one molecule of methyl pinacol phosphate as viewed down the *y* axis.

sublimation have better dimensions for collection of intensity data.

A crystal was mounted along its *b* axis and a precession camera was used in collecting 11 zones of intensity data. Mo Kα radiation was used. The zones collected were *hkx* and *xkl* (x = 0–3), *hkh*, *hk*(2*h*), and (2*l*)*kl*. Intensities were estimated visually from a series of timed exposures employing a standard series made from the same crystal. Lorentz-polarization corrections were computed;[10] no attempt was made to correct for absorption. A total of 729 unique, nonzero reflections were obtained.

Determination of the Structure. The 729 reflections were used in a three-dimensional Patterson synthesis from which the coordinates of the phosphorus atoms were obtained. A rank 4 minimum function revealed the locations of the four oxygen atoms in the molecular unit. A structure factor based on these five atoms gave a conventional *R* value of 0.31.

A Fourier synthesis based on the reflections phased by these five atoms gave the locations of the seven carbon atoms. A full-matrix least-squares refinement of all atomic positions and anisotropic temperature factors gave the present *R* of 0.09. A difference Fourier synthesis showed no significant intensity. The final atomic position parameters and the final anisotropic thermal parameters are listed in Tables I and II, respectively.[11]

Discussion

Tables III and IV compare bond distances and bond angles in methyl pinacol phosphate to those in methyl ethylene phosphate.[12] Bond distances are equivalent within experimental error in the two structures except for the ring C–C and C–O distances which are longer in methyl pinacol phosphate than in methyl ethylene phosphate. The effect of bond lengthening has an apparent effect on bond angles as well. The angles O_2–C_6–C_7 and O_3–C_6–C_7 in methyl pinacol phosphate are somewhat smaller than the corresponding angles in methyl ethylene phosphate. The angles subtended by groups attached to the ring carbon atoms are somewhat distorted from the normal tetrahedral angle of 109.5°.

Table I. Final Atomic Parameters for Methyl Pinacol Phosphate

Atom	*x*	*y*	*z*
P_1	0.1894 (3)[a]	0.2008 (2)	0.2222 (5)
O_2	0.102 (1)	0.1669 (7)	0.385 (1)
O_3	0.131 (1)	0.1208 (6)	0.088 (1)
O_4	0.3429 (9)	0.1707 (6)	0.274 (2)
O_5	0.180 (1)	0.3033 (6)	0.163 (1)
C_6	−0.013 (2)	0.0963 (9)	0.339 (2)
C_7	0.049 (1)	0.0386 (8)	0.175 (2)
C_8	0.466 (1)	0.244 (1)	0.214 (2)
C_9	−0.141 (2)	0.162 (1)	0.292 (3)
C_{10}	−0.039 (2)	0.030 (1)	0.498 (2)
C_{11}	0.154 (1)	−0.0420 (8)	0.228 (2)
C_{12}	−0.058 (2)	0.004 (1)	0.043 (2)

[a] The estimated standard deviation in the least significant figure is given in parentheses here and in subsequent tables.

Furthermore, the dihedral angles between the O_2–P–O_3 plane and the O_2–C_6–O_3 and O_2–C_7–O_3 planes in methyl pinacol phosphate are 12.2 ± 0.9° and 12.1 ± 0.9°, respectively, as compared to 10.9 and 1.8° for the same planes in methyl ethylene phosphate. These angles indicate a greater amount of puckering of the ring in methyl pinacol phosphate as compared to methyl ethylene phosphate. Presumably, these differences are associated with steric crowding of the methyl groups attached to the ring carbon atoms.

Conformation of groups about the C_6–C_7 bond suggests additional strain in methyl pinacol phosphate as compared to methyl ethylene phosphate. Consideration of the dihedral angles between planes defined by C_6–C_7–C_{11} and C_6–C_7–C_{10}, C_6–C_7–C_9 and C_6–C_7–C_{12}, C_6–C_7–O_3 and C_6–C_7–O_2 indicates that opposing groups are staggered by approximately 35° about the C_6–C_7 bond; this is 25° from the normal 60° angle and amounts to approximately one-third of the energy of rotation about the bond.

