Preparation and Crystal Structures of *trans*-Methyl *meso*-Hydrobenzoin Phosphite and Phosphate

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Abstract: The transesterification of trimethyl phosphite with *meso*-hydrobenzoin has been found to lead to the single isomeric product, *trans*-methyl *meso*-hydrobenzoin phosphite. The phosphite has been converted by ozonolysis to the analogous *trans*-methyl *meso*-hydrobenzoin phosphate. Single-crystal X-ray diffraction studies have been completed for both compounds. The phosphite, $C_{15}H_{15}PO_3$, crystallizes in space group $P2_12_12_1$ with cell dimensions a = 9.924 (3), b = 5.969 (1), c = 23.225 (5) Å, and Z = 4. The phosphate, $C_{15}H_{15}PO_4$, crystallizes in space group $Pna2_1$ with a = 18.559 (4), b = 6.609 (1), c = 23.614 (5) Å, and Z = 8. A comparison of the structural features of the phosphite and phosphate is reported. The results show that P-O bond lengths are longer and the O-P-O angles smaller in the phosphite than in the corresponding phosphate.

The rate enhancement observed in hydrolysis of cyclic five-membered ring phosphate esters and related compounds has received considerable attention over the past decade. The area has been reviewed by Westheimer[1] and more recently by Hudson and Brown.[2] Thus, ethylene phosphate,[3,4] methyl ethylene phosphate,[5] ethyl propylphostonate, and its lithium salt[6] hydrolyze in acid and base with exclusive P-O cleavage at rates millions of times faster than corresponding acyclic analologs. These enormous rate enhancements have been attributed in part to ring strain present in the parent ester which is relieved upon formation of a trigonal-bipyramidal phosphorus intermediate.[1,4,7] Studies of the heats of hydrolysis have shown that methyl ethylene phosphate does contain 5-6 kcal/mol excess energy over trimethyl phosphate.[8,9] Also, X-ray diffraction studies of several five-membered cyclic phosphate esters have established that a contracted OPO angle of approximately 99° exists in these systems.[10-13]

In addition to the strain factor, Aksnes and Bergesen have shown that the alkaline hydrolysis of ethyl propylphostonate is accompanied by a favorable entropy of activation in contrast to six- and seven-membered ring phosphonates and phosphinates.[14] Subsequently, Brown and Hudson[2] have suggested that the favorable entropy of activation in these systems is associated with a "loosening" of the ring pseudorotation in the activated complex.

In contrast to the phosphate esters, the heats of hydrolysis of five-membered ring phosphite esters are normal with respect to acyclic analogs.[15] In acidic solution, cyclic phosphites apparently show little or no kinetic acceleration in hydrolysis over corresponding acyclic phosphites, whereas rate ratios of approximately 10^3 are observed in alkaline solution.[15] Hudson and Brown[2] have attributed the observed rate increase in alkaline solution to a favorable entropy of activation.

Although the structures of several five-membered ring phosphate esters have been determined by X-ray diffraction,[10-13] structural information on phosphite triesters is very scanty. The electron diffraction measurements of triethyl and trivinyl phosphites constitute the only reported direct structural measurements for such systems.[16] Also, no direct structural comparisons of a phosphite ester with its phosphate analog have been reported.

In our studies of substituted phosphite esters, we have found that *meso*-hydrobenzoin undergoes ester exchange[17] with trimethyl phosphite to produce the single isomeric trans phosphite,[18] I, which can be converted stereospecifically[19] to the corresponding phosphate,[18] II, by ozonolysis. Because both I and II are crystalline substances, these compounds provided an excellent opportunity to compare directly the solid state structures of a phosphite and its analogous phosphate ester, and, in addition, the structural analysis would elucidate the stereochemistry of the esters. We now report the results of these studies.

I
(MHP)

II
(MHPO)
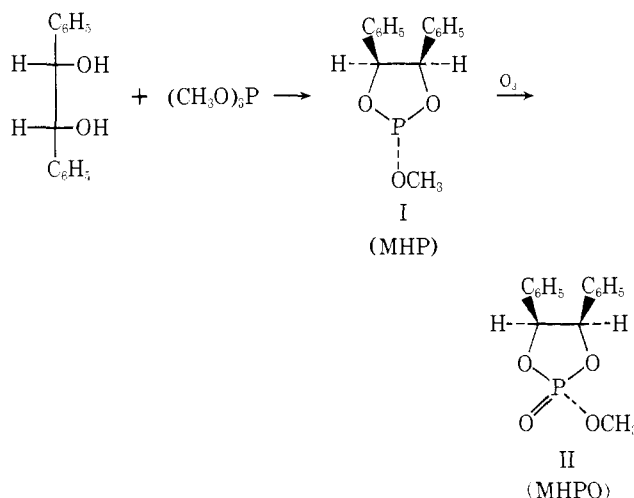
Experimental Section

Preparation of *trans*-Methyl *meso*-Hydrobenzoin Phosphite (I). *meso*-Hydrobenzoin was prepared according to the literature procedure[20] and dried by heating under vacuum. In a typical preparation of the methyl ester, 25 g (0.117 mol) of *meso*-hydrobenzoin and 75 ml (0.605 mol) of commercial trimethyl phosphite were heated at approximately 110° in a 250-ml round-bottom flask equipped with a distillation assembly. The methanol generated in the reaction distilled over for about a 4-hr period under these conditions. When production of methanol ceased, the excess trimethyl phosphite was distilled under vacuum, and the residue was allowed to cool to room temperature. Normally, the product solidified upon standing. If solidification did not occur, further heating under vacuum to remove the last traces of trimethyl phosphite and recooling produced a solid mass. The product was purified by vacuum distillation at 130-135° (0.05 mm) or by sublimation at 70° (0.1 mm): yield of purified product, 20.8 g (65%), mp 56-57°. The ester is quite unstable in the open atmosphere and develops an oily coating after only a brief exposure to the air. The trans stereochemistry of the product was established by the X-ray structure determination. The nmr spectra of the crude and purified ester showed none (<5.0%) of the alternate cis isomer: ir (CHCl₃) 3070 (w), 3010 (m), 2940 (m), 2840 (w), 1495 (w), 1450 (m), 1040 (m), 990 (s), 920 (m), 830 (m) cm⁻¹; nmr (CDCl₃, 100 MHz) δ 3.50 (d, J = 10.4 Hz, 3 H), 5.52 (d, J = 2.0 Hz, 2 H), 6.85 (m, 10 H).

Anal. Calcd for $C_{15}H_{15}PO_3$: C, 65.69; H, 5.51; P, 11.29. Found: C, 65.38; H, 5.41; P, 11.49.

Preparation of *trans*-**Methyl** *meso*-**Hydrobenzoin Phosphate (II).** In a typical preparation, a 4.3-g portion of the phosphite **I** was dissolved in 50 ml of methylene chloride and ozonized at $-30°$ using a potassium iodide indicator. The crude solid product obtained after removing CH_2Cl_2 solvent was purified by sublimation at 90° (0.05 mm), mp 74–75°. The trans stereochemistry of the product was established by the X-ray structure determination. No evidence of the alternate cis isomer was found in the nmr spectrum of the product: ir ($CHCl_3$) 3060 (w), 3005 (m), 2950 (m), 2850 (w), 1490 (w), 1450 (m), 1290 (s), 1205 (w), 1180 (m), 1080 (s), 1010 (vs), 955 (m), 895 (s), 860 (s), 800 (w); nmr ($CDCl_3$, 60 MHz), δ 3.76 (d, $J = 11.4$ Hz, 3 H), 5.45 (d, $J = 9.0$ Hz, 2 H), 6.74 (s, 10 H).

