Solid-State Studies on Crowded Molecules. Crystal and Molecular Structures of 2,2,3-Trimethyl-1-phenylphosphetane 1-Oxide[1a] and 2,2,3,3,4-Pentamethyl-1-phenylphosphetane 1-Oxide[1b]

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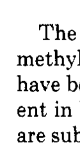
The crystal and molecular structures of the two unsymmetrically substituted phosphetane oxides, 2,2,3-trimethyl-1-phenylphosphetane 1-oxide (TPO) and 2,2,3,3,4-pentamethyl-1-phenylphosphetane 1-oxide (PPO), have been determined by X-ray analysis and the single methyl group was found to be trans to the phenyl substituent in both instances. Both structures exhibit P–C bond distances to the least substituted ring carbon atom that are substantially shorter [1.788 (5) Å, TPO; 1.799 (5) Å, PPO] than previously reported values for this class of compounds. The four-membered ring in TPO is puckered with an angle of 16.7°, while the ring in PPO is puckered at an angle of 29.8°. These two structures are compared to five structures from the literature which contain the phosphetane ring system. The degree of puckering has been related (qualitatively) to the number of interactions between methyl substituents on the four-membered ring. The ring systems all pucker such that a lone methyl substituent on the ring occupies a pseudoequatorial position. Both compounds crystallize in the monoclinic space group $P2_1/c$ with TPO having unit cell dimensions of a = 10.582 (7), b = 12.688 (7), c = 10.229 (4) Å, and β = 119.03 (4)° and PPO having unit cell dimensions of a = 17.165 (16), b = 7.226 (2), c = 11.365 (10) Å, and β = 102.24 (7)°. The final R values are 0.047 for TPO and 0.065 for PPO.

The chemistry of the four-membered heterocyclic phosphetanes has received considerable attention over the past nine years.[3] This is due in part to the fact that ring constraint in this system provides a structural asset for the analysis of phosphorus stereochemistry (particularly in polytopal rearrangements).[4] Also, a ring methyl substituent bearing a cis or trans relationship to a functional group on phosphorus (structures 1–3) provides a convenient probe for following stereochemical changes about phosphorus in chemical reactions.[5a,b]



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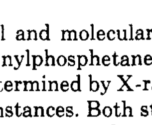

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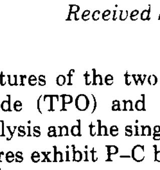


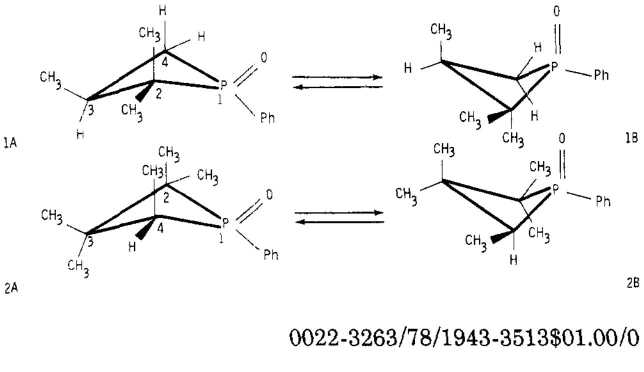
3

R = ALKYL, ARYL, Cl, OH, OCH_3

Previous X-ray studies have focused on derivatives of 3[6a,c,d] and the resultant isomer assignments have been valuable for spectral and stereochemical correlations.[7] The X-ray results of 2 have already been applied in a ^{13}C NMR study and the X-ray data for 1 is in agreement with the assignments in that same study.[7b]

Moreover, the inherent properties of ring strain, ring puckering, and conformational preference provided special interest in carrying out the X-ray work. With regard to conformational aspects, the following equilibria can be considered (Scheme I).

Scheme I



Although the preference in the solid state may not parallel that in solution, several features are noted. The conformational energy difference between **1A** and **1B** is not clear cut. The C(3)–CH_3 group might be expected to favor a pseudoequatorial position (**1A**); however, because of the long P–C bonds (relative to C–C) the usual preference rules for carbocyclics may not be applicable. Conformational analysis involving second row elements may require different considerations.[8] Conformer **2B** with pseudoequatorial groups at positions 1 and 4 does not contain the apparent energetically unfavorable nonbonded repulsions ($CH_3 \cdots CH_3$ and $CH_3 \cdots Ph$) found in **2A**, thus indicating **2B** as the more stable conformer.