The most significant difference in the structure of methyl pinacol phosphate and that of methyl ethylene phosphate is the position of the methyl ester group; in methyl ethylene phosphate, the methyl group is over the ring and, within experimental error, centered between the two ring oxygens;[13] in methyl pinacol phosphate, the methyl group is over the phosphoryl oxygen. In both cases, the four atoms, O′–P–O–C (O′ is the phosphoryl oxygen), are almost coplanar. Although a change in the methyl position is required because of steric crowding by the staggered methyls of the pinacol group, one of which projects over the ring, it seems unusual that the methyl ester group should rotate 180°. The short C–O distances (3.01 and 2.98 in methyl ethylene phosphate; 2.94 in methyl pinacol phosphate) could be taken as evidence of hydrogen bonding,[14] and hydrogen bonding could thus determine the methyl position; we feel, however, that this effect

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(10) All computations were made on the Burroughs B-5500 computer. Programs for LP corrections, Fourier summations, and minimum functions were written by J. A. B.; translations of the Busing, Martin, and Levy ORFLS least-squares refinement and ORFEE function and error programs were used.

(11) A table of the resulting F_c listed with the observed values, F_o, is available from the authors and will be sent on request.

(12) T. A. Steitz and W. N. Lipscomb, *J. Am. Chem. Soc.*, 87, 2488 (1965).

(13) In all discussion of structures, we have used the molecular parameters from the original articles when possible; since O–C distances and some of the dihedral angles were not given in the original articles, we have calculated these from the published structure parameters. In the calculations for methyl ethylene phosphate, we found it necessary to change the sign of the *y* coordinate of O_5 to reproduce the published molecular parameters and, thus, used −0.2137 for that coordinate in all of our calculations.

(14) D. J. Sutor, *J. Chem. Soc.*, 1105 (1963).

Table II. Final Thermal Parameters for Methyl Pinacol Phosphate

Atom	$\beta_{1,1}$	$\beta_{2,2}$	$\beta_{3,3}$	$\beta_{1,2}$	$\beta_{1,3}$	$\beta_{2,3}$
P_1	0.0073 (3)	0.0032 (2)	0.0141 (8)	−0.0002 (2)	0.0004 (6)	0.0005 (3)
O_2	0.011 (1)	0.0052 (6)	0.013 (2)	−0.0029 (8)	0.001 (2)	−0.003 (1)
O_3	0.009 (1)	0.0046 (6)	0.011 (2)	−0.0006 (7)	0.004 (2)	0.0002 (9)
O_4	0.008 (1)	0.005 (6)	0.026 (3)	−0.0007 (7)	−0.002 (2)	0.001 (1)
O_5	0.012 (1)	0.0039 (5)	0.021 (2)	0.0012 (9)	−0.001 (2)	0.000 (1)
C_6	0.012 (2)	0.0033 (7)	0.015 (3)	0.000 (1)	0.003 (3)	−0.001 (1)
C_7	0.008 (2)	0.0032 (6)	0.014 (3)	−0.0007 (9)	0.001 (2)	0.000 (1)
C_8	0.007 (1)	0.007 (1)	0.015 (4)	0.000 (1)	−0.002 (2)	0.001 (2)
C_9	0.008 (2)	0.007 (1)	0.028 (5)	0.002 (1)	−0.003 (3)	−0.003 (2)
C_{10}	0.013 (2)	0.007 (1)	0.014 (3)	−0.003 (1)	0.007 (3)	0.001 (2)
C_{11}	0.012 (2)	0.0023 (6)	0.027 (4)	0.0013 (9)	0.005 (3)	0.000 (1)
C_{12}	0.013 (2)	0.0057 (9)	0.016 (4)	−0.003 (1)	−0.004 (3)	−0.002 (2)

Table III. Comparison of Bond Lengths in Methyl Pinacol Phosphate and Methyl Ethylene Phosphate

Bond	Methyl pinacol phosphate, A	Methyl ethylene phosphate, A
P_1–O_2	1.57 (1)	1.57 (1)
P_1–O_3	1.59 (1)	1.57 (1)
P_1–O_4	1.56 (1)	1.57 (1)
P_1–O_5	1.44 (1)	1.44 (1)
O_2–C_6	1.49 (2)	1.41 (2)
O_3–C_7	1.50 (1)	1.45 (2)
O_4–C_8	1.44 (1)	1.44 (2)
C_6–C_7	1.59 (2)	1.52 (2)
C_6–C_9	1.53 (2)	. . .
C_6–C_{10}	1.52 (2)	. . .
C_7–C_{11}	1.51 (2)	. . .
C_7–C_{12}	1.51 (2)	. . .