Anal. Calcd for $C_{15}H_{15}PO_4$: C, 62.07; H, 5.21; P, 10.67. Found: C, 62.60; H, 5.35; P, 10.60.

X-Ray Structure Determination of Methyl *meso*-**Hydrobenzoin Phosphite.** Long needle-like crystals of **I** were obtained by sublimation of the ester at 70° (0.15 mm). Because the crystals were partially decomposed by only a short exposure to the atmosphere, the sublimate was cut directly from the cold finger into vaseline under nitrogen in a dry bag. When coated with vaseline, the crystals could be easily handled in the open air. An appropriate crystal was selected and mounted inside a glass capillary. Precession photographs revealed an orthorhombic system elongated along c, the rotation axis. Systematic absences uniquely identified the space group as $P2_12_12_1$. The crystal was transferred to an Enraf-Nonius CAD-3 diffractometer, and the cell dimensions and orientation matrix were calculated from 15 accurately centered reflections near $\theta = 30°$. Table I summarizes the pertinent crystal data. No

Table I. Summary of Crystallographic Data for *trans*-Methyl *meso*-Hydrobenzoin Phosphite

Molecular formula: $C_{15}H_{15}PO_3$
Molecular weight: 274.3
Linear absorption coefficient, μ: 17.77 cm⁻¹ (for Cu Kᾱ)
Calculated density: 1.32 g/cm³ for $Z = 4$
Crystal dimensions: 0.6 × 0.4 × 0.3 mm
Space group $P2_12_12_1$
Cell constants: $a = 9.924$ (3), $b = 5.969$ (1), $c = 23.225$ (5) Å, $\alpha = \beta = \gamma = 90.0°$, $V = 1375.8$ Å³, $Z = 4$

experimental density could be obtained because of the solubility in or reactivity with most solvents.

Intensity data were automatically collected on the CAD-3 diffractometer to a maximum θ of 65° using Ni-filtered Cu Kᾱ radiation (λ 1.54180 Å) and ω–2θ scan technique. No decomposition of the sample during data collection was detected in the control reflections which were measured after each block of 50 reflections. In all, 1930 diffraction maxima were measured and recorded. The data were corrected for Lorentz–polarization effects[21] but not for absorption. The standard deviation, σ_{F_o}, of each reflection was estimated from counting statistics.[22] A final total of 1202 unique nonzero reflections[23] with $I_r > 1.5\sigma_I$ were used in the subsequent analysis.

A sharpened Patterson map[24] revealed a set of vectors consistent with a phosphorus atom located at $x = -0.040$, $y = 0.240$, $z = 0.123$. An electron density map[25] generated using phases calculated from the phosphorus position gave reasonable starting positions for two of the three oxygen atoms. Successive electron density maps eventually provided starting positions for all nonhydrogen atoms. Several cycles of full-matrix least-squares refinement[26] of the 19 atomic positions using isotropic temperature factors gave a conventional unweighted R of 0.12. Further refinement using anisotropic temperature factors and weights of $1/\sigma_{F_o}^2$ reduced R to 0.08. Twelve of the fifteen H atoms were located from a difference map in chemically reasonable positions but refined to positions that gave untenable bond lengths and angles. Also, the isotropic temperature factors for these hydrogen atoms became unreasonably large during refinement. The final positional coordinates and anisotropic temperature factors for nonhydrogen atoms obtained from the last cycle of least-squares refinement are listed in Table II. The numbering scheme used in the analysis is shown in Figure 1.
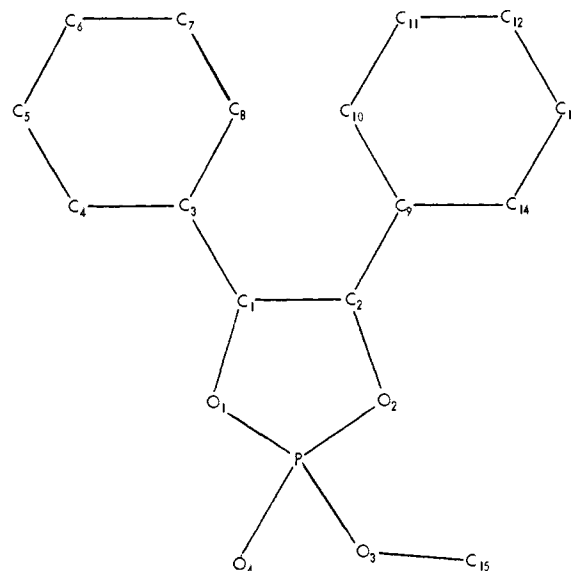
Figure 1. The numbering scheme used in the X-ray analysis for the phosphite, MHP (without O_4), and for both conformers of the phosphate, MHPO(A) and -(B).

X-Ray Structure Determination of *trans*-**Methyl** *meso*-**Hydrobenzoin Phosphate.** Needle crystals of **II** suitable for the X-ray analysis were obtained by sublimation of the ester at 90° (0.05 mm). A crystal was selected and mounted inside a glass capillary. Initial precession photographs identified an orthorhombic system elongated about the shortest direct cell axis, and systematic absences established the space group as either $Pnma$ or $Pna2_1$. Cell dimensions and the orientation matrix were obtained from 23 reflections which were accurately centered on the CAD-3 diffractometer. Table III lists the pertinent crystal data.

Intensity data were collected on the CAD-3 system using Cu Kᾱ radiation (λ 1.5418 Å) and ω–2θ scan technique to a maximum θ of 65°. A total of 2758 diffraction maxima were recorded, of which 2299 were considered to have nonzero values[21-23] and were used in the subsequent analysis. Several attempts were made to locate the phosphorus atoms from a sharpened Patterson map[24] in both $Pnma$ and $Pna2_1$ but without success. The statistical distribution of E's[27] did not give a definite assignment for a centric or acentric system, possibly because the weak reflections were not included in the statistical evaluation. It was noted during the collection of intensity data that reflections with h odd were apparently systematically weaker than those with h even. This proved to be correct upon examination of the average E^2 for the hkl (h even) and hkl (h odd) groups. The E's were rescaled so that each parity group with h odd and h even gave an average E^2 of 1.0.[28] Use of the rescaled data in space group $Pna2_1$ with MULTAN[29] produced a correct phase set with the highest absolute figure of merit of 1.37. Initial coordinates for 16 atoms including the two independent phosphorus atoms were obtained from the E map calculated from the phases produced by MULTAN. The remaining nonhydrogen atoms were located from a subsequent electron density map using the phases calculated from the coordinates of the 16 atoms. Full-matrix least-squares refinement[26] of the positional parameters and isotropic temperature factors using unit weights gave an R value of 0.14. Subsequent stages of refinement of positional parameters and anisotropic temperature factors of one molecule at a time using weights of $1/\sigma_{F_o}^2$ gave a final conventional unweighted $R = 0.07$. A difference map at this stage revealed 15 reasonable H coordinates but, similar to the phosphite ester structure, were not well behaved upon refinement.