Moret and Trefonas[6b] have suggested that a study of an unsymmetrically substituted phosphetane ring should be carried out to determine whether the 1,2 P–C bond distance would be longer than the 1,4 P–C bond as suggested by its ring-opening reactions or whether they would be equivalent. In fact, subsequent chemical reactions have shown that the ring can be cleaved at either position depending on the cleavage reagent. For example, treatment of 1,2,2,3,3-pentamethyl-1-phenylphosphetanium bromide with phenyllithium opens the ring at the more substituted P–C bond,[5e] whereas sodium hydroxide treatment of either 1,2,2,3-tetramethyl-1-phenylphosphetanium iodide or 1,2,2,3,3-pentamethyl-1-phenylphosphetanium iodide gave ring opening at the least-substituted P–C bond.[5f] Alkaline hydrolysis of PPO also opens the ring at the least-substituted position.[5f] The basis for the direction of ring opening is dependent on the relative ground state–transition state free-energy differences. It is really not valid to relate the direction of cleavage to the relative length of the P–C bonds in the starting material.

The heterocycles 2,2,3-trimethyl-1-phenylphosphetane 1-oxide (**1**, TPO, with R = phenyl) and 2,2,3,3,4-pentamethyl-1-phenylphosphetane 1-oxide (**2**, PPO, with R = phenyl) represent the first examples of unsymmetrically substituted phosphetane oxides whose three-dimensional structures have been determined.

Experimental Section

Crystal Data. Both TPO and PPO were recrystallized from cyclohexane. The compounds were prepared by published methods[5c,d]

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Table I. Crystal Data and Experimental Conditions

	TPO ($C_{12}H_{17}PO$)	PPO ($C_{14}H_{21}PO$)
a, Å	10.582 (7)	17.165 (16)
b, Å	12.688 (7)	7.226 (2)
c, Å	10.229 (4)	11.365 (10)
β, deg	119.03 (4)	102.24 (7)
Z	4	4
D_{calcd}, g/cm^3	1.150	1.14
D_{expt}, g/cm^3	1.140	1.12
μ, cm^{-1}	2.01	1.78
vol of unit cell, Å^3	1200	1379
crystal dimensions, mm	0.63 × 0.38 × 0.32	0.18 × 0.64 × 0.65
θ–2θ scan time		
background count and time, s	10	10
take off angle, deg	4	4
scan rate, deg/min	2	2
scan width, deg	2	2
total reflections scanned	1215	1712
obsd reflections	997($I > 2\sigma I$)	1244($I > 3\sigma I$)
radiation MoKα	0.71069	0.71069
final R factor	0.047	0.065
R_w	0.042	0.080

Table II. Selected Bond Distances and Angles for TPO and PPO with Their Standard Deviations in Parentheses

TPO		PPO	
	Bond Distances, Å		
P-O	1.472 (3)	P-O	1.477 (4)
P-C(2)	1.835 (4)	P-C(2)	1.840 (5)
P-C(4)	1.788 (5)	P-C(4)	1.799 (5)
P-C(8)	1.800 (3)	P-C(10)	1.819 (5)
C(2)-C(3)	1.548 (7)	C(2)-C(3)	1.584 (7)
C(2)-C(5)	1.535 (6)	C(2)-C(8)	1.515 (8)
C(2)-C(6)	1.504 (6)	C(2)-C(9)	1.527 (8)
C(3)-C(4)	1.536 (6)	C(3)-C(4)	1.584 (7)
C(3)-C(7)	1.515 (9)	C(3)-C(6)	1.525 (8)
C(8)-C(9)	1.366 (8)	C(3)-C(7)	1.519 (8)
C(8)-C(13)	1.345 (6)	C(4)-C(5)	1.513 (8)
C(9)-C(10)	1.388 (9)	C(10)-C(11)	1.350 (7)
C(10)-C(11)	1.362 (9)	C(11)-C(12)	1.387 (8)
C(11)-C(12)	1.359 (10)	C(12)-C(13)	1.393 (10)
C(12)-C(13)	1.374 (8)	C(13)-C(14)	1.331 (11)
	Bond Angles, deg		
C(2)-P-C(4)	79.4 (2)	C(2)-P-C(4)	80.8 (2)
O-P-C(8)	111.4 (2)	O-P-C(10)	109.4 (2)
O-P-C(2)	121.3 (2)	O-P-C(2)	116.2 (2)
O-P-C(4)	122.3 (2)	O-P-C(4)	117.4 (2)
C(2)-P-C(8)	108.9 (2)	C(2)-P-C(10)	116.8 (2)
C(4)-P-C(8)	109.4 (2)	C(4)-P-C(10)	114.1 (2)
P-C(2)-C(3)	89.3 (2)	P-C(2)-C(3)	86.9 (3)
C(2)-C(3)-C(4)	97.3 (3)	C(2)-C(3)-C(4)	96.3 (4)
C(3)-C(4)-P	87.8 (2)	C(3)-C(4)-P	88.3 (3)

