

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

CONFORMATIONAL PREFERENCES OF PENTACOORDINATE SPIROCYCLIC PHOSPHORUS COMPOUNDS

Robert R. Holmes^a

^a Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Holmes, Robert R.(1995) 'CONFORMATIONAL PREFERENCES OF PENTACOORDINATE SPIROCYCLIC PHOSPHORUS COMPOUNDS', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 98: 1, 75 — 88

To link to this Article: DOI: 10.1080/10426509508036943

URL: <http://dx.doi.org/10.1080/10426509508036943>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

CONFORMATIONAL PREFERENCES OF PENTACOORDINATE SPIROCYCLIC PHOSPHORUS COMPOUNDS

ROBERT R. HOLMES

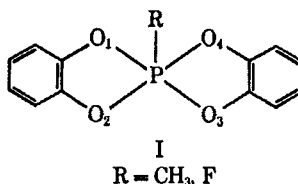
*Contribution from the Department of Chemistry, University of Massachusetts,
Amherst, Massachusetts 01002*

(Received December 1, 1973)

It is shown that existing nmr data on spirocyclic oxyphosphoranes are consistent with square pyramidal structures in agreement with X-ray data on these systems. Previously, the nmr data has been exclusively interpreted in terms of trigonal bipyramidal formulations. Structural principles are outlined for the square pyramidal model and appropriate mechanisms governing intramolecular exchange phenomena are advanced. Both reduced ring strain and enhanced electronic balance are cited as important factors stabilizing a square pyramidal conformation for spirocyclics containing highly electronegative atoms directly attached to phosphorus. Increasing distortion toward a trigonal bipyramid for these spirocyclics as the atom electronegativity is decreased is consistent with VSEPR theory.

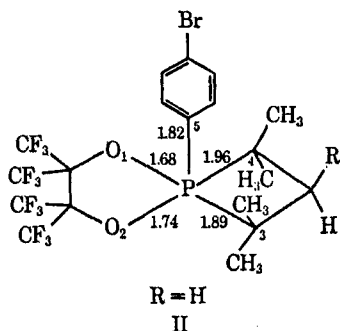
As is well known, the structure of simple pentacoordinated phosphorus compounds is trigonal bipyramidal.¹ For more complex derivatives detailed structural parameters are available in a few cases,^{2–10} although most structural assessments have resulted from nmr interpretations on a wide variety of derivatives.¹¹

In a recent X-ray study dealing with the spiro oxyphosphoranes I, a “square” pyramidal conformation has been reported.¹² This conformation is close to that



predicted by a simple point charge model,¹³ *i.e.*, one having an axial-basal angle of approximately 105° with the basal angles near 88°. The analogous compound with sulfur in place of oxygen (R = CH₃) is intermediate in structure between a square pyramid and a trigonal bipyramid based on an X-ray analysis.¹⁴ A summary of pertinent parameters on these derivatives is found in Table I.¹⁵

Also “square” pyramidal structures have been observed *via* X-ray diffraction for 1,3,2-dioxaphospholans II (R = H, CH₃) containing both a five- and a four-membered ring.¹⁶



	Angle (deg)
C_5PC_4	105.6
C_5PC_3	110.7
C_5PO_1	101.6
C_5PO_2	100.0
C_4PC_3	78.1
O_1PO_2	85.0
C_4PO_2	154.2
C_5PO_1	147.7

In view of the many spirocyclic phosphorus systems whose structures have been inferred as trigonal bipyramidal by nmr spectroscopy,¹¹ it becomes necessary to reassess the structural conclusions and establish whether the nmr data are effective in discriminating between the two basic pentacoordinate conformations. It is important to determine the consequences of any structural reassignment, especially if the square pyramid becomes the dominant form for these spirocyclic systems.

STRUCTURAL PRINCIPLES

Before proceeding with a proper treatment, it is worthwhile to recall two established principles of pentacoordinate behavior. These principles are particularly important in application to mechanisms involving the dynamic stereochemistry of some of the derivatives that will be discussed.