Table IV lists the positional coordinates and anisotropic temperature factors for nonhydrogen atoms obtained from the final least-squares refinement. The numbering scheme used in the analysis is shown in Figure 1. The designations of like atoms have been made to correspond between the structures of **I** and both conformers of **II**. The two independent molecules are conformational isomers which differ primarily in the orientation of the methoxyl group. The coordinates in Table IV that are assigned to unprimed atom designations define the conformer with the methoxyl group point-

Table II. Positional Coordinates and Temperature Factors^a for Methyl *meso*-Hydrobenzoin Phosphite

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P$_1$	0.46384 (20)	0.25070 (36)	0.87167 (10)	0.01067 (21)	0.02438 (58)	0.002772 (49)	0.00213 (78)	-0.00078 (19)	0.00085 (35)
O$_1$	0.60537 (47)	0.18638 (86)	0.90164 (25)	0.01189 (61)	0.0252 (18)	0.00356 (15)	0.0012 (16)	0.00121 (52)	-0.00515 (83)
O$_2$	0.46194 (51)	0.03639 (84)	0.82856 (21)	0.01110 (57)	0.0339 (11)	0.00257 (11)	-0.0007 (20)	-0.00154 (48)	-0.00315 (79)
O$_3$	0.35179 (51)	0.16209 (90)	0.91770 (25)	0.01323 (64)	0.0336 (18)	0.00316 (14)	0.0044 (18)	0.00091 (51)	-0.00027 (93)
C$_1$	0.63200 (74)	-0.0537 (13)	0.89665 (34)	0.01267 (95)	0.0203 (23)	0.00255 (19)	0.0011 (24)	-0.00116 (72)	0.0002 (11)
C$_2$	0.57856 (66)	-0.1111 (12)	0.83487 (30)	0.00916 (79)	0.0292 (26)	0.00201 (16)	-0.0023 (23)	-0.00122 (57)	0.0006 (10)
C$_3$	0.77667 (71)	-0.0980 (12)	0.90823 (29)	0.01070 (83)	0.0272 (26)	0.00159 (15)	-0.0009 (24)	-0.00160 (58)	-0.0033 (10)
C$_4$	0.81322 (79)	-0.2923 (13)	0.93678 (32)	0.0155 (11)	0.0326 (30)	0.00196 (16)	0.0003 (30)	-0.00186 (70)	0.0027 (12)
C$_5$	0.94685 (87)	-0.3424 (14)	0.94924 (34)	0.0151 (11)	0.0372 (28)	0.00257 (20)	0.0148 (34)	-0.00088 (83)	0.0002 (13)
C$_6$	1.04989 (85)	-0.1886 (15)	0.93275 (36)	0.0142 (10)	0.0435 (34)	0.00256 (19)	0.0046 (35)	-0.00166 (80)	-0.0007 (14)
C$_7$	1.01114 (77)	0.0063 (15)	0.90193 (36)	0.0124 (10)	0.0367 (31)	0.00249 (18)	-0.0019 (27)	-0.001587 (71)	-0.0026 (14)
C$_8$	0.87778 (73)	0.0493 (15)	0.89086 (32)	0.01151 (95)	0.0383 (29)	0.00227 (18)	-0.0063 (29)	-0.00185 (70)	0.0026 (12)
C$_9$	0.67293 (70)	-0.0765 (12)	0.07879 (28)	0.01082 (87)	0.0306 (25)	0.00164 (15)	0.0027 (25)	-0.00203 (60)	-0.0021 (11)
C$_{10}$	0.68102 (78)	0.1257 (12)	0.75575 (32)	0.01349 (98)	0.0242 (24)	0.00188 (15)	-0.0026 (26)	-0.00205 (68)	0.0006 (11)
C$_{11}$	0.77523 (87)	0.1497 (13)	0.71118 (37)	0.0128 (10)	0.0286 (26)	0.00305 (21)	-0.0056 (29)	-0.00148 (83)	-0.0011 (14)
C$_{12}$	0.86830 (86)	-0.0152 (16)	0.69918 (34)	0.0139 (11)	0.0468 (36)	0.00239 (19)	0.0022 (35)	0.00023 (78)	-0.0009 (15)
C$_{13}$	0.85817 (88)	-0.2250 (15)	0.73098 (33)	0.0168 (11)	0.0383 (31)	0.00193 (15)	0.0075 (36)	-0.00068 (75)	-0.0031 (13)
C$_{14}$	0.76433 (78)	-0.2488 (14)	0.77368 (31)	0.01446 (94)	0.0272 (24)	0.00225 (16)	0.0076 (32)	-0.00152 (72)	-0.0040 (13)
C$_{15}$	0.3012 (10)	0.3193 (18)	0.95840 (44)	0.0213 (15)	0.0556 (41)	0.00370 (24)	0.0129 (44)	0.0026 (11)	-0.0129 (19)

^{a} Anisotropic temperature factors (β_{ij}) have the form $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

Table III. Summary of Crystallographic Data for *trans*-Methyl *meso*-Hydrobenzoin Phosphate

Molecular formula: $C_{15}H_{15}PO_4$
Molecular weight: 290.3
Linear absorption coefficient, μ: 19.41 cm^{-1} (for Cu K$\bar{\alpha}$)
Calculated density: 1.33 g/cm^3 for $Z = 8$
Crystal dimensions: 0.5 × 0.3 × 0.3 mm
Space group: $Pnma$ or $Pna2_1$ ($Pna2_1$ determined)
Cell constants: $a = 18.559$ (4), $b = 6.609$ (1), $c = 23.614$ (5) Å,
$\alpha = \beta = \gamma = 90.0°$, $V = 2896.4$ Å^3, $Z = 8$

ing away from the ring. The primed atom designations are coordinates for the conformer with the methoxyl group pointing over the ring.

Results and Discussion

The production of the single isomeric trans phosphite, I, in the transesterification reaction is rather unique although not surprising. Denney, *et al.*[19] have found that isomer ratios in other five-membered ring phosphites with similar cis-trans arrangements are sensitive to steric requirements of the attached groups. Thus, the cyclic methyl phosphite ester of 1,2-propanediol is formed in a 62:38 isomer ratio, whereas the same ester of *meso*-2,3-butanediol is found in an 87:13 isomer ratio. Denney assumed that the major isomer was trans. The presence of two phenyl groups on the same side of the five-membered ring thus induces the apparently exclusive production of the single trans isomer. A more exact understanding of the nature of the steric requirements in this reaction must await a more detailed concept of the transesterification process in trialkyl phosphites.[17] The identification of the stereochemistry of I lends credence to the assignment of trans stereochemistry to the major isomers in other similar phosphites by Denney, *et al.*[19]

The conversion of I to the corresponding phosphate, II, by ozonolysis shows conclusively that this oxidation occurs stereospecifically with retention of configuration. This finding confirms the conclusion by Denney, *et al.*,[19] that ozonolysis of phosphites to phosphates occurs with retention of configuration.

Bond lengths, bond angles, selected dihedral angles, and intramolecular distances are compiled in Tables V-VIII, respectively, for *trans*-methyl *meso*-hydrobenzoin phosphite (MHP) and both conformers of the corresponding phosphate (MHPO(A) and MHPO(B)). The numbering scheme shown in Figure 1 is consistent among all three structures.

In MHP, the phosphite moiety is a rather distorted pyramidal structure with OPO angles of 95.1, 98.1 and 103.5°, and P is 0.78 Å above the plane of the three O atoms. The average of the OPO angles, 98.9°, falls midway in value between normal sp^3 and p^3 hybrid angles. These OPO angles are in reasonable agreement with those measured for triethyl (96.5°) and trivinyl phosphite (100.0°)[16] and P_4O_6 (99°)[30] by electron diffraction. It seems likely that the interior OPO ring angle of 95.1° is somewhat contracted by restrictions imposed by the five-membered ring since it is smaller than all the OPO angles not involved in the five-membered ring. Thus, assuming a normal unrestricted OPO angle of 99°, the ring OPO angle is contracted by about 4°.