and the melting points were in agreement with values from the literature (TPO = 84–86 °C, PPO = 135–136 °C). Table I gives lattice parameters and experimental conditions.

Both data sets were reduced in the usual manner after application of Lorentz and polarization corrections.[9] Form factors for P, O, and C were taken from the International Tables.[10a] The hydrogen scattering factors were from Stewart, Davidson, and Simpson.[11] Anomalous scattering corrections for phosphorus were also included.[10b] The PPO data were corrected for absorption[12] (μ = 1.78 cm^{-1}), but no correction was applied to the TPO data.

Structure Determination and Refinement. The structures of both TPO and PPO were solved by Patterson syntheses. Both structures were refined by full-matrix least-squares techniques. Difference Fourier syntheses were used to locate the position of the hydrogen atoms at an intermediate state (R = 0.091 for TPO, R = 0.084 for PPO). In the final stages of the refinements, atomic coordinates and anisotropic thermal parameters were adjusted for the P, O, and C atoms and positional and isotropic parameters were allowed to vary for the H atoms. The weighting scheme used in the final stages of refinement was a statistical one based on that suggested by Stout and Jensen.[13] The residuals for TPO were R = 0.047 and R_w = 0.042 and R = 0.065 and R_w = 0.080[14] for PPO.

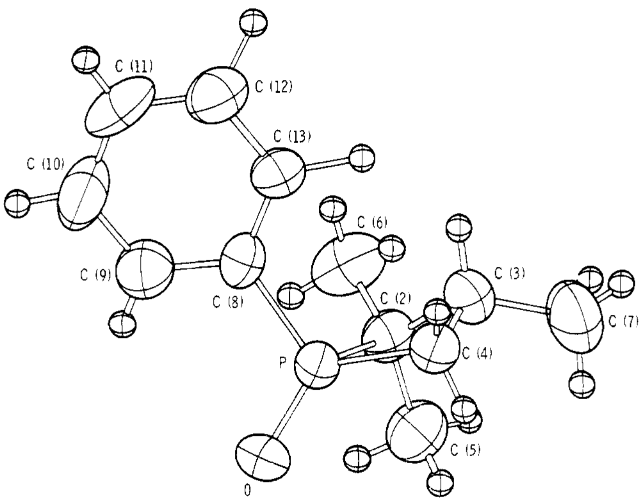

Figure 1. ORTEP plot of TPO at the 50% probability level. The hydrogen atoms are arbitrarily assigned isotropic temperature factors of 1.0 in this illustration.

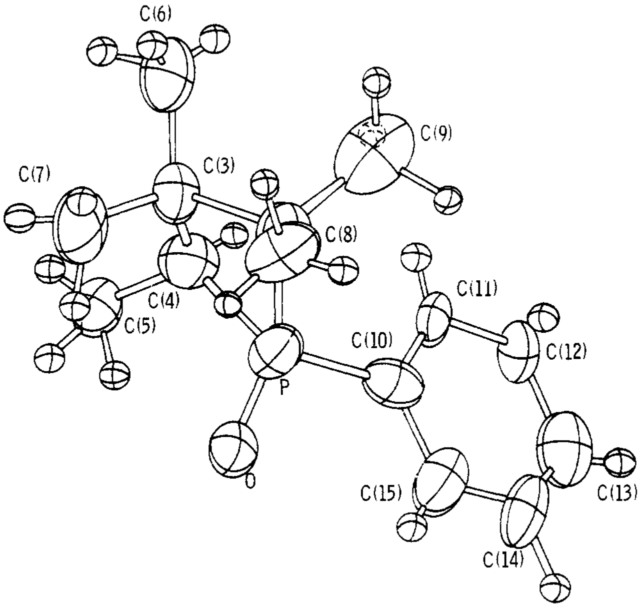

Figure 2. ORTEP plot of PPO at the 50% probability level. The hydrogen atoms are arbitrarily assigned isotropic temperature factors of 1.0 in this illustration.

