

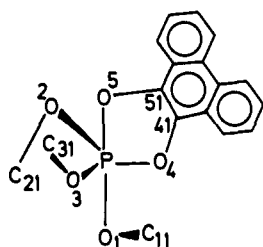
Crystal and Molecular Structure of Pentaphenoxyphosphorane, $(C_6H_5O)_5P$. The Configuration of Acyclic, Monocyclic, and Spirobicyclic Pentaoxyphosphoranes

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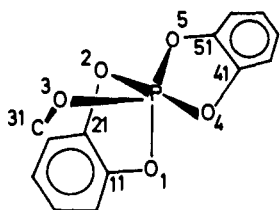
Abstract: The crystal and molecular structure of pentaphenoxyphosphorane, $(C_6H_5O)_5P$, was determined by single-crystal x-ray diffraction techniques. Intensity data were collected using a computer controlled CAD4 automatic diffractometer with nickel filtered Cu $K\alpha$ radiation; 5076 unique reflections with $\theta \leq 75^\circ$ were collected using $(\theta-2\theta)$ scan and a scan width of 1.0° . The space group is $P\bar{1}$ with two molecules per unit cell of dimensions $a = 9.686 \pm 0.005 \text{ \AA}$, $b = 11.315 \pm 0.005 \text{ \AA}$, $c = 11.693 \pm 0.005 \text{ \AA}$, $\alpha = 83.66 \pm 0.06^\circ$, $\beta = 79.66 \pm 0.06^\circ$, and $\gamma = 77.58 \pm 0.04^\circ$. The final R factor for 5076 independent reflections is 7.5%. The phosphorus is at the center of a nearly perfect PO_5 trigonal bipyramid (D_{3h} symmetry). The two apical P-O bonds are virtually identical, 1.662 (5) and 1.663 (5) \AA , and longer than the three equatorial P-O bonds, 1.602 (5), 1.596 (5), 1.600 (5) \AA . The C-O (apical) bonds are shorter, 1.372 (7) and 1.389 (7) \AA , than the C-O (equatorial) bonds, 1.403 (8), 1.404 (8), and 1.409 (8) \AA . It is suggested that the electrons on the apical oxygens are less involved in p-d π -bonding to the phosphorus atom and consequently are more available for delocalization into the phenyl rings, than the electrons on the equatorial oxygens. The five phenyl rings distribute themselves on the trigonal bipyramidal skeleton so as to minimize the considerable intramolecular crowding. The molecular structures and the ^{31}P NMR chemical shifts of acyclic, monocyclic, and spirobicyclic pentaoxyphosphoranes are correlated.

The first determination of the molecular structure of a pentaoxyphosphorane² by x-ray crystallography was performed on the monocyclic compound **1**.³ Four significant observations were made in that investigation.³ (1) The geometry about the phosphorus atom is very close to that of the regular TBP.⁴ (2) The five-membered ring occupies an apical-equatorial skeletal position. (3) The apical P-O bonds are longer than the corresponding equatorial P-O bonds, and the endocyclic P-O bonds are longer than the exocyclic P-O bonds of the same kind. (4) There is a great deal of crowding about the phosphorus, as reflected in several relatively short nonbonded distances, e.g., $C(31)\cdots O(5) = 2.63 \text{ \AA}$.



1. $C_{11}, C_{21}, C_{31} \equiv 150-C_3H_7$; $\delta^{31}P = +48.6 \text{ ppm}$
2. $C_{11}, C_{21}, C_{31} = C_6H_5$; $\delta^{31}P = +58.6 \text{ ppm}$

The molecular structure of the spirobicyclic pentaoxyphosphorane, **3**, is known from x-ray crystallography.⁶ The geometry about the phosphorus in **3** does not resemble a



3. $C_{31} \equiv C_6H_5$; $\delta^{31}P = +30.2 \text{ ppm}$

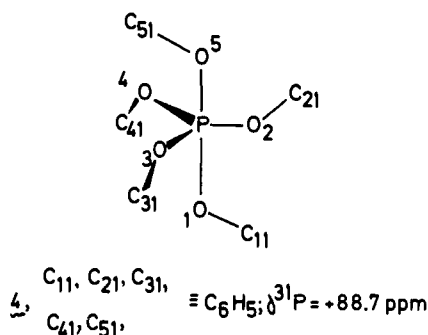
regular TBP,⁴ nor a regular TP,⁴ but is adequately described as a 15° -TR⁴ configuration.^{7,8} The term "static TR-configuration" is a convenient designation for those phosphoranes which clearly do not resemble a TBP about the phosphorus atom. As originally conceived (ref 7), "TR-configuration" had only a dynamic connotation; however, this concept now seems more general and capable of providing an adequate description of the molecular geometry of certain complex phosphoranes. X-Ray analyses carried out since the submission of this paper have uncovered other examples of 5,5-spirobicyclic homophosphoranes (five oxygen ligands), and 5-monocyclic heterophosphoranes (two oxygen and three carbon ligands) whose geometry conforms to the definition of static TR-configuration.

The remarkable differences in the molecular structures of the pentaoxyphosphoranes, **1** and **3**, led us to investigate the structure of the parent acyclic compound, pentaphenoxyphosphorane, $(C_6H_5O)_5P$, first synthesized in 1968.⁹ A summary of the results is given in partial formula **4**, which will be utilized in the Discussion Section to correlate the molecular structures of the three types of pentaoxyphosphoranes, **1**, **3**, and **4**.

In a previous paper⁶ we had concluded that homophosphoranes, i.e., those with five ligands of the same type, tend to adopt the TBP skeletal geometry in the absence of certain structural restrictions.¹⁰ Two five-membered rings in a spiro configuration, as in **3**, apparently constitute the type of restriction that prevents the establishment of the regular TBP skeletal geometry. It is not clear at this time why this should be so. A conceivable hypothesis is that the simultaneous incorporation of one P atom into two 1,3,2-dioxaphospholene rings prevents, to some extent, the involvement of the electrons of the oxygens in p-d π -bonding with the pentavalent phosphorus, which could decrease the tendency of the latter to adopt the TBP skeletal geometry. This effect could also operate in other spirobicyclic oxyphosphoranes containing combinations of 1,3,2-dioxaphospholane, 1,3,2-dioxaphospholene, 1,2-oxaphosphetane, and other analogous rings. Another type of restriction against TBP geome-

try of the PO₅ skeleton could involve steric hindrance among the five groups surrounding the phosphorus, i.e., repulsions among the carbon atoms attached to the oxygen ligands,¹¹ and the oxygens and carbons of the other four groups. Information on the molecular structure of pentaoxyphosphorane (4) should throw light on this question.