The three PO bond lengths average 1.623 Å. Although the exo PO bond is slightly longer than the PO bonds in the ring, all three PO bond lengths are within 2 σ of their average value. The bond lengths calculated for MHP are longer than those found in triethyl and trivinyl phosphite (1.600 Å)[16] but shorter than those in P_4O_6 (1.65 Å).[30]

The five-membered ring is an envelope conformation with C$_1$ in the flap position and 0.55 Å out of the plane defined by P, O$_1$, O$_2$, and C$_2$. A projection of the molecule

Table IV. Positional Coordinates and Temperature Factors[a] for Methyl *meso*-Hydrobenzoin Phosphate

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	0.14286 (10)	0.23959 (25)	0.17725 (00)	0.003101 (55)	0.01627 (35)	0.001543 (31)	−0.00002 (24)	−0.000071 (89)	−0.00107 (20)
O₁	0.20861 (24)	0.15034 (72)	0.21198 (21)	0.00276 (16)	0.0237 (14)	0.00202 (11)	−0.00234 (74)	−0.00075 (22)	0.00081 (59)
O₂	0.00897 (25)	0.05773 (65)	0.18519 (22)	0.00349 (17)	0.0204 (11)	0.001702 (99)	−0.00081 (70)	−0.00116 (23)	0.00024 (60)
O₃	0.16120 (32)	0.22742 (89)	0.11237 (21)	0.00496 (23)	0.0338 (17)	0.00157 (11)	0.0025 (11)	0.00054 (26)	0.00088 (69)
O₄	0.11979 (32)	0.43648 (77)	0.19562 (26)	0.00524 (24)	0.0201 (13)	0.00279 (14)	0.00220 (88)	0.00061 (31)	−0.00199 (67)
C₁	0.20244 (36)	−0.0680 (10)	0.21450 (31)	0.00253 (22)	0.0173 (17)	0.00189 (15)	−0.00007 (95)	0.00054 (31)	−0.00144 (77)
C₂	0.12018 (38)	−0.1038 (10)	0.22026 (32)	0.00284 (23)	0.0184 (17)	0.00190 (16)	−0.0005 (10)	0.00041 (32)	0.00069 (80)
C₃	0.24845 (38)	−0.1480 (11)	0.26215 (31)	0.00246 (21)	0.0246 (20)	0.00174 (15)	0.0006 (11)	−0.00066 (32)	−0.00020 (87)
C₄	0.28050 (42)	−0.34060 (11)	0.25463 (36)	0.00329 (27)	0.0021 (19)	0.00253 (19)	−0.0015 (12)	−0.00022 (32)	−0.00029 (96)
C₅	0.32340 (47)	−0.4223 (13)	0.29891 (44)	0.00352 (30)	0.0285 (26)	0.00330 (26)	−0.0022 (14)	0.00031 (47)	0.0048 (13)
C₆	0.33294 (48)	−0.3106 (16)	0.34868 (40)	0.00357 (29)	0.0425 (32)	0.00215 (21)	−0.0032 (17)	−0.00025 (42)	0.0036 (13)
C₇	0.30025 (47)	−0.1211 (14)	0.35626 (38)	0.00343 (30)	0.0395 (30)	0.00217 (20)	−0.0015 (15)	−0.00046 (40)	0.0008 (12)
C₈	0.25738 (41)	−0.0392 (12)	0.31193 (32)	0.00299 (25)	0.0289 (21)	0.00165 (15)	−0.0004 (12)	0.00091 (34)	−0.00158 (93)
C₉	0.08980 (37)	−0.0959 (10)	0.27881 (32)	0.00255 (22)	0.0193 (17)	0.00179 (15)	0.0015 (10)	0.00033 (30)	−0.00156 (81)
C₁₀	0.05969 (48)	0.0792 (13)	0.30180 (37)	0.00431 (33)	0.0286 (24)	0.00220 (20)	0.0021 (14)	0.00140 (43)	−0.0021 (10)
C₁₁	0.03179 (56)	0.0757 (15)	0.35776 (42)	0.00552 (43)	0.0382 (31)	0.00260 (23)	0.0015 (18)	0.00265 (53)	−0.0057 (14)
C₁₂	0.03504 (50)	−0.0961 (16)	0.39056 (41)	0.00405 (33)	0.0408 (33)	0.00242 (21)	0.0024 (17)	−0.00135 (45)	0.0018 (13)
C₁₃	0.06505 (48)	−0.2735 (14)	0.36733 (39)	0.00382 (32)	0.0338 (32)	0.00236 (20)	0.0030 (15)	−0.00048 (42)	0.0017 (12)
C₁₄	0.09171 (41)	−0.2718 (13)	0.31160 (35)	0.00317 (27)	0.0318 (24)	0.00194 (16)	0.0033 (13)	−0.00037 (35)	0.0023 (11)
C₁₅	0.19252 (54)	0.4113 (15)	0.08519 (40)	0.00494 (38)	0.0400 (31)	0.00245 (20)	0.0015 (17)	0.00062 (48)	0.0079 (13)
P′	0.39449 (10)	0.18314 (26)	0.15524 (10)	0.003094 (61)	0.01994 (40)	0.001694 (34)	0.00059 (26)	0.000171 (89)	0.00092 (20)
O₁′	0.46576 (24)	0.11626 (70)	0.12212 (22)	0.00318 (16)	0.0279 (14)	0.00221 (10)	−0.00199 (73)	0.00082 (21)	−0.00030 (58)
O₂′	0.34798 (22)	−0.01137 (64)	0.14316 (19)	0.00284 (14)	0.0258 (12)	0.00201 (10)	−0.00043 (66)	−0.00069 (20)	−0.00138 (57)
O₃′	0.40911 (27)	0.18742 (79)	0.21946 (20)	0.00435 (19)	0.0324 (15)	0.00193 (10)	0.00063 (86)	0.00006 (23)	−0.00346 (65)
O₄′	0.36431 (28)	0.37568 (68)	0.13701 (25)	0.00506 (21)	0.0248 (13)	0.00280 (13)	0.00140 (87)	−0.00011 (28)	0.00037 (66)
C₁′	0.46548 (36)	−0.0979 (10)	0.10915 (29)	0.00288 (23)	0.0262 (19)	0.00188 (15)	−0.0029 (10)	−0.00027 (30)	0.00045 (81)
C₂′	0.38334 (34)	−0.15566 (91)	0.10402 (29)	0.00278 (21)	0.0205 (16)	0.00209 (15)	−0.00055 (98)	−0.00037 (29)	−0.00026 (76)
C₃′	0.51081 (34)	−0.1399 (10)	0.05846 (29)	0.00237 (20)	0.0278 (19)	0.00190 (14)	0.0014 (10)	−0.00016 (29)	−0.00046 (82)
C₄′	0.54712 (40)	−0.3278 (12)	0.05614 (33)	0.00360 (26)	0.0314 (21)	0.00222 (17)	0.0019 (12)	0.00023 (36)	−0.00050 (96)
C₅′	0.59171 (45)	−0.3748 (13)	0.01067 (40)	0.00386 (30)	0.0389 (27)	0.00284 (21)	0.0054 (14)	−0.00028 (41)	0.0045 (13)
C₆′	0.59879 (43)	−0.2323 (15)	−0.03441 (35)	0.00357 (29)	0.0435 (27)	0.00213 (17)	0.0008 (15)	0.00079 (36)	0.0026 (12)
C₇′	0.56252 (40)	−0.0527 (13)	−0.03230 (34)	0.00322 (26)	0.0365 (25)	0.00245 (19)	−0.0007 (13)	0.00077 (37)	−0.0008 (10)
C₈′	0.51765 (38)	−0.0051 (12)	0.01458 (31)	0.00314 (26)	0.0346 (22)	0.00197 (15)	0.0019 (12)	−0.00062 (33)	−0.00380 (98)
C₉′	0.35120 (34)	−0.1412 (10)	0.04532 (29)	0.00261 (21)	0.0243 (18)	0.00180 (14)	0.00180 (99)	−0.00042 (29)	−0.00092 (78)
C₁₀′	0.32462 (44)	0.0377 (12)	0.02413 (34)	0.00402 (30)	0.0354 (24)	0.00205 (17)	0.0027 (14)	−0.00109 (35)	0.0017 (10)
C₁₁′	0.29708 (50)	0.0397 (14)	−0.03344 (41)	0.00499 (36)	0.0385 (29)	0.00296 (23)	−0.0002 (16)	−0.00054 (46)	0.0015 (13)
C₁₂′	0.29677 (49)	−0.1292 (15)	−0.06525 (40)	0.00428 (33)	0.0434 (31)	0.00272 (20)	0.0028 (16)	0.00018 (44)	−0.0045 (14)
C₁₃′	0.32329 (47)	−0.3114 (14)	−0.04338 (41)	0.00398 (33)	0.0426 (31)	0.00309 (24)	0.0047 (16)	−0.00005 (45)	−0.0061 (14)
C₁₄′	0.34984 (42)	−0.3202 (11)	0.01330 (37)	0.00355 (37)	0.0304 (21)	0.00259 (18)	0.0018 (13)	−0.00033 (38)	−0.0037 (10)
C₁₅′	0.44098 (44)	0.0134 (13)	0.24982 (33)	0.00454 (31)	0.0367 (24)	0.00213 (18)	0.0013 (14)	0.00077 (39)	0.0059 (10)