Results

Figures 1 and 2 are ORTEP[9] drawings of TPO and PPO. Selected bond distances and angles are listed in Table II.

Structural Details of the Phosphetane Ring System. The lone ring methyl group [C(7) in TPO and C(5) in PPO] is trans to the phenyl group in both structures.

The structural details that will be emphasized are those for which differences are observed between these compounds and previous structures. Structural data on several phosphetane derivatives are shown in Figure 5 for purposes of comparison. The P–C bond lengths involving an unsubstituted α carbon (1.788 (5) Å, TPO) and a monosubstituted α carbon (1.799 (5) Å, PPO) are the shortest distances of this type reported to date. Previously reported values range from 1.83 to 1.94 Å. The

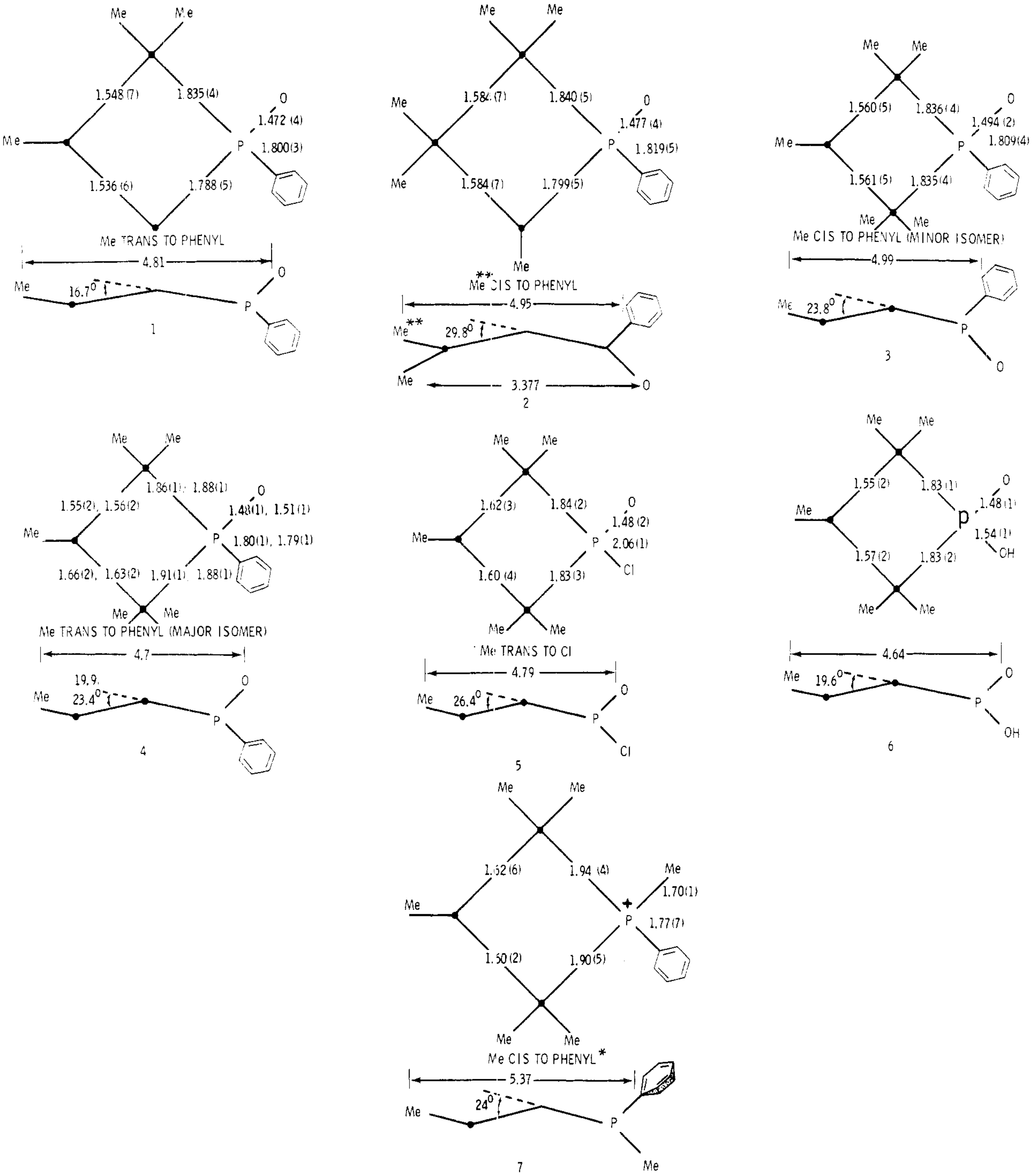

Figure 5. Summary of pertinent data for several phosphetane structures. Structures 1 and 2 are from this work. Structures 3–5 were reported by Haque,[6c,d] structure 6 was reported by Swank and Caughlan,[6a] and structure 7 was reported by Moret and Trefonas.[6b] Estimated standard deviations are in parentheses.

(*) The phenyl group is rotated by 90° with respect to the phenyl substituents on P in structures 1–4.

phosphoryl bond lengths (1.472 (3) Å, TPO; 1.477 (4) Å, PPO) are both shorter than previously observed values[6] (1.48–1.51 Å) though still longer than the normal phosphoryl distance of 1.45 Å.[15]

The C–C distances in the four-membered ring of TPO are shorter than have been observed in phosphetane ring systems in the past. For TPO, these distances are 1.548 (7) Å and 1.536 (4) Å. Previously reported values range from 1.55 (2) to 1.66 (2) Å.

Table IV summarizes the intramolecular distances that are less than or approximately equal to the sum of the van der Waals radii.[16] Since TPO contains fewer substituents than previous phosphetane derivatives, the number of substituent–substituent interactions is reduced to where the ring C–C distances approach normal values. The P=O bond is shortened and the P–C(4) bond length approaches the average found in other compounds containing tetravalent phosphorus.