Recent investigations¹²⁻¹⁶ have disclosed significant departures from the regular TBP geometry in a variety of spirobicyclic phosphoranes having combinations of P-O and P-C, P-O and P-F, P-S and P-C, and P-O, P-S, and P-C bonds in the same molecule. Interesting as these results are,¹²⁻¹⁶ they cannot reveal the purely steric effects which affect the phosphorane valence bond skeleton, since in all cases the pertinent compounds lack "ligand subset symmetry",^{7,8} i.e., neither the apical nor the equatorial subsets of ligands in them can be made up of the same element, and electronic, as well as steric factors, will contribute to the observed molecular geometry. The literature¹⁷⁻²⁵ contains several examples of phosphoranes with P-C bonds, or combinations of P-C, P-N, and P-O bonds with partial ligand subset symmetry, X₂PY₃, and in these cases the molecules approach the TBP geometry, although with significant distortions.



Experimental Section

Preparation of Pentaoxyphosphorane (4). This substance was prepared as described.⁹ The crystals for x-ray analysis were obtained from *n*-hexane; they had mp 103–104°, and $\delta^{31}\text{P} + 88.7$ ppm vs. H₃PO₄ (CH₂Cl₂ solution). Crystal data (compound 4): C₃₀H₂₅O₅; triclinic, *P*₁; *a* = 9.686 ± 0.005, *b* = 11.315 ± 0.005, *c* = 11.693 ± 0.005 Å; α = 83.66 ± 0.06, β = 79.66° ± 0.06, γ = 77.58 ± 0.04°; volume of unit cell = 1256 Å³; *Z* = 2; *d*(calcd) = 1.310, *d*(measd) = 1.306 g/cm³, in bromoform-hexane.

Data Collection and Structure Determination. The crystals were sensitive to atmospheric moisture and were sealed inside a capillary tube with a small amount of P₂O₅ at one end of the tube.

Intensity data were collected using a computer controlled CAD4 automatic diffractometer using nickel filtered Cu K α (λ 1.542 Å) radiation; 5076 unique reflections with $\theta \leq 75^\circ$ were collected using (θ - 2θ) scan and a scan width of 1.0°. Three reflections were measured periodically to monitor any crystal deterioration. No such effects were observed during data collection. Ninety six separate measurements were made during each scan, the first 16 and the last 16 measurements were summed to provide the background measurements for each reflection. There were about 300 reflections with $|F_o|^2$ less than or equal to $2\sigma(|F_o|^2)$; the σ was estimated from counting statistics.

Since the crystal was sealed inside a capillary tube, an empirical absorption correction²⁶ was applied, this correction was determined by performing an azimuth scan for a reflection occurring at a χ value of approximately 90°. The transmission factor varied from a value of 1.00 to about 1.22 during an azimuth scan of 180°.

The structure amplitudes derived in the usual way after correction for Lorentz, polarization, and absorption factors were used to perform statistical tests to distinguish between the centrosymmetric (*P*₁) and noncentrosymmetric (*P*₁) space groups.²⁷ This was done by grouping reflections into regions of $\sin \theta$, namely 0.0 to 0.2, 0.2 to 0.4, etc., and in each range the local average intensity (*I*) was determined. This was assumed to be the same for all re-

Table I. Atomic Coordinates and Their Standard Deviations × 10⁴

Atom	X	Y	Z
PHOS	0.1390 (1)	0.1782 (1)	0.2289 (1)
O (1)	-0.0356 (2)	0.1850 (2)	0.2380 (2)
O (2)	0.1616 (2)	0.0340 (2)	0.2274 (2)
O (3)	0.1157 (2)	0.2511 (2)	0.3400 (2)
O (4)	0.1449 (2)	0.2578 (2)	0.1098 (2)
O (5)	0.3145 (2)	0.1633 (2)	0.2246 (2)
C (11)	-0.1171 (3)	0.0989 (3)	0.2752 (2)
C (12)	-0.2123 (3)	0.0837 (3)	0.2064 (3)
C (13)	-0.3025 (4)	0.0013 (4)	0.2444 (3)
C (14)	-0.2955 (4)	-0.0661 (4)	0.3485 (4)
C (15)	-0.2013 (4)	-0.0491 (4)	0.4164 (3)
C (16)	-0.1105 (4)	0.0336 (3)	0.3791 (3)
C (21)	0.2887 (3)	-0.0533 (2)	0.2088 (3)
C (22)	0.3581 (4)	-0.0678 (3)	0.0984 (3)
C (23)	0.4775 (4)	-0.1623 (3)	0.0792 (4)
C (24)	0.5213 (4)	-0.2398 (3)	0.1697 (4)
C (25)	0.4507 (4)	-0.2240 (4)	0.2783 (4)
C (26)	0.3314 (4)	-0.1287 (3)	0.2993 (3)
C (31)	-0.0022 (3)	0.3421 (3)	0.3768 (3)
C (32)	-0.0899 (4)	0.3184 (4)	0.4788 (3)
C (33)	-0.1986 (5)	0.4155 (5)	0.5196 (4)
C (34)	-0.2149 (5)	0.5278 (5)	0.4612 (4)
C (35)	-0.1263 (5)	0.5486 (4)	0.3584 (5)
C (36)	-0.0177 (4)	0.4541 (3)	0.3173 (3)
C (41)	0.0432 (3)	0.2748 (3)	0.0358 (3)
C (42)	-0.0754 (5)	0.3677 (4)	0.0490 (4)
C (43)	-0.1715 (5)	0.3826 (4)	-0.0281 (4)
C (44)	-0.1480 (4)	0.3074 (4)	-0.1166 (4)
C (45)	-0.0271 (5)	0.2140 (5)	-0.1259 (4)
C (46)	0.0696 (4)	0.1993 (4)	-0.0502 (3)
C (51)	0.3846 (3)	0.2510 (3)	0.2465 (3)
C (52)	0.4539 (4)	0.2279 (4)	0.3412 (3)
C (53)	0.5382 (4)	0.3084 (5)	0.3590 (4)
C (54)	0.5483 (5)	0.4118 (4)	0.2833 (5)
C (55)	0.4754 (5)	0.4337 (4)	0.1916 (5)
C (56)	0.3941 (3)	0.3523 (3)	0.1729 (3)
H (12)	-0.2097 (39)	0.1377 (33)	0.1298 (30)
H (13)	-0.3693 (42)	-0.0086 (35)	0.1923 (32)
H (14)	-0.3661 (40)	-0.1200 (35)	0.3693 (32)
H (15)	-0.1911 (37)	-0.1004 (32)	0.4955 (29)
H (16)	-0.0358 (38)	0.0502 (31)	0.4185 (29)
H (22)	0.3227 (41)	-0.0085 (35)	0.0283 (32)
H (23)	0.5186 (55)	-0.1740 (47)	-0.0082 (42)
H (24)	0.6090 (44)	-0.3108 (38)	0.1511 (35)
H (25)	0.4789 (43)	-0.2845 (36)	0.3558 (33)
H (26)	0.2822 (39)	-0.1092 (34)	0.3712 (31)
H (32)	-0.0749 (50)	0.2349 (42)	0.5354 (39)
H (33)	-0.2564 (51)	0.3954 (42)	0.6003 (41)
H (34)	-0.2799 (50)	0.6039 (41)	0.4908 (38)
H (35)	-0.1223 (45)	0.6339 (38)	0.3129 (36)
H (36)	-0.0249 (43)	0.4592 (35)	0.2329 (34)
H (42)	-0.0898 (34)	0.4237 (29)	0.1182 (26)
H (43)	-0.2499 (48)	0.4598 (40)	-0.0175 (37)
H (44)	-0.2216 (48)	0.3188 (40)	-0.1732 (37)
H (45)	0.0003 (45)	0.1637 (39)	-0.2094 (36)
H (46)	0.1469 (39)	0.1202 (32)	-0.0491 (30)
H (52)	0.4478 (41)	0.1543 (35)	0.3927 (32)
H (53)	0.6036 (43)	0.2811 (37)	0.4271 (33)
H (54)	0.6186 (43)	0.4737 (36)	0.2886 (33)
H (55)	0.4880 (42)	0.5178 (36)	0.1274 (33)
H (56)	0.3464 (35)	0.3692 (30)	0.1008 (28)