[a] Anisotropic temperature factors (β_{ij}) have the form $h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}$.

Table V. Comparison of Bond Distances[a] in MHP, MHPO(A), and MHPO(B)

Bond	MHP	MHPO(A)	MHPO(B)
		Distance, Å	
$P-O_1$	1.614 (5)	1.584 (4)	1.599 (5)
$P-O_2$	1.624 (5)	1.575 (4)	1.574 (5)
$P-O_3$	1.631 (6)	1.571 (5)	1.541 (5)
$P-O_4$		1.443 (5)	1.455 (5)
O_1-C_1	1.462 (9)	1.449 (8)	1.448 (8)
O_2-C_2	1.462 (8)	1.470 (8)	1.481 (8)
O_3-C_{15}	1.424 (12)	1.492 (10)	1.479 (10)
C_1-C_2	1.567 (10)	1.551 (9)	1.576 (9)
C_1-C_3	1.485 (10)	1.508 (9)	1.489 (10)
C_2-C_9	1.452 (9)	1.494 (10)	1.512 (9)
C_3-C_4	1.384 (10)	1.416 (10)	1.414 (10)
C_3-C_8	1.394 (10)	1.388 (10)	1.372 (10)
C_4-C_5	1.390 (12)	1.421 (12)	1.391 (12)
C_5-C_6	1.427 (12)	1.399 (13)	1.427 (13)
C_6-C_7	1.419 (12)	1.403 (13)	1.365 (13)
C_7-C_8	1.373 (11)	1.422 (11)	1.420 (11)
C_9-C_{10}	1.422 (10)	1.395 (10)	1.375 (10)
C_9-C_{14}	1.411 (11)	1.397 (10)	1.404 (10)
$C_{10}-C_{11}$	1.402 (11)	1.419 (12)	1.452 (12)
$C_{11}-C_{12}$	1.378 (12)	1.376 (13)	1.345 (13)
$C_{12}-C_{13}$	1.457 (12)	1.409 (13)	1.400 (13)
$C_{13}-C_{14}$	1.368 (11)	1.406 (11)	1.427 (13)

[a] Bond distances have not been corrected for thermal motion. The estimated standard deviations do not contain cell constant errors.

Table VI. Comparison of Bond Angles in MHP, MHPO(A), and MHPO(B)

Atoms	MHP	MHPO(A)	MHPO(B)
		Angle, deg	
O_1-P-O_2	95.1 (3)	98.2 (2)	98.0 (2)
O_1-P-O_3	103.5 (3)	108.6 (3)	109.9 (3)
O_1-P-O_4		113.6 (3)	114.5 (3)
O_2-P-O_3	98.1 (3)	102.4 (3)	106.8 (3)
O_2-P-O_4		117.5 (3)	116.7 (3)
O_3-P-O_4		114.7 (3)	110.0 (3)
$P-O_1-C_1$	110.9 (4)	109.3 (4)	111.8 (4)
$P-O_2-C_2$	113.8 (4)	111.8 (4)	113.3 (4)
$P-O_3-C_{15}$	117.5 (5)	117.5 (5)	122.2 (5)
$O_1-C_1-C_2$	103.0 (6)	103.5 (5)	104.9 (5)
$O_1-C_1-C_3$	109.6 (6)	109.6 (5)	110.5 (5)
$C_2-C_1-C_3$	117.0 (6)	116.0 (5)	116.1 (6)
$O_2-C_2-C_1$	103.2 (5)	103.2 (5)	103.0 (5)
$O_2-C_2-C_9$	110.5 (6)	110.3 (5)	110.9 (5)
$C_1-C_2-C_9$	115.9 (6)	116.6 (6)	115.9 (5)
$C_1-C_3-C_4$	119.3 (6)	117.3 (6)	117.7 (6)
$C_1-C_3-C_8$	122.1 (6)	121.2 (6)	122.6 (6)
$C_4-C_3-C_8$	118.6 (7)	121.4 (6)	119.8 (7)
$C_3-C_4-C_5$	122.0 (7)	119.0 (7)	120.6 (7)
$C_4-C_5-C_6$	119.3 (8)	119.2 (7)	118.9 (8)
$C_5-C_6-C_7$	117.9 (7)	121.6 (8)	120.1 (8)
$C_6-C_7-C_8$	120.6 (8)	119.2 (8)	120.7 (7)
$C_3-C_8-C_7$	121.5 (8)	119.5 (7)	119.9 (7)
$C_2-C_9-C_{10}$	123.5 (6)	122.7 (6)	122.0 (6)
$C_2-C_9-C_{14}$	119.2 (6)	118.3 (6)	116.6 (6)
$C_{10}-C_9-C_{14}$	117.3 (6)	119.0 (7)	121.5 (7)
$C_9-C_{10}-C_{11}$	120.8 (7)	119.7 (7)	118.3 (7)
$C_{10}-C_{11}-C_{12}$	121.6 (7)	121.4 (8)	121.1 (9)
$C_{11}-C_{12}-C_{13}$	117.7 (7)	119.0 (8)	120.4 (9)
$C_{12}-C_{13}-C_{14}$	120.2 (8)	119.8 (8)	120.2 (8)
$C_9-C_{14}-C_{13}$	122.2 (7)	121.1 (7)	118.5 (7)

which shows the ring conformation sighting down the C_1-C_2 bond is given in Figure 2. The O_1 and O_2 atoms are unequally spaced above and below the $P-C_1-C_2$ plane with O_1, 0.54, and O_2, 0.31 Å out of plane. The dihedral angles, $C_3-C_1-C_2-C_9$ and $O_1-C_1-C_2-O_2$ of 34.4 and 35.0°, respectively, are similar in magnitude to those estimated for other five-membered ring phosphite triesters from nmr coupling constants.[31]

Table VII. Comparison of Selected Dihedral Angles[a] in MHP, MHPO(A), and MHPO(B)