For trigonal bipyramids, it is generally observed¹ that the most electronegative ligands preferentially reside in the axial positions. The presence of cyclic systems imposes an additional constraint limiting the stereochemical possibilities. Derivatives containing four- or five-membered rings, which represent the most widely studied systems, assume a conformation with the rings spanning axial-equatorial positions.²⁻¹⁰ Only if the ring ligand atoms directly attached to the phosphorus atom are of low electronegativity is there some evidence that a ring may span an equatorial-equatorial set.^{1a} As shown by X-ray results on some ring-containing compounds,²⁻¹⁰ the typical structural arrangement will position the most electronegative ring component in an axial position if the ring ligands differ in character. Because ring strain is minimized in the axial-equatorial compared to the equatorial-equatorial conformation, the ring arrangement will take preference in occupying an axial position, even at the expense of displacing a more electronegative atom of an acyclic substituent from this location.

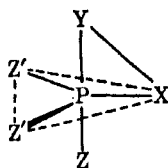
Accordingly, most published data¹¹ on monocyclic containing pentacoordinate

TABLE I
Selected Bond Parameters for Spirocyclic Phosphoranes

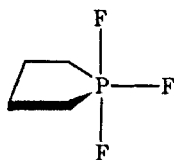
	R = F, X = O (ref 12)	R = CH ₃ , X = O ^b (ref 12)	R = CH ₃ , X = S (ref 14)
Bond Distances, Å			
P-X ₁	1.629	1.652	2.153
P-X ₂	1.659	1.668	2.206
P-X ₃	1.625	1.654	2.131
P-X ₄	1.658	1.673	2.202
P-R	1.546	1.776	1.817
Bond Angles, deg			
X ₁ PX ₂	91.2	90.1	90.6
X ₁ PX ₄	91.7	90.2	91.5
X ₂ PX ₃	85.7	82.9	
X ₁ PX ₃	84.5	83.9	
X ₁ PX ₄	146.1	147.9	132.0
X ₂ PX ₄	168.2	156.6	158.1
X ₁ PR	107.3	106.0	107.5
X ₂ PR	96.0	102.2	101.4
X ₃ PR	106.6	106.0	109.1
X ₄ PR	95.8	101.3	100.5

^a On the basis of electron pair repulsions (R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963)), the presence of strongly electronegative ligands leads to decreased repulsion between bond pairs and reduces the slight preference in stability accorded the trigonal bipyramid relative to the idealized square pyramid. This effect may be invoked to rationalize the data in this table. Replacement of the unique fluorine atom by the more electropositive methyl groups produces a general lengthening of PO distances. Introduction of less electronegative sulfur atoms into the spiro system results in enhanced electron pair repulsions, in line with the observed lengthening of the P-C bond of the methyl groups and the increased structural deformation toward a trigonal bipyramid. ^b Two kinds of molecules with slightly different parameters appear in the unit cell for this derivative.¹² The ones given here are average values for the two structures.

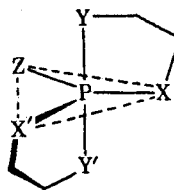
phosphorus compounds agree with the general structural representation where X-Y refers to either a four- or five-membered ring and the electronegativities of the five-coordinated atoms, which may be the same or different, follow the order $Z > Z'$, $Y > X$, and X and Y may take on any value relative to Z and Z'. Only



the case of $(\text{CH}_2)_4\text{PF}_3$ does ^{19}F nmr data suggest^{1a} that the cyclic system is in the equatorial plane.



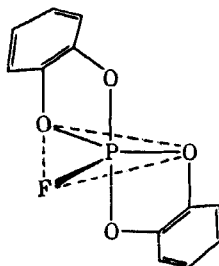
Extension of these principles to spirocyclic systems containing rings of the same size suggests a structure similar to that for monocyclic derivatives which is in accord with most available nmr data.¹¹ The electronegativities of the atoms follow the



order $Y(Y') \geq X(X')$, and Z may take on a range of values relative to either X or Y. The atoms X, Y, X', Y', and Z may be the same or different.