[17a,b] The greater length of the 1,2 versus the 1,4 P–C bond (about 0.04 Å) may have a steric origin and may be related to the C(8)–O (PPO) and C(5)–O (TPO) distance (Table IV); the apparent discrepancy for compound 4 is not completely understood at this time.

Although TPO apparently shows a methyl-phenyl interaction, based on sums of van der Waals radii (see Table IV), this interaction is of less importance than the methyl–methyl and methyl–phosphoryl oxygen interactions. The P–C (phenyl) distance of 1.800 (3) Å is in good agreement with values reported in the literature[17b] and does not differ from values

Table IV. Intramolecular Distances in TPO and PPO That Are Less Than or Approximately Equal to the Sum of the van der Waals Radii

	PPO	TPO
methyl–methyl[a]	C(5)–C(7) = 3.011 Å C(6)–C(9) = 2.885 Å C(7)–C(8) = 2.882 Å	C(5)–C(7) = 2.966 Å
methyl–methyl (diaxial)	C(5)–C(8) = 4.858 Å	
methyl–phenyl[b]	C(9)–C(10) = 3.287 Å	C(6)–C(8) = 3.250 Å
methyl–oxygen[c]	C(5)–O = 3.314 Å C(8)–O = 3.169 Å C(7)–O = 3.37 Å[d]	C(5)–O = 3.178 Å

[a] Bondi[16] estimates r_w ($C_{aliphatic}$) = 1.70 Å; therefore, an intramolecular distance <3.4 Å may be significant. [b] Bondi[16] estimates r_w ($C_{aromatic}$) = 1.77 Å, and since the effective size of the phenyl group is related to its rotational position an intramolecular distance <3.4–3.5 Å may be significant. [c] Bondi[16] estimates r_w (=O, normal to bond axis) = 1.6–1.7 Å; therefore, an intramolecular distance <3.3–3.4 Å may be significant. [d] The C(7)–O distance of 3.377 Å in PPO is a diaxial cross-ring interaction and probably serves to prevent further puckering of the phosphetane ring.

previously observed for this class of compounds.[6c,d] No apparent shortening of the P–C (phenyl) bond due to a decreased amount of crowding is observed in TPO.