lections in the particular group, and the values of $|F|/\sqrt{I} = y$ were computed. The number of reflections having values of *y* between *y* and *y* + *dy* were determined, and from these the value of the function *P*(*y*) at the midpoints of the ranges was calculated. The distribution of *P*(*y*) as a function of *y* indicated quite unambiguously that the structure is centrosymmetric.

A sharpened Patterson map was used to locate the position of the phosphorus atom. The remaining nonhydrogen atoms were located from a series of weighted (β' syntheses using $w(|F_N|/|F_H|) \exp(i\phi_p)$ as coefficients.²⁸ In this expression $|F_N|$ is the observed structure amplitude, $|F_H| \exp(i\phi_p)$ corresponds to the contribution to the calculated structure factor from the *P* known atoms in the unit cell, and *w* the weighting factor is equal to $\tanh (|F_N|/|F_H|)$

Table II. Anisotropic Thermal Parameters for all the Nonhydrogen Atoms in the Structure (Standard Deviations $\times 10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	0.0086 (1)	0.0061 (1)	0.0086 (1)	-0.0041 (1)	-0.0016 (1)	-0.0016 (1)
O (1)	0.0092 (2)	0.0087 (1)	0.0116 (2)	-0.0047 (3)	-0.0023 (3)	0.0006 (3)
O (2)	0.0101 (2)	0.0074 (1)	0.0148 (2)	-0.0040 (3)	-0.0014 (4)	-0.0024 (3)
O (3)	0.0099 (2)	0.0130 (2)	0.0083 (1)	-0.0026 (3)	-0.0014 (3)	-0.0042 (3)
O (4)	0.0112 (2)	0.0104 (2)	0.0089 (1)	-0.0076 (3)	-0.0032 (3)	-0.0003 (3)
O (5)	0.0091 (2)	0.0077 (1)	0.0114 (2)	-0.0034 (3)	-0.0026 (3)	-0.0031 (3)
C (11)	0.0087 (2)	0.0088 (2)	0.0086 (2)	-0.0040 (4)	-0.0011 (4)	-0.0020 (3)
C (12)	0.0107 (3)	0.0107 (2)	0.0093 (2)	-0.0052 (4)	-0.0031 (4)	-0.0038 (4)
C (13)	0.0116 (3)	0.0118 (3)	0.0127 (3)	-0.0082 (5)	-0.0054 (5)	-0.0056 (5)
C (14)	0.0125 (3)	0.0112 (3)	0.0133 (3)	-0.0101 (5)	-0.0024 (6)	-0.0021 (5)
C (15)	0.0154 (4)	0.0130 (3)	0.0115 (3)	-0.0098 (5)	-0.0032 (6)	0.0031 (5)
C (16)	0.0135 (3)	0.0129 (3)	0.0095 (2)	-0.0098 (5)	-0.0051 (5)	0.0012 (5)
C (21)	0.0104 (3)	0.0074 (2)	0.0108 (2)	-0.0052 (4)	-0.0012 (4)	-0.0025 (4)
C (22)	0.0154 (4)	0.0097 (3)	0.0110 (3)	-0.0062 (6)	-0.0002 (6)	-0.0033 (5)
C (23)	0.0177 (5)	0.0109 (3)	0.0149 (3)	-0.0068 (6)	0.0047 (7)	-0.0074 (5)
C (24)	0.0129 (4)	0.0085 (3)	0.0183 (5)	-0.0049 (5)	-0.0021 (7)	-0.0044 (6)
C (25)	0.0143 (4)	0.0102 (3)	0.0160 (4)	-0.0056 (6)	-0.0086 (7)	0.0004 (6)
C (26)	0.0143 (3)	0.0102 (2)	0.0114 (3)	-0.0056 (5)	-0.0041 (5)	0.0005 (4)
C (31)	0.0096 (3)	0.0118 (3)	0.0093 (2)	-0.0053 (4)	-0.0016 (4)	-0.0062 (4)
C (32)	0.0134 (4)	0.0161 (4)	0.0101 (3)	-0.0072 (6)	0.0026 (5)	-0.0068 (5)
C (33)	0.0142 (5)	0.0190 (5)	0.0135 (3)	-0.0069 (8)	0.0029 (7)	-0.0156 (6)
C (34)	0.0144 (5)	0.0161 (4)	0.0156 (4)	-0.0026 (8)	-0.0027 (8)	-0.0177 (6)
C (35)	0.0191 (6)	0.0125 (3)	0.0168 (4)	-0.0042 (7)	-0.0062 (8)	-0.0103 (6)
C (36)	0.0161 (4)	0.0118 (3)	0.0126 (3)	-0.0054 (6)	-0.0021 (6)	-0.0056 (5)
C (41)	0.0111 (3)	0.0094 (2)	0.0086 (2)	-0.0068 (4)	-0.0032 (4)	-0.0003 (4)
C (42)	0.0188 (5)	0.0106 (3)	0.0133 (3)	0.0007 (7)	-0.0099 (7)	-0.0028 (6)
C (43)	0.0180 (5)	0.0135 (4)	0.0144 (4)	0.0014 (8)	-0.0117 (7)	0.0004 (7)
C (44)	0.0159 (4)	0.0151 (4)	0.0115 (3)	-0.0083 (7)	-0.0087 (6)	0.0005 (6)
C (45)	0.0195 (5)	0.0172 (5)	0.0135 (3)	-0.0032 (9)	-0.0123 (6)	-0.0073 (6)
C (46)	0.0152 (4)	0.0139 (4)	0.0108 (3)	-0.0016 (7)	-0.0067 (5)	-0.0070 (5)
C (51)	0.0079 (2)	0.0082 (2)	0.0100 (2)	-0.0028 (4)	-0.0015 (4)	-0.0047 (3)
C (52)	0.0114 (3)	0.0137 (3)	0.0113 (3)	-0.0016 (6)	-0.0036 (5)	-0.0062 (5)
C (53)	0.0129 (4)	0.0183 (5)	0.0147 (4)	-0.0018 (8)	-0.0049 (7)	-0.0099 (7)
C (54)	0.0142 (5)	0.0144 (4)	0.0187 (5)	-0.0080 (7)	-0.0018 (8)	-0.0098 (7)
C (55)	0.0177 (5)	0.0118 (4)	0.0201 (6)	-0.0092 (7)	-0.0031 (9)	-0.0024 (8)
C (56)	0.0137 (3)	0.0091 (2)	0.0136 (3)	-0.0090 (4)	-0.0070 (5)	-0.0014 (5)