Atoms	MHP	MHPO(A)	MHPO(B)
		Angle, deg	
$O_2-P-O_1-C_1$	-24.0 (5)	+22.5 (5)	-14.6 (5)
$O_3-P-O_1-C_1$	+75.6 (5)	-83.6 (4)	96.6 (5)
$O_4-P-O_1-C_1$		147.5 (4)	-138.9 (4)
$O_1-P-O_2-C_2$	+0.3 (5)	1.3 (4)	-5.8 (4)
$O_3-P-O_2-C_2$	-104.2 (5)	112.5 (4)	-119.5 (4)
$O_4-P-O_2-C_2$		-120.9 (4)	116.9 (4)
$O_1-P-O_3-C_{15}$	94.6 (6)	-95.4 (5)	-51.9 (6)
$O_2-P-O_3-C_{15}$	-168.1 (6)	161.4 (5)	53.4 (6)
$O_4-P-O_3-C_{15}$		33.0 (6)	-179.0 (5)
$P-O_1-C_1-C_2$	38.0 (6)	-36.9 (6)	28.3 (6)
$P-O_1-C_1-C_3$	163.2 (5)	-161.3 (4)	154.0 (4)
$P-O_2-C_2-C_1$	20.9 (6)	-22.3 (6)	21.8 (6)
$P-O_2-C_2-C_9$	-103.6 (6)	102.9 (5)	-102.8 (5)
$O_1-C_1-C_2-O_2$	-35.0 (6)	35.7 (6)	-29.8 (6)
$O_1-C_1-C_2-C_9$	85.9 (7)	-85.3 (6)	91.4 (6)
$C_3-C_1-C_2-O_2$	-155.3 (6)	+155.8 (5)	-152.0 (5)
$C_3-C_1-C_2-C_9$	-34.3 (9)	34.7 (8)	-30.8 (8)
$O_1-C_1-C_3-C_4$	144.2 (7)	-147.1 (6)	147.8 (6)
$O_1-C_1-C_3-C_8$	-36.3 (9)	34.5 (8)	-32.8 (9)
$C_2-C_1-C_3-C_4$	-99.0 (8)	96.2 (7)	-93.0 (7)
$C_2-C_1-C_3-C_8$	80.5 (9)	-82.2 (8)	86.4 (8)
$O_2-C_2-C_9-C_{10}$	24.2 (9)	-22.6 (9)	31.7 (8)
$O_2-C_2-C_9-C_{14}$	-157.2 (6)	157.3 (6)	-148.3 (6)
$C_1-C_2-C_9-C_{10}$	-92.7 (8)	94.6 (8)	-85.2 (8)
$C_1-C_2-C_9-C_{14}$	85.9 (8)	-85.5 (7)	94.8 (7)

[a] The dihedral angle has a positive sign if vector **K-L** is clockwise from vector **J-I** when viewed down vector **J-K**, and a negative sign if counterclockwise. Note that MHPO(A) is enantiomeric to both MHP and MHPO(B) as shown by the signs of the dihedral angles.

Table VIII. Comparison of Selected Intramolecular Nonbonded Distances for MHP, MHPO(A), and MHPO(B)

Atoms	MHP	MHPO(A)	MHPO(B)
		Distance, Å	
$P \cdots C_1$	2.534	2.476	2.524
$P \cdots C_2$	2.587	2.522	2.553
$P \cdots C_{15}$	2.614	2.620	2.644
$O_1 \cdots C_2$	2.372	2.356	2.398
$O_2 \cdots C_1$	2.374	2.367	2.393
$O_1 \cdots O_2$	2.389	2.389	2.395
$O_1 \cdots C_{15}$	3.389	3.468	3.125
$O_2 \cdots C_{15}$	3.807	3.838	3.058
$O_4 \cdots C_{15}$		2.960	3.854
$P \cdots C_{10}$	3.529	3.487	3.492
$O_4 \cdots C_{10}$		3.606	3.555

The ring C–O bond lengths of 1.462 (9) Å in MHP are longer by 4 σ than normal C–O bonds (1.426 Å) in aliphatic alcohols and ether,[32] whereas the O_3-C_{15} bond length of 1.42 (1) Å is normal. The exo $P-O_3-C_{15}$ angle of 117.5° in MHP is similar to P–O–C angles observed in a large number of phosphate esters.[10-13,33] The internal ring P–O–C angles of 110.9 and 113.8° are much smaller than the exo angle presumably because of the restrictions imposed by the five-membered ring.

Another effect of the geometrical requirements of the five-membered ring is found in the bond angles around C_1 and C_2. The $O_1-C_1-C_2$ and $O_2-C_2-C_1$ angles are about 6° smaller than a normal tetrahedral angle. This effect is accompanied by an increase of about 7° over a normal tetrahedral angle in the $C_2-C_1-C_3$ and $C_1-C_2-C_9$ angles. The average of the three angles around both C_1 and C_2 is 109.9°.

Both phenyl rings are essentially planar with standard deviations of distances from the best least-squares planes of 0.018 Å. The $C_{sp^2}-C_{sp^2}$ distances in the aromatic rings average 1.402 Å, and the 16 aromatic C_{sp^2} angles average

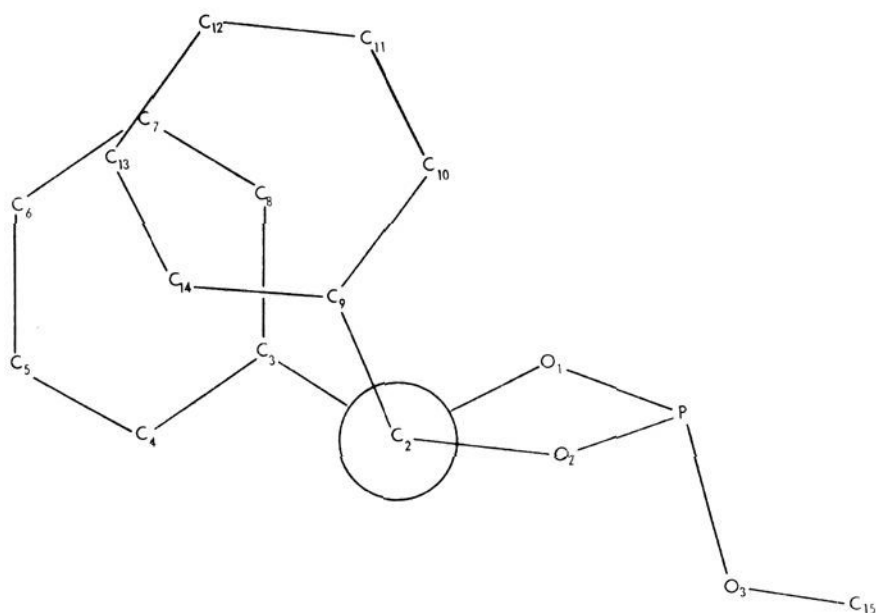**Figure 2.** A view of MHP sighting down the C_1-C_2 bond in the five-membered ring.

120.2°. The angle between vectors normal to the phenyl rings is 45.1°. The plane of the phenyl ring attached to C_1 is approximately perpendicular (92.5°) to the $C_1C_2O_2$ plane.

A partial list of intramolecular distances is compiled in Table VIII. The two C $\cdots$ O nonbonded distances in the five-membered ring are essentially equal (2.37 Å). The O $\cdots$ O contact distance across the ring is 2.39 Å. The P $\cdots$ C contact distances for C_1, C_2, and C_{15} are quite similar, ranging from 2.53 to 2.61 Å. The unsymmetrical positioning of the methoxyl group can be seen from a comparision of the $O_1 \cdots C_{15}$ distance of 3.39 Å with the $O_2 \cdots C_{15}$ distance of 3.81 Å

A 3-D molecular packing diagram prepared by ORTEP-II[34] is shown in Figure 3. There are five intermolecular contacts < 3.60 Å: $C_7 \cdots O_3$, 3.53 (1) Å $(1 + x, y, z)$; $C_{15} \cdots C_3$, 3.51 (1) Å $(-\frac{1}{2} + x, \frac{1}{2} - y, 2 - z)$; $C_{14} \cdots O_2$, 3.51 (1) Å $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$; $C_{10} \cdots O_2$, 3.44 (1) Å $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$; $C_{11} \cdots O_2$, 3.42 (1) Å $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$. There are 15 intermolecular contacts < 3.75 Å including those listed above.