Of the three apparent methyl–phosphoryl oxygen interactions in PPO only one is significantly less than the sum of the van der Waals radii. This reduction in the number of significant Me–O interactions in PPO (relative to the symmetrical pentamethyl isomers) apparently allows the P–C(4) bond length to approach the expected value for this type of bond and the P–O bond to be shortened (although perhaps not significantly). The P–C phenyl bond length of 1.819 (5) Å is within the limits for a normal bond of this type, again indicating that no undue crowding of the phenyl substituent takes place in the symmetrically substituted compounds.

All phosphetane ring structures to date exhibit puckering of the four-membered ring. The amount of pucker in the four-membered ring is defined as the angle between the planes C(2)–P–C(4) and C(2)–C(3)–C(4). For TPO the amount of pucker is 16.7°, while PPO is puckered with an angle of 29.8°. Qualitatively, these variations may be explained in terms of the number of substituent interactions; packing interactions have been assumed to be negligible as there are very few intermolecular distances significantly less than the sums of the van der Waals radii. The number and type of substituent interactions for several phosphetane derivatives are summarized in Table V. An interaction is considered to exist only between substituents which are attached to adjacent ring atoms and cis to one another with respect to the phosphetane ring system (the diaxial cross-ring Me–O interaction observed in PPO is also included).

Energetically, the most important interactions are the methyl–methyl interactions as they result in distances substantially less than 3.4 Å distance based on van der Waals radii (see Table IV). Variations in puckering due to the type of substituent on the P atom are expected to be small relative to the variation in puckering due to different numbers of substituent interactions. PPO with three methyl–methyl interactions is puckered to a greater extent than any other phosphetane ring system, while TPO with only one methyl–methyl interaction displays less puckering than any of the symmetrically substituted compounds which have two methyl–methyl interactions.

The average puckering angle for the symmetrically substituted compounds is 22.9° with a standard deviation of 2.6° and a standard deviation of the mean of 1.1°.[18] The two unsymmetrical structures have puckering angles that are substantially different from this mean value. One might expect that an unsubstituted phosphetane ring system would exhibit less puckering than any of the structures studied to date.

In the solid state, TPO exists in the form **1A** with an O–C(7) distance of 4.81 Å. For PPO, which is in form **2B** in the crystalline state, the C(7)–O distance of 3.37 Å and the methyl–phenyl distance [C(6)–C(10)] of 4.95 Å agree well with distances measured from the molecular model of **2B.** Both structures contain methyl–oxygen distances [C(5)–O = 3.178 Å in TPO; C(8)–O = 3.169 Å] that are somewhat less than the sum of the van der Waals radii (3.3–3.4 Å).[16]

Some observations can be made concerning the direction of puckering and the substitution pattern of the ring system. On examination of Figure 5 (compounds 1 and 3–7) and Figure 2 (compound 2), it is apparent that the direction of puckering is such that a single methyl group attached to a ring carbon is pseudoequatorial in all examples studied to date. A more detailed analysis (still of a qualitative nature) can be based on the substituents on C(3) and P; some of the possible puckering forms are illustrated in Figure 6. In six cases (compounds 1 and 3–7 in Figure 5), there is a single methyl substituent on C(3). The phosphetane ring system puckers such that cross-ring interactions between the substituents on P and C(3) are minimized. Since interactions involving a pseudoaxial C(3)–H substituent are relatively small, the larger possible diaxial cross-ring interaction between the other substituent on C(3) and the substituent on P determines the direction of puckering in these phosphetane ring systems. Form **1A** is the minimum energy form for compounds 1 and

Table V. Summary of Number and Type of Substituent Interactions in Phosphetane Ring Systems

compd	registry no.	no. of methyl–methyl interactions	no. of methyl–X interactions	no. of methyl–Y interactions	puckering angle, deg
1	34136-10-2	1	1 (X = Ph)	1 (Y = O)	16.7
2	35623-55-3	3	1 (X = Ph)	1 (Y = O)[a]	29.8
3	20047-46-5	2	2 (X = Ph)	2 (Y = O)	23.8
4	16083-91-3	2 (1)[b]	2 (X = Ph)	2 (Y = O	19.9, 23.4
5	26674-18-0	2	2 (X = Cl)	2 (Y = O)	26.4
6	17405-94-6	2	2 (X = O)	2 (Y = O)	19.6
7	35623-39-3	2	2 (X = Ph)[c]	2 (Y = CH_3)	24

[a] Compound 2 contains two Me–O interaction distances that appear to be too long to be significant in this analysis. The distances are both >3.3 Å and are shown in Table IV. Therefore, only one of these three interactions has real significance (see Table IV and text). [b] Value in parentheses involves possible cross-ring diaxial methyl–methyl interactions. Compound 4 exhibits cross-ring Me–Me distances of 3.52 (molecule 1) and 3.48 Å (molecule 2) which are probably not significant relative to the interactions between methyl groups that are cis to each other and attached to neighboring ring carbon atoms. [c] The plane of the phenyl group is oriented ~90° away from the phenyl group plane in the other structures containing a phenyl substituent on the P atom.