STRUCTURAL CORRELATIONS BETWEEN TRIGONAL BIPYRAMIDS AND SQUARE PYRAMIDS

In this context the trigonal bipyramidal structure originally proposed^{17,18} for the spiro dioxaphosphole I (with $R = F$) based on ^{19}F chemical shift data is reasonable

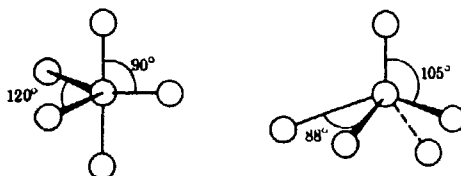


and shows the rings favorably positioned, displacing the more electronegative fluorine atom from its usual position at an axial site. The value of the chemical shift, 70.4 ppm relative to CCl_3F , is close to that commonly observed for equatorially positioned fluorine atoms compared to downfield values associated with axially oriented fluorine atoms.^{17,18}

Although it is possible to argue that the square pyramidal structure found for this compound by X-ray analysis may be a result of lattice constraints, especially since energy differences between the two basic five-coordinate geometries are predictably small,^{13,19-21} structural investigations on simpler pentacoordinate phosphorus derivatives give no evidence for the occurrence of this kind of isomeric conversion with a change of state.^{1c,d} In a somewhat related example, SbPh_5 , which

exists as a distorted square pyramid in the solid,²² shows evidence for retention of this structure in solution.²³

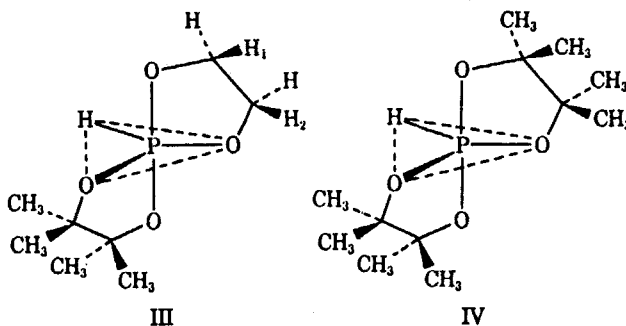
Although it is not known what chemical shift values are expected for square pyramids, electron-pair repulsion considerations, with reference to the idealized five-coordinate geometries, suggest a correspondence in bond properties between



the basal bonds of the square pyramid and the axial bonds of the trigonal bipyramid.²⁴ As a consequence, ^{19}F chemical shifts for basal fluorine atoms should appear to the low field side of ^{19}F resonances for axial fluorine atoms in the square pyramid. Hence the relatively positive chemical shift value observed^{17,18} for the fluorine derivative I is not at variance with the X-ray structure¹² showing an axial fluorine atom in a square pyramidal configuration.

NMR INTERPRETATIONS ON SPIROCYCLIC OXYPHOSPHORANES

If square pyramidal representations become prevalent for spirophosphoranes, it is necessary to establish that such structures are supported by more complex spectral observations. Examination of the results of nmr studies shows that suitable interpretations are available. For example, a temperature-dependent nmr study of the spiro tetroxyhydridophosphoranes, formulated as trigonal bipyramids,²⁵ shows the presence of two types of methyl signals at reduced temperatures but one methyl peak at higher temperatures (T_c , 37° for III and 95° for IV). Similar behavior is



observed for the ring protons in the less methylated compound. Furthermore, the process is intramolecular since the doublets, corresponding to the protons directly bonded to the phosphorus atom, remain unchanged over the temperature range studied, and the coupling constant for the ring protons J_{PH} in III at high temperatures is the mean value of the J_{PH} coupling constants obtained in the lower temperature AA'BB'X system. Detailed analysis²⁵ indicates that at reduced temperatures the ring substituents that are trans to the proton atom directly bonded to