Table IV. Comparison of Bond Angles in Methyl Pinacol Phosphate and Methyl Ethylene Phosphate

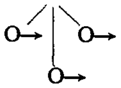
Bonds	Methyl pinacol phosphate, deg	Methyl ethylene phosphate, deg
O_5–P–O_4	112.6 (6)	108.7 (6)
O_5–P–O_2	119.4 (6)	116.0 (6)
O_5–P–O_3	113.9 (6)	117.3 (6)
O_4–P–O_2	102.2 (7)	105.7 (6)
O_4–P–O_3	108.9 (6)	109.2 (6)
O_2–P–O_3	98.4 (5)	99.1 (6)
P–O_2–C_6	112.3 (8)	112.0 (9)
P–O_3–C_7	112.0 (8)	112.0 (9)
P–O_4–C_8	123.4 (9)	118.8 (9)
O_2–C_6–C_7	102 (1)	107.8 (9)
C_6–C_7–O_3	101.4 (9)	106.0 (9)
O_2–C_6–C_9	106 (1)	. . .
O_2–C_6–C_{10}	107 (1)	. . .
O_3–C_7–C_{11}	107 (1)	. . .
O_3–C_7–C_{12}	105 (1)	. . .
C_7–C_6–C_9	112 (1)	. . .
C_7–C_6–C_{10}	115 (1)	. . .
C_6–C_7–C_{11}	112 (1)	. . .
C_6–C_7–C_{12}	116 (1)	. . .
C_9–C_6–C_{10}	113 (1)	. . .
C_{11}–C_7–C_{12}	114 (1)	. . .

and the bond angle at oxygen (in both esters approximately 120°) are related primarily to π-bonding effects.

Structure information is available for one acyclic triester, triphenyl phosphate,[15] and one diester acid, dibenzyl hydrogen phosphate.[16] There are several structural features which are common to these four compounds and thus seem general for triesters. (1) In each case, one oxygen exhibits a much shorter P–O bond distance than the other three. (2) The remaining three oxygen bond distances are identical within experimental error. (3) The *normal* bond angle at oxygen appears to be 120°; this is also true of the monoester structures which have been studied.[17] This angle is, of course, greatly distorted in the five-membered ring. (4) One of the ester groups appears to be aligned in such a way that the four atoms, O′–P–O–C are almost planar; the dihedral angle between the planes formed by O′–P–O and P–O–C are 6.8, 9.1, 16.6, and 20.7° in dibenzyl hydrogen phosphate, triphenyl phosphate, methyl ethylene phosphate, and methyl pinacol phosphate, respectively.

There has been at least one attempt to discuss d–p π bonding of phosphates in terms of symmetry arguments;[18] the PO_4 group was considered to be tetrahedral. Since the esters and the acid show three oxygens with equal bond distances and one with a much shorter bond distance, it would appear to be more reasonable to consider the symmetry to be somewhat lower. If the symmetry is first considered to be C_{3v}, the phosphorus d orbitals give rise to an A_1 (d_{z^2}) and two E ($d_{x^2-y^2}$, d_{xy} and d_{xz}, d_{yz}) representations. If the unique (phosphoryl) oxygen, which exhibits a much shorter P–O bond, is considered to form two π bonds,[19] the phosphorus orbitals involved could be the mutually perpendicular d_{xz} and d_{yz}, leaving the A_1 and an E set for π bonding to the remaining oxygens.