Table III. Isotropic Thermal Parameters for the Hydrogen Atoms (Standard Deviations)

H (12)	5.0 (0.8)	H (34)	7.8 (1.1)
H (13)	5.4 (0.9)	H (35)	6.8 (1.0)
H (14)	5.3 (0.9)	H (36)	7.0 (1.1)
H (15)	4.7 (0.8)	H (42)	4.3 (0.7)
H (16)	4.5 (0.8)	H (43)	7.7 (1.1)
H (22)	6.0 (0.9)	H (44)	7.1 (1.1)
H (23)	9.4 (1.3)	H (45)	6.4 (1.0)
H (24)	6.9 (1.0)	H (46)	6.1 (0.8)
H (25)	6.1 (1.0)	H (52)	5.6 (0.9)
H (26)	5.4 (0.9)	H (53)	6.1 (0.9)
H (32)	8.1 (1.2)	H (54)	8.2 (0.9)
H (33)	8.3 (1.2)	H (55)	5.8 (0.9)
		H (56)	4.1 (0.7)

$\sum_j f^2 Q_j$),²⁹ $f Q_j$ corresponding to the scattering factor of the unknown atoms Q. The first β' synthesis using the phosphorus atoms for the known part of the structure revealed the positions of the five oxygen atoms and these were included in the second β' synthesis which revealed the positions of the remaining atoms in the structure. The positional and thermal parameters of all the atoms were refined using a standard full-matrix least-squares program that minimized $\sum w(\Delta F)^2$. The weighting scheme used was of the form $w = 1/(a + |F_d| + c|F_d|^2)$ where a and c were of the order of $2F$ min and $2F$ max, respectively.³⁰ Three innermost reflections affected by extinction errors were completely omitted from the least-squares refinement. The lowest residual $R = \sum |\Delta F| / \sum |F|$ calculated using positions of all the nonhydrogen atoms was 9.3%. A difference electron density map was used to locate the positions of all the hydrogen atoms and the final R value for 5076 reflections was 7.5%. Table I lists the final positional parameters for all the atoms of one molecule. Table II lists the anisotropic thermal parameters for all the nonhydrogen atoms in the structure and Table III lists the isotropic thermal parameters for all the hydrogen atoms. The

observed and calculated structure factors are given in Table IV; see paragraph at end of paper regarding supplementary material.

Discussion of Results

Molecular Structure of Pentaphenoxyphosphorane (4).

The interatomic distances^{31,32} and bond angles and their standard deviations are listed in Table V. Some intramolecular distances between nonbonded atoms are collected in Table VI. Equations of least-squares planes and deviations of certain atoms from these planes are given in Table VII. The dihedral angles formed by pairs of these planes are shown in Table VIII. A computer generated drawing of the molecule is reproduced in Figure 1. Figure 2 is the result of a 180°-rotation about one of the twofold axes of the TBP shown in Figure 1.

The data clearly show that the phosphorus in pentaphenoxyphosphorane (4) is at the center of a nearly perfect TBP. The pertinent bond angles are very close to the ideal 180°, 120°, and 90° of the D_{3h} symmetry. The only deviations that might be slightly outside experimental error are those associated with one of the equatorial oxygens, O(3), as shown by the following bond angles: O(2)-P-O(3) = 125.51 (0.7)°, O(3)-P-O(4) = 117.9 (0.6)°, and O(3)-P-O(5) = 87.93 (0.4)°. In retrospect, one finds the same trend in the monocyclic system 1: O(2)-P-O(4) = 125°, O(2)-P-O(3) = 117°, and O(2)-P-O(5) = 85°.

The planes expected in the TBP geometry of PO₅ are observable; cf. planes 1, 2, 3, and 4 in Table VII. The orthogonality between the equatorial plane, P, O(2), O(3), O(4), and the three planes containing two apical and one equatorial ligand can be seen in Table VIII.