The most remarkable feature of the structure of MHPO is the coexistence of two conformers in the solid state which differ primarily in the orientation of the methoxyl ester function. These conformers will be designated in the discussion as MHPO(A) and MHPO(B). The methoxyl group in MHPO(A) is directed away from the five-membered ring and forms dihedral angles O_1-P-O_3-C_{15} and O_2-P-O_3-C_{15} that are almost identical with those in MHP. MHPO(B) has the methoxyl group folded over the five-membered ring and nearly perfectly staggered between O_1 and O_2 with an O_4-P-O_3-C_{15} dihedral angle of 179°. These conformers have precedents in earlier systems; i.e., the orientation of the methoxyl group in methyl ethylene phosphate[10] and in methyl acetoinenediol phosphate[12] are similar to MHPO(B), whereas in methyl pinacol phosphate[11] the methoxyl group is oriented similarly to that in MHPO(A). Such conformational effects in solution have been seen in the P=O stretching frequency in the infrared spectra.[35]

The coordinates in Table IV for MHPO(B) are approximately related to those of MHPO(A) by $x_B = x_A + 0.2552$, $y_B = y_A - 0.0489$, $z_B = 0.3298 - z_A$. These factors were calculated using P, O_1, O_2, O_3, O_4, C_1, and C_2 but work reasonably well for all atoms except C_{15}. The translational factor of approximately $\frac{1}{4}$ in the relationship of the x coordinates of the two conformers is apparently responsible for the systematic weakening of the structure factor amplitudes of odd h indices.

The internal OPO ring angle in both conformers agrees with values measured for other five-membered ring phosphate esters[10-13] and is about 5° smaller than the normal average O(C)–P–O(C) angle of 103.0°[13] measured in six-membered cyclic and acyclic esters. The three O(C)–P–O(C) angles in MHPO(A) average 103.1° and in MHPO(B) average 104.9°. The average of the three O=P–O(C) angles in MHPO(A) is 115.3° and in MHPO(B) is 113.7°. The sum of the four P–O bond lengths is 6.173 Å for MHPO(A) and 6.169 Å for MHPO(B), in excellent agreement with the value of 6.177 ± 0.030 Å observed by Calleri and Speakman.[36] The average P–O single bond length in both conformers is 1.574 Å.

A survey of several recent phosphate ester structures reveals that C–O bonds in C–O–P=O bonding situations are longer than normal aliphatic or aromatic C–O bonds (ali-
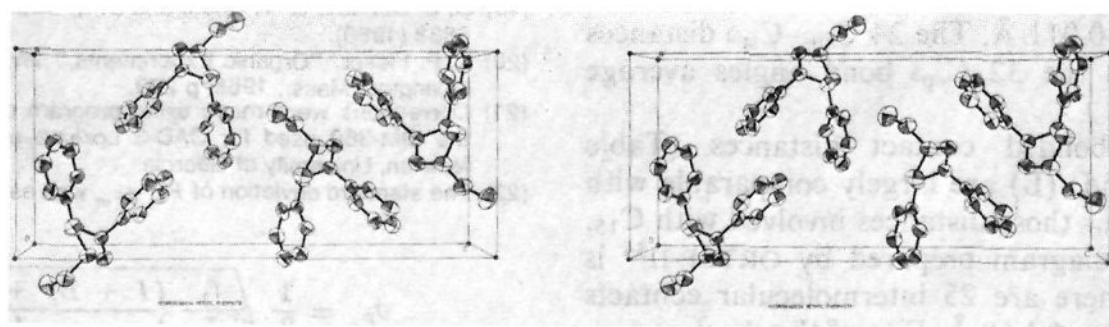

Figure 3. A stereoscopic packing diagram of one unit cell of *trans*-methyl *meso*-hydrobenzoin phosphite.
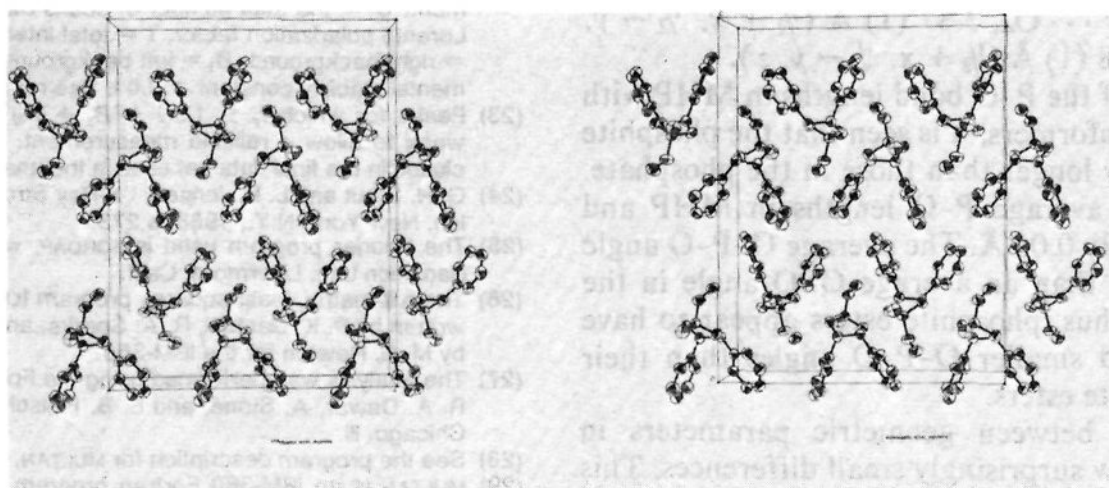

Figure 4. A stereoscopic packing diagram of one unit cell of *trans*-methyl *meso*-hydrobenzoin phosphate.

phatic C–O, 1.43 Å; aromatic C–O, 1.36 Å)[32] by about 0.03–0.04 Å. Thus, the average of the aliphatic C_{sp^3}–O bonds in methyl ethylene phosphate,[10] methyl pinacol phosphate,[11] acetoinenediol phosphate,[12] propane-1,3-diol cyclic phosphate,[37] sodium β-cytidine 2′,3′-cyclic phosphate, [38] 2α-bromo-5β-bromomethyl-5α-methyl-2β-oxo-1,3,2-dioxaphosphorinane,[39] the borane adduct of 2-methoxy-*cis*-4,6-dimethyl-1,3,2-dioxaphosphorinane,[40] and both conformers of MHPO is 1.466 Å. The 12 C_{sp^2} O distances in acetoinenediol phosphate,[12] catechol cyclic phosphate,[13] 4-carbethoxyanilinium bis-*p*-nitrophenyl phosphate,[41] triphenyl phosphate,[42] and tri-*p*-nitrophenyl phosphate[43] average 1.395 Å. It was also noted earlier that C–O bond lengths in MHP are apparently elongated with respect to normal aliphatic C–O single bonds.

Values of normal unrestricted P–O–C angles observed in a large number of phosphate esters[33] are approximately 120°. In contrast, the internal P–O–C ring angles in both MHPO conformers and in other five-membered ring phosphate esters[10-13] are 7–10° smaller than the normal value. This contraction in P–O–C angle is one of the major differences between five-membered ring phosphate esters and larger ring or acyclic esters. Whereas reduced O–P–O angles in five-membered ring esters have received considerable attention, little emphasis has been given to reduced P–O–C angles even though the difference in angles is considerably larger.