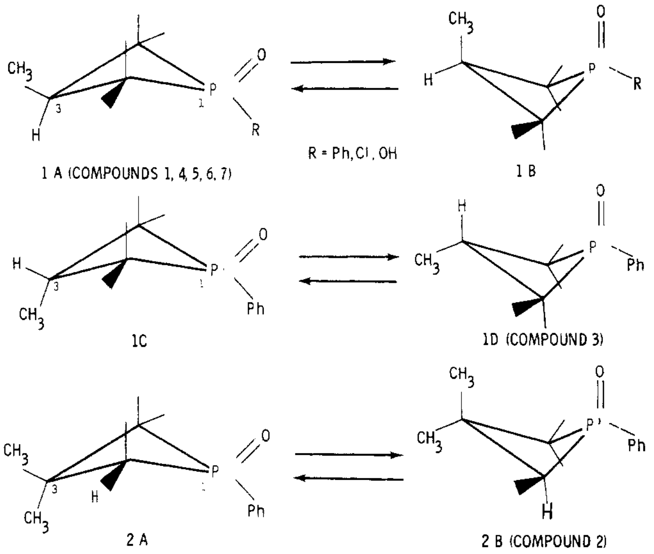

Figure 6. Puckering direction of the four-membered rings in several phosphetane derivatives.

4–7. Compound **3** exists in form **1D** (Figure 6) and is different from compounds **1, 4, 5,** and **7** when the substituents on P are taken into consideration; the phenyl group, which is larger than the oxygen substituent, is cis to the C(3)-methyl group and occupies a pseudoequatorial position.

Compound **2**, with two methyl groups on C(3), is a case where the relative size of the two substituents on P become important when the possible diaxial cross-ring interactions are considered in terms of the direction of ring puckering. In this work, compound **2** was found to exist in form **2B**, which is very similar to form **1D** in terms of diaxial cross-ring interactions. There are two possible diaxial cross-ring interactions to consider in compound **2**; a methyl–oxygen interaction (form **2B**) or a methyl–phenyl interaction (form **2A**). The methyl–phenyl diaxial interaction would be an energetically unfavorable situation, whereas the methyl–oxygen interaction that occurs in form **2B** is the minimum energy form for this system.

Based on these observations, it is reasonable to suggest that the direction of ring puckering is determined by the possible diaxial cross-ring interactions between substituents on C(3) and P in the phosphetane ring systems. The two possible sets of cross-ring interactions between cis-pseudoaxial substituents in any phosphetane derivative must be considered, and the lowest energy cross-ring interaction form will correspond to the observed puckering form. Forms **3A** and **3B** (Scheme II) illustrate the situation in general terms. When $R_3 \approx R_4$ in size (based on van der Waals radii) and $R_1 \gg R_2$, then the phosphetane ring system will exist in form **3A.** If $R_2 \gg R_1$ and $R_3 \approx R_4$, the ring system will exist in form **3B.** For the case where $R_1 \approx R_2$ and $R_3 > R_4$, the most stable form for the ring system will be form **3A.** If $R_1 \approx R_2$ and $R_3 < R_4$, then the ring will be puckered in form **3B.** For the two cases where (a) $R_1 > R_2$ and $R_3 < R_4$ or (b) $R_1 \approx R_2$ and $R_3 \approx R_4$, the probability of a correct prediction for the form of ring puckering is decreased.

Both ^{13}C and ^1H NMR analyses of TPO and PPO in solution with lanthanide shift reagents, which includes angular as well as distance considerations, indicate that the structures in solution parallel that of the crystalline state. The details of this study will be published elsewhere.[19]

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Supplementary Material Available: Positional and thermal parameters and structure factors for both TPO and PPO (Tables IIIa and IIIb) and all of the bond angles and distances (Figures 3 and 4) (12 pages). Ordering information is given on any current masthead page.

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