The two apical P-O bond distances in 4 are virtually identical and are significantly larger than the three equato-

Table V. Bond Distances (Å) and Angles (deg), and Their Standard Deviations^a (in Parentheses), for (C₆H₅O)₃P

(i) In PO ₅ Group			
Bond Angles (deg)		Bond Distances (Å)	
O(1)-P-O(5)	176.57 (1.2)	P-O(1)	1.662 (5)
O(2)-P-O(3)	125.51 (0.7)	P-O(5)	1.663 (5)
O(2)-P-O(4)	118.27 (0.6)	P-O(2)	1.602 (5)
O(3)-P-O(4)	116.19 (0.6)	P-O(3)	1.596 (5)
O(1)-P-O(3)	92.08 (0.4)	P-O(4)	1.600 (5)
O(1)-P-O(4)	91.62 (0.4)		
O(4)-P-O(5)	91.44 (0.4)		
O(2)-P-O(5)	88.99 (0.4)		
O(1)-P-O(2)	88.21 (0.4)		
O(3)-P-O(5)	87.93 (0.4)		
(ii) In Phenoxy Ligands			
Bond Angles (deg)		Bond Distances (Å)	
P-O(1)-C(11)	130.74 (0.9)	O(1)-C(11)	1.372 (7)
P-O(5)-C(51)	126.53 (0.8)	O(5)-C(51)	1.389 (7)
P-O(2)-C(21)	129.76 (0.9)	O(2)-C(21)	1.403 (8)
P-O(3)-C(31)	126.47 (0.9)	O(3)-C(31)	1.404 (8)
P-O(4)-C(41)	125.71 (0.8)	O(4)-C(41)	1.409 (8)
O(1)-C(11)-C(12)	117.31 (1.0)		
O(1)-C(11)-C(16)	121.76 (1.1)		
O(5)-C(51)-C(52)	117.24 (1.0)		
O(5)-C(51)-C(56)	121.26 (1.2)		
O(2)-C(21)-C(22)	118.60 (1.1)		
O(2)-C(21)-C(26)	118.70 (1.1)		
O(3)-C(31)-C(32)	117.86 (1.2)		
O(3)-C(31)-C(36)	119.00 (1.2)		
O(4)-C(41)-C(42)	120.27 (1.2)		
O(4)-C(41)-C(46)	117.53 (1.2)		
(iii) In Phenyl Rings ^b			
Bond Angles (deg)		Bond Distances (Å)	
C(11)-C(12)-C(13)	118.90 (1.2)	C(11)-C(12)	1.385
C(12)-C(13)-C(14)	120.69 (1.3)	C(12)-C(13)	1.397
C(13)-C(14)-C(15)	119.70 (1.4)	C(13)-C(14)	1.395
C(14)-C(15)-C(16)	120.01 (1.4)	C(14)-C(15)	1.381
C(15)-C(16)-C(11)	119.82 (1.3)	C(15)-C(16)	1.404
C(16)-C(11)-C(12)	120.86 (1.2)	C(16)-C(11)	1.381
C(21)-C(22)-C(23)	118.40 (1.4)	C(21)-C(22)	1.379
C(22)-C(23)-C(24)	119.88 (1.5)	C(22)-C(23)	1.398
C(23)-C(24)-C(25)	120.73 (1.6)	C(23)-C(24)	1.385
C(24)-C(25)-C(26)	120.14 (1.5)	C(24)-C(25)	1.363
C(25)-C(26)-C(21)	118.46 (1.3)	C(25)-C(26)	1.412
C(26)-C(21)-C(22)	122.38 (1.4)	C(26)-C(21)	1.370
C(31)-C(32)-C(33)	116.76 (1.4)	C(31)-C(32)	1.392
C(32)-C(33)-C(34)	121.01 (1.6)	C(32)-C(33)	1.411
C(33)-C(34)-C(35)	120.97 (1.7)	C(33)-C(34)	1.372
C(34)-C(35)-C(36)	118.80 (1.6)	C(34)-C(35)	1.399
C(35)-C(36)-C(31)	119.65 (1.5)	C(35)-C(36)	1.391
C(36)-C(31)-C(32)	122.79 (1.5)	C(36)-C(31)	1.379
C(41)-C(42)-C(43)	118.15 (1.5)	C(41)-C(42)	1.376
C(42)-C(43)-C(44)	121.22 (1.7)	C(42)-C(43)	1.398
C(43)-C(44)-C(45)	118.53 (1.7)	C(43)-C(44)	1.388
C(44)-C(45)-C(46)	120.56 (1.7)	C(44)-C(45)	1.388
C(45)-C(46)-C(41)	119.35 (1.5)	C(45)-C(46)	1.392
C(46)-C(41)-C(42)	122.15 (1.5)	C(46)-C(41)	1.366
C(51)-C(52)-C(53)	118.65 (1.3)	C(51)-C(52)	1.392
C(52)-C(53)-C(54)	119.93 (1.4)	C(52)-C(53)	1.399
C(53)-C(54)-C(55)	120.00 (1.5)	C(53)-C(54)	1.403
C(54)-C(55)-C(56)	119.91 (1.5)	C(54)-C(55)	1.397
C(55)-C(56)-C(51)	120.15 (1.4)	C(55)-C(56)	1.386
C(56)-C(51)-C(52)	121.33 (1.3)	C(56)-C(51)	1.376

The C-H bond distances range from 0.98 to 1.17 Å with an average value of 1.092 Å.

^a The standard deviations in bond distances refer to the least significant digits and the standard deviations in bond angles are in degrees. ^b The average standard deviation in bond distances in the rings is 0.014 Å.

rial P-O distances. Conversely, the two C-O (apical) bonds, O(1)-C(11) and O(5)-C(51), are shorter than the three C-O (equatorial) bonds, O(2)-C(21), O(3)-C(31), and O(4)-C(41). This supports the view that the electrons on the apical oxygens are less involved in p-d π bonding to the phosphorus atom, and consequently are more available

Table VI. Intramolecular Nonbonded Distances^a ≤ 3.5 Å

P...C(41)	2.675 (7)	P...C(51)	2.726 (9)
P...C(31)	2.688 (7)	P...C(11)	2.759 (6)
P...C(21)	2.720 (6)		
O(3)...O(5)	2.276 (6)	O(1)...O(3)	2.360 (6)
O(1)...O(2)	2.285 (6)	O(3)...O(4)	2.720 (7)
O(2)...O(5)	2.300 (6)	O(2)...O(4)	2.760 (7)
O(4)...O(5)	2.344 (6)	O(2)...O(3)	2.864 (7)
O(1)...O(4)	2.350 (6)		
O(1)...C(12)	2.339 (9)	O(3)...C(36)	2.380 (10)
O(1)...C(16)	2.406 (9)	O(3)...C(32)	2.396 (10)
O(4)...C(46)	2.354 (10)	O(2)...C(22)	2.391 (9)
O(4)...C(42)	2.420 (10)	O(2)...C(26)	2.392 (9)
O(5)...C(52)	2.359 (9)		
O(5)...C(56)	2.410 (9)		
O(5)...C(21)	2.547 (8)	O(3)...C(52)	3.223 (9)
O(1)...C(41)	2.571 (8)	O(1)...C(32)	3.309 (10)
O(2)...C(11)	2.618 (8)	O(5)...C(26)	3.313 (9)
O(3)...C(51)	2.646 (8)	O(1)...C(36)	3.335 (10)
O(1)...C(31)	2.676 (8)	O(3)...C(11)	3.354 (7)
O(1)...C(42)	2.920 (10)	O(3)...C(56)	3.403 (10)
O(2)...C(16)	2.929 (9)	O(1)...C(46)	3.411 (10)
O(4)...C(51)	3.052 (8)	O(3)...C(16)	3.575 (9)
O(4)...C(56)	3.065 (10)	O(2)...C(12)	3.589 (8)
O(5)...C(22)	3.072 (9)		