As observed in MHP, both conformers of MHPO have O_1–C_1–C_2 and O_2–C_2–C_1 angles that are smaller and C_2–C_1–C_3 and C_1–C_2–C_9 angles that are larger than normal tetrahedral value. The average of the three angles around C_1 and C_2 in MHPO(A) is 109.7 and 110.0°, respectively, and for MHPO(B) is 110.5 and 109.9°.

The ring conformation in both MHPO(A) and -(B) is essentially an envelope with C_1 in the flap position. The dihedral angle for O_1–P–O_2–C_2 in MHPO(A) is 1.3° and in MHPO(B) is 5.8° as compared with 0.3° in MHP. The dihedral angles O_1–C_1–C_2–O_2 and C_3–C_1–C_2–C_9 of 35.7 and 34.7°, respectively, in MHPO(A) correspond closely to those found in MHP, whereas the angles in MHPO(B) are smaller, 29.8 and 30.8°, respectively.

The phenyl rings in MHPO(A) and -(B) are planar with a maximum standard deviation of distances from the best least-squares planes of 0.011 Å. The 24 C_{sp^2}–C_{sp^2} distances average 1.402 Å, and the 32 C_{sp^2} bond angles average 119.9°.

Intramolecular nonbonded contact distances (Table VIII) in MHPO(A) and -(B) are largely comparable with those in MHP except for those distances involved with C_{15}. A molecular packing diagram prepared by ORTEP-II[34] is shown in Figure 4. There are 25 intermolecular contacts <3.75 Å of which 13 are < 3.60 Å. Five of the shortest contact distances are $C_2 \cdots O_4$, 3.09 (1) Å (x, $-1 + y$, z); $C_2' \cdots O_4'$, 3.21 (1) Å (x, $-1 + y$, z); $C_{14} \cdots O_4$, 3.37 (1) Å (x, $-1 + y$, z); $O_1' \cdots O_4$, 3.37 (1) Å ($\frac{1}{2} + x$, $\frac{1}{2} - y$, z); and $O_1' \cdots O_2$, 3.48 (1) Å ($\frac{1}{2} + x$, $\frac{1}{2} - y$, z).

From comparisons of the P–O bond lengths in MHP with those in the MHPO conformers, it is seen that the phosphite ester bonds are slightly longer than those in the phosphate. The difference in the average P–O lengths in MHP and MHPO is approximately 0.05 Å. The average O–P–O angle in MHP is 5° smaller than an average OPO angle in the MHPO conformers. Thus, phosphite esters appear to have longer P–O bonds and smaller O–P–O angles than their corresponding phosphate esters.

Other comparisons between geometric parameters in MHP and MHPO show surprisingly small differences. This can best be seen in Table VII by comparing the dihedral angles for the three structures. Agreement of the values be-

tween MHP and MHPO(A) is indeed excellent; somewhat larger deviations are noted between MHP and MHPO(B), but the overall agreement is obvious. (Dihedral angles in MHPO(B) involving C_{15} will, of course, not agree with values in MHP or MHPO(A).)

Supplementary Material Available. Listings of h, k, l, F_o, and F_c for MHP and MHPO will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20x reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-7790.

References and Notes

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$$\sigma_{F_o} = \frac{1}{2}\sqrt{\frac{f_i}{S_i L_p}}\left\{\frac{I + B_r + B_l + (\nu I_r)^2}{I_r}\right\}$$

where f_i = filter factor for the attenuation filter used in the measurement, S_i = the total number of scans made in the measurement, L_p = Lorentz polarization factor, I = total intensity including backgrounds, B_r = right background, B_l = left background, $I_r = I - B_l - B_r$, ν = instrumental stability constant = 0.01. See ref 24, p 454.
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Isolation and Characterization of Peroxy-Y Base from Phenylalanine Transfer Ribonucleic Acid of the Plant, *Lupinus luteus*

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Abstract: The peroxy-Y structure **3** has been determined for the fluorescent base Y_L isolated from the phenylalanine tRNA of the plant *Lupinus luteus*. This compound had been shown to be present in the phenylalanine tRNA of beef, calf, chicken, and rat livers, but owing to the limited amount (*ca.* 5 μg from each source) it was only possible to measure the uv and mass spectra. The amount of material isolated from the plant (30 μg) provides additional evidence for this highly unique structure.

So far the following three hydrophobic fluorescent bases have been characterized from various sources of tRNA^{Phe}: Y_{sc} base **1** from Baker's yeast,[2,3] Y_t base **2** from *Torulopsis utilis*,[4] and peroxy-Y base **3** from livers of beef, calf, rat, and chicken.[5,6] The Y base first discovered in 1967, located next to the 3' end of the anticodon loop,[7] can be selectively excised at pH 2.9.[8] It is intimately related to the codon–anticodon binding and has been shown by X-ray studies to be quite exposed (in the solid state of a salt).[9] Recently, guanine has been shown to be a biogenetic precursor of the Y base.[10]
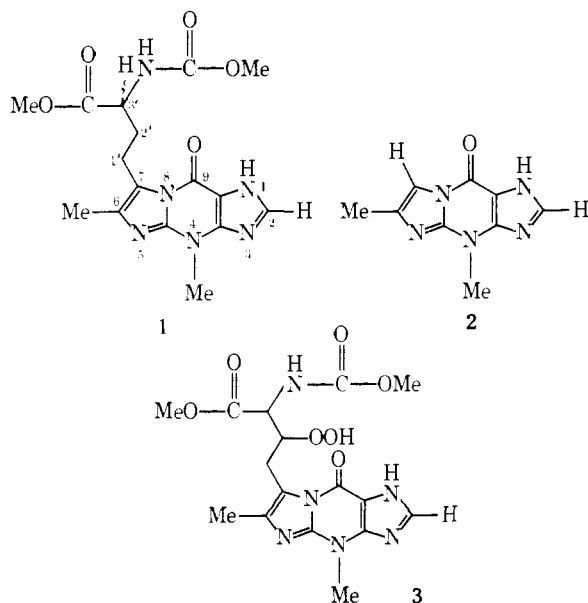
Based on observations that the fluorescent bases present in wheat germ tRNA^{Phe} [11] and beef tRNA^{Phe} [5] are chromatographically and chemically similar, it was inferred that the wheat germ base could be represented by **3**.[6] The peroxy-Y base obtained from the various liver sources was very limited in amount (*ca.* 5 μg) of the base, so that the structure was derived solely from uv and mass spectra data. The plant *Lupinus luteus* (*Papilionaceae*) has provided a larger amount (30 μg) of the base and has thus enabled us to carry out CD measurements, and a microcolor reaction sensitive to peroxides. This has provided us with additional evidence supporting the very unique hydroperoxy structure **3**. As far as we know, this appears to be the first and only natural product characterized so far to have a hydroperoxy function.

Experimental Section

In view of the frequent difficulties encountered in the isolation of Y bases with satisfactory uv and fluorescent spectra, the isolation procedure is described in some detail. In this procedure, the base is excised directly from the crude tRNA mixture, and hence the laborious isolation of pure tRNA^{Phe} is obviated.

Isolation of tRNA. All operations were performed at 5–8° in the cold room. The total tRNA mixture was isolated according to the following procedure. To a liter polyethylene container, 40 l. of freshly distilled phenol saturated with water was added, followed by 40 l. of distilled water containing 0.002 mol/l. of EDTA, 0.002 mol/l. of sodium thiosulfate, and 0.01 mol/l. of MgCl$_2$. The mixture was brought to pH 6.8–7.0 by addition of solid sodium acetate with stirring. Ten kilograms of freshly milled *Lupinus luteus* seeds was added with constant stirring, which was continued for 4 hr. The next day the separated upper phase was siphoned off to another polyethylene container. The lower phase was again stirred for 1 hr with 10 l. of 0.01 *M* MgCl$_2$, and the separated upper phase was also siphoned off to the same second container.