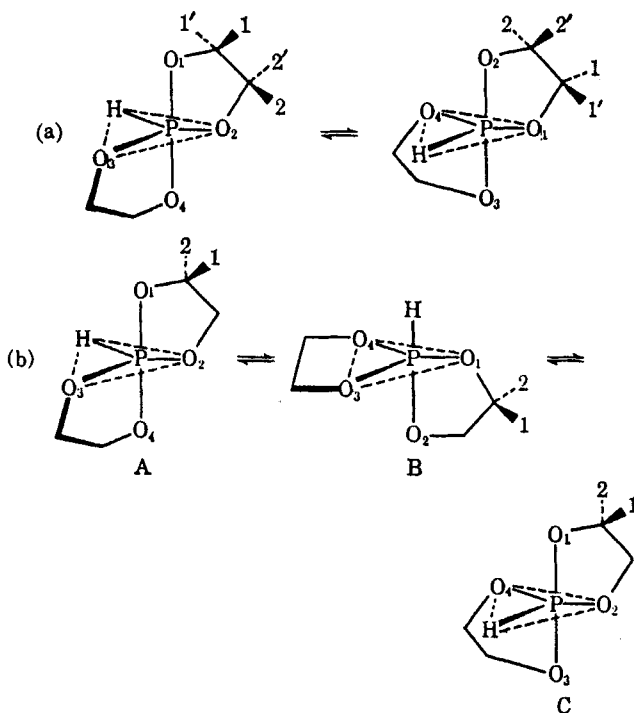
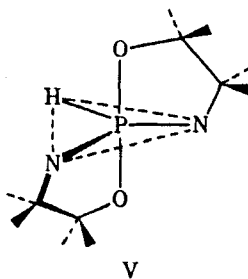


FIGURE 1 (a) Low temperature process, (b) high temperature process.

phosphorus form equivalent pairs and are different from the analogous *cis* substituents which form equivalent pairs. In the high temperature process, all substituents of one ring become equivalent.

The process has been described²⁵ as a double intramolecular one since, in the trigonal bipyramid assumed, four types of protons in III and four kinds of methyl groups in III and IV are expected for rigid forms. A simple Berry pseudorotation²⁶ operating from the lowest temperature studied (-70°) accounts for the presence of only two types of ring protons or methyl groups, Figure 1(a), whereas a more complex multistage pseudorotation has been advanced²⁵ to account for the appearance of a single type of ring proton or methyl group above the coalescence temperatures, Figure 1(b).

In related amino derivatives of the type



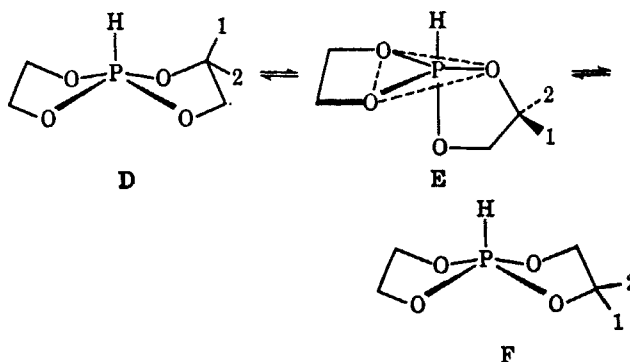
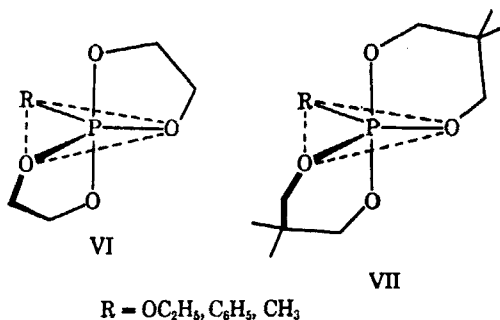


FIGURE 2 Non-Berry exchange based on a square pyramidal ground state for a spirocyclic derivative.

no intramolecular exchange is evident even at room temperature.²⁷ The latter behavior is consistent with the proposed exchange scheme since the occurrence of exchange would imply the formation of unfavorable trigonal bipyramidal intermediates with the less electronegative nitrogen atoms situated in axial positions.