^a The standard deviation in parentheses refers to the least significant digits.

for delocalization into the phenyl rings, than the electrons on the equatorial oxygens.^{2,3,7,8}

The data on P-O bond distances in the three types of pentaoxyphosphoranes **4**, **1**,³ and **3**⁶ lead to the tentative generalization that significant differences in the lengths of P-O bonds of comparable electronic type should be expected only when the skeletal geometry of the PO₅ group approaches that of the TBP. In compound **3** four P-O bonds are virtually identical in length.⁶

Table VI discloses the crowding that exists about the phosphorus atom in an oxyphosphorane.^{2,3} The distances that separate an apical oxygen from the three equatorial oxygens are significantly shorter (in the range 2.276-2.360 Å), than the distances that separate any two equatorial oxygens (in the range 2.720-2.864 Å). This observation quantifies the inference that the 90° apical-equatorial ligand-ligand interactions are more significant than the 120° di-equatorial ligand-ligand interactions.^{2,7,8} Therefore, a ligand in an apical position of the TBP is subject to more steric interference from other ligands,¹¹ than one in an equatorial position, since the apical ligand is subject to three relatively short 90° interactions, while the equatorial ligand is subject to only two such interactions. From a purely steric point of view a relatively large monovalent ligand, such as the chlorine atom, should tend to occupy the less hindered equatorial position unless electronic factors³³⁻³⁷ outweigh these steric considerations.

The situation pertaining to the steric hindrance of the groups attached to the oxygen ligands is more complicated. Note in Table VI the distances which separate the carbons directly attached to the oxygens, namely, C(11), C(21), C(31), C(41), and C(51) from the oxygen ligands to which they are not bonded. These distances do not vary much, and range from 2.547 (8) Å for the distance between C(21) (equatorial)...O(5) (apical), to 2.676 (8) Å for C(31) (equatorial)...O(1) (apical). The remaining distances in Table VI are significantly longer, from 2.920 (10) to 3.589 (8) Å; they are given in order to define the conformations of the five rings about the PO₅ TBP skeleton.

The conformations of the five phenyl rings are obtained from the data in Tables VI, VII, and VIII. Ring 1, on one of the apical oxygens, O(1), occupies the space available between two equatorial oxygens, O(2) and O(3). Ring 5, on

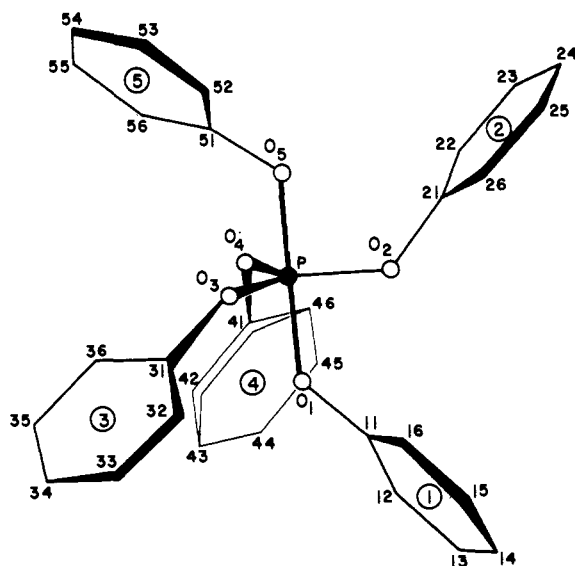


Figure 1. Computer generated drawing of one molecule of pentaphenoxyphosphorane (4).

Table VII. Least-Squares Planes^a

1. P, O(2), O(3), O(4)	$0.9904X + 0.1212Y - 0.0659Z = 1.8849$ P, -0.014; O(2), 0.005; O(3), 0.005; O(4), 0.004
2. P, O(1), O(2), O(5)	$0.0499X - 0.0165Y + 0.9986Z = 2.7463$ P, -0.020; O(1), 0.010; O(2), 0.000; O(5), 0.010
3. P, O(1), O(3), O(5)	$-0.1400X + 0.7918Y - 0.5945Z = 0.1854$ P, 0.037; O(1), -0.014; O(3), -0.005; O(5), -0.016
4. P, O(1), O(4), O(5)	$-0.0978X + 0.8650Y + 0.4922Z = 3.3899$ P, 0.016; O(1), -0.008; O(4), 0.000; O(5), -0.008
5. Ring 1	$-0.6344X + 0.6359Y + 0.4395Z = 2.5827$ [0.007 largest deviation for C(13)]
6. Ring 2	$0.6290X + 0.7671Y + 0.1267Z = 2.4847$ [0.007 largest deviation for C(23)]
7. Ring 3	$0.7209X + 0.4688Y + 0.5105Z = 4.8104$ [0.0035 largest deviation for C(33) & C(34)]
8. Ring 4	$0.4223X + 0.6805Y - 0.5989Z = 2.1721$ [-0.010 largest deviation]
9. Ring 5	$-0.7239X + 0.4178Y + 0.5491Z = 0.2695$ [0.011 largest deviation]
10. Ring 1 plus O(11)	$-0.6408X + 0.6268Y + 0.4434Z = 2.6082$ O(1), 0.025; C(11), -0.022; C(12), -0.017; C(13), 0.011; C(14), 0.007; C(15), 0.005; C(16), -0.009
11. Ring 2 plus O(21)	$0.6084X + 0.7826Y + 0.1317Z = 2.3917$ O(2), -0.058; C(21), 0.044; C(22), 0.022; C(23), -0.004; C(24), -0.029; C(25), -0.013; C(26), 0.035
12. Ring 3 plus O(31)	$0.7021X + 0.4860Y + 0.5204Z = 4.9637$ O(3), 0.057; C(31), -0.046; C(32), -0.028; C(33), 0.007; C(34), 0.032; C(35), 0.008; C(36), -0.030
13. Ring 4 plus O(41)	$0.4200X + 0.6802Y - 0.6008Z = 2.1747$ O(4), 0.007; C(41), -0.016; C(42), 0.006; C(43), -0.006; C(44), 0.010; C(45), -0.006; C(46), 0.006
14. Ring 5 plus O(51)	$0.7831X - 0.3680Y - 0.5014Z = 0.4219$ O(5), -0.103; C(51), -0.110; C(52), -0.021; C(53), 0.112; C(54), 0.116; C(55), -0.010; C(56), -0.097

^a X, Y, and Z are in orthogonal coordinates with deviations of the individual atoms from the planes given in Å. The Y axis is parallel to the crystallographic b axis and the x axis is in the a,c plane.