As the three equivalent oxygens in such a picture are essentially sp^2 hybridized (120° angle at oxygen) and one of these is known to be aligned with its sp^2 plane coincident with a C_{3v} symmetry plane (O′–P–O–C plane), the oxygen π orbitals are considered to be perpendicular to the symmetry planes (I). Such a set of π orbitals would give rise to a representation reducible to E + A_2 and, since there is no A_2 orbital available on phosphorus, only two π bonds can be formed.



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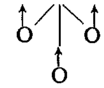

II

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(15) W. O. Davies and E. Stanley, *Acta Cryst.*, **15**, 1092 (1962).

(16) J. D. Dunitz and J. S. Rollett, *ibid.*, **9**, 327 (1956).

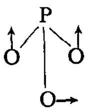
(17) See, for example, E. Alver and S. Furberg, *Acta Chem. Scand.*, **13**, 910 (1959); K. N. Trueblood, P. Horn, and V. Luzzati, *Acta Cryst.*, **14**, 965 (1961); J. Kraut, *ibid.*, **14**, 1146 (1961); E. Shefter and K. N. Trueblood, *ibid.*, **18**, 1067 (1965).

(18) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

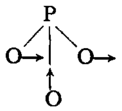
(19) E. A. Lucken and M. A. Whitehead, *ibid.*, 2459 (1961).

If the π orbitals are rotated 90° (II), a set of π orbitals reducible to $E + A_1$ results, and three π bonds are possible. That such an arrangement is not found in any of the compounds studied suggests that the π bonds of the ester oxygens and those of the phosphoryl group are not *completely* independent, as considered here, but interact to form molecular orbitals with greater delocalization.

It is possible to consider even lower symmetry, C_s, for the three oxygens, requiring only that at least one π orbital remain aligned perpendicular to its O′–P–O–C plane to agree with experimental evidence. In C_s, the three d orbitals available transform as A', A', and A''; there are two possible arrangements of the oxygen π orbitals (III and IV). One set (III) gives rise to a representation reducible to $A' + A'' + A''$ and only two π bonds are possible; the other set (IV) gives rise to a representation which reduces to $A' + A' + A''$ and three π bonds are possible.



III



IV

Since IV allows three π bonds to the set of three oxygens and five π bonds over-all, it might be expected that this would be the normal arrangement. Triphenyl phosphate approaches this arrangement, the π-bond planes (normal to sp^2 or P–O–C plane) of two oxygens being approximately perpendicular (dihedral angles between O′–P–O and P–O–C are 93 and 172°); the dihedral angle between O′–P–O and P–O–C for the third oxygen is 154° and it therefore deviates considerably from the expected 180°; however, considerable involvement of all d orbitals in π bonding is still expected.

The arrangement in methyl ethylene phosphate and methyl pinacol phosphate approach arrangement III. In methyl ethylene phosphate, as indicated previously, the methyl ester group deviates only 16° from the O′–P–O plane and the π orbital is perpendicular to this plane; the dihedral angles between CH_3–O–P plane and the other two C–O–P planes are 84 and 89°.

It seems significant that in the cyclic esters there are only four π bonds while in other esters there are five; this is in agreement with the proposal,[20] based on other evidence, that the π bonding is decreased in these cyclic esters and that the decrease in resonance energy contributes to the thermochemical strain.

Quantitative estimates of the thermochemical strain of methyl ethylene phosphate[21] and of the factor by which its rate of hydrolysis is accelerated with respect to that of trimethyl phosphate[10a] show that the observed rate of nucleophilic attack upon the phosphorus atom of the cyclic ester is greater by several orders of magnitude than that which would have been predicted on the basis of the assumption that the demonstrated strain is relieved quantitatively in the transition state and that the only effect of the ring is to reduce the activation enthalpy by this amount. Since one of the d orbitals of the cyclic esters is not used in π bonding and the availability of such an orbital should facilitate nucleophilic attack at phosphorus as well as facilitate formation of a transition state with d sp^3 hybridization, this effect is suggested in addition to the thermochemical strain to explain the very rapid hydrolysis of five-membered cyclic esters as compared to normal esters.

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(20) (a) A. Eberhard and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 253 (1965); (b) E. T. Kaiser, M. Panar, and F. H. Westheimer, *ibid.*, **85**, 602 (1963); (c) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).

(21) J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 129 (1959).