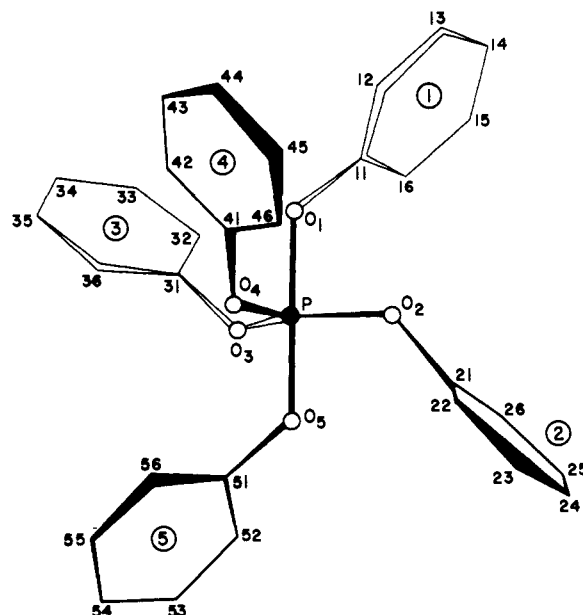


Figure 2. Result of a 180° rotation of the molecule in Figure 1 about one of the twofold axes passing through P-O(2) of the TBP.

Table VIII. Some Dihedral Angles between Planes^a

Plane a	Plane b	Angle (deg)
P, O(2), O(3), O(4)	P, O(1), O(2), O(5)	89
P, O(2), O(3), O(4)	P, O(1), O(3), O(5)	90
P, O(2), O(3), O(4)	P, O(1), O(4), O(5)	89
Ring 1	Ring 5	15
Ring 1	Ring 2	82
Ring 1	Ring 3	86
Ring 1	Ring 4	84
Ring 5	Ring 2	86
Ring 5	Ring 3	87
Ring 5	Ring 4	69
Ring 2	Ring 3	29
Ring 3	Ring 4	71
Ring 4	Ring 2	45

^a The planes are defined in Table VII. The dihedral angles, θ , are expressed as $\leq 90^\circ$.

the second apical oxygen, O(5), places itself between another pair of equatorial oxygens, O(3) and O(4). The remaining three phenyl rings, 2, 3, and 4, which are attached to equatorial oxygens, take on the most favorable conformations to avoid steric repulsions among themselves, and from the two apical rings and the oxygen ligands. Note that ring 2 moves up and comes relatively close to O(5), to avoid ring 1. Ring 3 moves down, fairly close to O(1), to avoid ring 5, but it must avoid also ring 1. The last ring, 4, has no option, it must choose a location near one of the two apical oxygens, O(1) or O(5). The actual placement of ring 4 seems to be determined by the precise conformations of the pair of rings 1, 3 vs. 5, 2, with the former arrangement being the most favorable one.

The two rings, 1, 5, on apical oxygens are not far from being parallel to each other (dihedral angle of 15°). On the other hand, ring 1 is nearly orthogonal to the three rings, 2, 3, and 4, attached to equatorial oxygens (dihedral angles of 82, 86, and 84°); see also Figure 2. Ring 5 is nearly orthogonal to only two of the equatorial rings, 2 and 3 (dihedral angles of 86 and 87°); the third equatorial ring, 4, forms a 69° dihedral angle with apical ring 5, reflecting the unique situation of the "fifth group" in a penta-oxyphosphorane. The dihedral angles formed by the three equatorial rings among themselves, 29, 71, and 45°, reveal a distorted propeller arrangement of the rings in the equatorial plane. The disposition of the five phenyl rings about the PO₅ skeleton is

undoubtedly determined by the bulkiness of this group, whose half-thickness has been estimated as 1.85 Å.³⁸

This study suggests that, in *acyclic* penta-oxyphosphoranes, the bulkiest of a set of five groups should occupy one of the equatorial positions, since this allows for a minimum of interference from the remaining ligands; cf. distances O(1)---C(31), O(1)---C(32), and O(1)---C(36). The second and third groups should occupy the two apical positions; cf. distances O(3)---C(51), O(4)---C(51), O(4)---C(56), O(3)---C(52), and O(3)---C(56), for one ring, and O(2)---C(11), O(2)---C(16), O(3)---C(11), O(3)---C(16), and O(2)---C(12), for the other ring. The fourth and fifth groups, in order of decreasing size, should go to equatorial positions as the crowding increases; cf. distances O(1)---C(41), O(5)---C(21), and all other distances which involve these two carbon atoms.

In the *monocyclic* compound 1, there is a slight steric advantage in placing the bulkiest of the three exocyclic groups in an apical position, since the C(11)---O(3) and C(11)---O(4) distances are somewhat longer than the C(31)---O(5) and C(21)---O(1) distances.³

The evidence now at hand on the stereochemistry of compounds with five-coordinate phosphorus^{2,3,6-8,12-25} suggests that the constellation of electronic and steric factors which determine the configuration and conformation of these molecules is too complicated to permit generalizations applicable to all types of phosphoranes. However, if one restricts those generalizations to particular types of phosphoranes, the following pattern is discernible.

(1) The TBP skeletal geometry is preferred by *homophosphoranes*. PX₅, with monovalent ligands, e.g., PF₅, and by both *acyclic* and *monocyclic* types containing divalent ligands such as oxygen, e.g., compounds 4 and 1. Homophosphoranes with trivalent and tetravalent ligands, such as nitrogen and carbon, probably tend also toward the TBP geometry, in both the *acyclic* and the *monocyclic* types; however, with the exception of pentaphenylphosphorane,¹⁷ (C₆H₅)₅P, which has TBP geometry, there are no data on the molecular structure of phosphoranes in this category.

(2) The X^o-TR configuration⁶⁻⁸ is preferred by *homophosphoranes* of the *spirobicyclic* type with divalent ligands, e.g., 3. The same is probably true for other homophosphoranes with *spirobicyclic* systems having trivalent and tetravalent ligands, but the pertinent data are not available to support this conclusion.

(3) The TBP geometry is favored by *heterophosphoranes* which possess ligand subset symmetry^{7,8,33} of the type shown below. This appears to be true for compounds with mono-, di-, and trivalent ligands, and in the *acyclic* and *monocyclic* types.



(4) The *spirobicyclic heterophosphoranes* do not have TBP skeletal geometry.¹²⁻¹⁶ The structure of the *spirobicyclic homophosphorane* 3 has been interpreted to be a 15^o-TR configuration on the basis of the relevant bond angles and dihedral angles determined by x-ray diffraction analysis.⁶ However the results of the x-ray analysis of other spiro compounds¹²⁻¹⁶ have been regarded as indicative of a tetragonal (square) pyramid or as "mixes of TBP and TP¹⁶".

³¹P NMR Chemical Shifts and the Structure of Penta-oxyphosphoranes. The introduction of a five-membered ring into pentaphenoxyporphorane (4) to give 2 causes a relatively large displacement of the ³¹P NMR chemical shift toward lower magnetic field, Δδ³¹P (4 → 2) = -30 ppm.²

The introduction of a second five-membered ring to give 3 has a very similar effect, Δδ³¹P (2 → 3) = -29 ppm.⁵ This relatively large decrease in the shielding of the phosphorus nucleus by electrons in the series 4 → 2 → 3 can be qualitatively explained on the assumption that the presence of the five-membered ring inhibits the back-donation of electron density from the oxygen ligands into the vacant d orbitals of phosphorus. This "steric inhibition" of p-d π-bonding, by the five-membered ring does not contribute to the loss of TBP skeletal geometry when it is associated with one ring only (cf. 1 and 4); however, the combined effect of two rings is severe enough to affect the configuration of the PO₅ group. These arguments are related to those used previously to account for the differences in P-O and O-C bond distances in compound 4.

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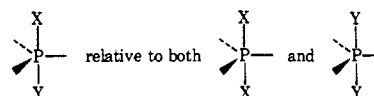
Supplementary Material Available: Table IV, structure factors (47 pages). Ordering information is given on any current masthead page.

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- (11) The term "ligand" is reserved for the atom directly bonded to the phosphorus.
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disclose that there is always a weakening of the bond system in oxyphosphorane



- The same is true for the equatorial subset. It appears that the contribution of a ligand to the total chemical binding energy of the phosphorane is less in the "heterosystem" than the mean of the contribution of the same ligand in the "homosystem". LSS affects also the ^{31}P NMR chemical shift resulting from a given set of ligands: a molecule with LSS gives resonance at a higher magnetic field than another without it, even though they may have the same number of ligands of the same electronegativity (ref 2, 5, 7, 21, 22).
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Thyroid Hormone Stereochemistry. IV.¹ Molecular Conformation of 3'-Isopropyl-3,5-diiodo-L-thyronine in the Crystal and in Solution

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Abstract: The three-dimensional structure of 3'-isopropyl-3,5-diiodo-L-thyronine (ip-T₂), the most potent known thyromimetic agent, has been determined by a single-crystal x-ray diffraction study of ip-T₂ hydrochloride trihydrate. The unit cell dimensions are $a = 30.408$, $b = 5.308$, $c = 17.176$ Å; $\beta = 117.93^\circ$; space group C2, with four molecules per cell. The structure was solved by Patterson methods and refined to $R = 0.051$. The planes of the α - and β -phenyl rings make dihedral angles of 97° and -26° , respectively, with the plane of the inter-ring linkage, and the β -ring orientation is such that the 3'-isopropyl group is positioned proximal to the α ring. High-resolution NMR studies of ip-T₂ in methanol and methanol-acid indicate that the 3'-substituent proximal conformation is favored in acidic media and that the 3'-distal conformation predominates in alcohol.

3'-Isopropyl-3,5-diiodo-L-thyronine (ip-T₂) is chemically very similar to 3,5,3'-triiodo-L-thyronine (T₃), the most potent naturally occurring thyroid hormone; the two molecules differ in chemical structure only in the replacement of the iodine at the 3' position of the β ring of T₃ by an isopropyl group in ip-T₂. The hormonal activity of ip-T₂ is 50-100% greater than that of T₃, making it the most potent thyromimetic agent known.^{3,4}

The conformational characteristics of T₃ and its analogues have been the subject of much interest. The presence of iodines at the 3 and 5 positions of the α ring, ortho to the phenolic β ring, favors a roughly mutually perpendicular arrangement of the two aromatic rings, and the question of whether the β ring is then oriented with its 3'-substituent proximal or distal (the 120° angle at the inter-ring ether link makes these positions conformationally nonequivalent) to the α ring has been extensively investigated. On the basis of studies utilizing fixed-conformation analogues, the 3'-iodine distal arrangement for T₃ was concluded to be the biologically active conformation.^{3,5} However, structure determinations of T₃ hydrochloride⁶ and ethyl 3,5,3'-triiodothypropionate⁷ (T₃P) revealed that both of these molecules

adopt conformations having the 3'-iodine proximal to the α ring in the crystalline state. The great hormonal potency of ip-T₂, its close structural resemblance to T₃, and its possession of an isopropyl group instead of iodine at the 3' position, thereby eliminating any possibility of intermolecular electrostatic effects involving that substituent stabilizing a particular conformation, combine to make a three-dimensional molecular structure determination of ip-T₂ highly desirable.⁸

Recently crystal structures have also been reported⁹ in which T₃ and analogues exist in the 3'-iodine distal conformation. These crystals were obtained from alcoholic solutions, in some cases containing excesses of urea or salicylic acid, while the crystals in which the 3'-substituent proximal conformation is found were prepared from alcohol-HCl solutions. Thus solution conditions appear to exert a profound influence on conformational stability in these thyromimetics, and an NMR investigation of the structure of 3,5,3'-triiodothypropionic acid in differing media has indicated that acidic solutions stabilize the 3'-substituent proximal conformation.¹⁰ A similar NMR investigation of acidic and neutral solutions of ip-T₂ is of great interest in determining