Alternatively, if a square pyramid is assumed for compounds III and IV, a "rigid" form would exhibit but two types of ring protons or methyl groups (cis and trans to the unique directly bonded proton) in agreement with the lower temperature nmr data on the tetraoxy derivatives²⁵ and, accordingly, negate the need for a double intramolecular mechanism. The higher temperature data may proceed by a multi-stage Berry process or may simply be interpreted in terms of a non-Berry single stage exchange process proceeding through a trigonal bipyramidal intermediate formed by displacing one of the basal ligands in the original square pyramid to an axial position in the trigonal bipyramid.²⁸

The process depicted in Figure 2 is applicable to a number of other kinds of spiro systems including the dioxaphospholans II which were initially interpreted in terms of trigonal bipyramidal ground state structures.²⁹ For the five- and six-membered spirocyclic oxyphosphoranes³⁰ VI and VII, interpretations in terms of intramolecular exchange among trigonal bipyramidal formulations, similar to the processes shown in Figure 1, satisfactorily account for the nmr data. For the five-membered spirocyclics, like that for the spiro hydrido derivatives, both exchange processes were involved,³⁰ the only difference being that a higher coalescence temperature ($T_c = 172^\circ$ for $R = OC_2H_5$) was observed to bring about equivalence of the ring protons compared to the hydrido derivatives. In the case of the phenyl

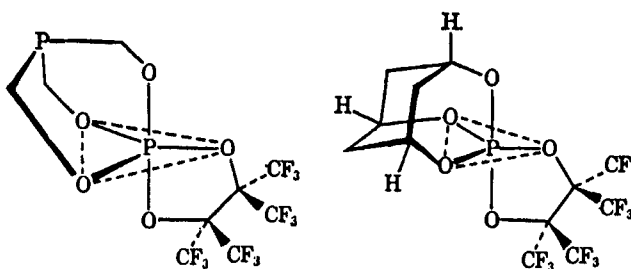


and methyl derivatives, changes occurred in the ^1H spectra on heating, but a simple doublet (phosphorus coupling) pattern was not reached.

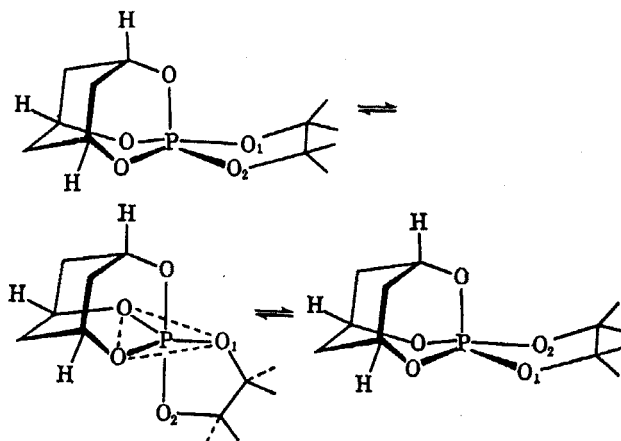
For the six-membered spirocyclics VII, predictably greater exchange rates are indicated by the appearance of equivalent ring methyl protons as well as equivalent ring methylene protons in their nmr spectra at room temperature.³⁰ This is because less strain should be experienced by the six-membered ring located in the diequatorial position in the postulated³⁰ exchange intermediate B for the higher temperature process in Figure 1. Furthermore, on cooling to -65° , no change was observed for the ^1H spectrum associated with the ethoxy compound whereas, in the case of the phenyl derivative, the single absorption for the hydrogens of the ring methyl groups splits into two absorptions of equal intensity, and the methylene doublet became two poorly resolved multiplets. The spectrum of the methyl derivative showed similar but less-resolved spectral changes. Consequently, both processes of Figure 1 are indicated to be occurring for all three derivatives of VII at room temperature and the higher temperature process is "stopped" for the phenyl and methyl derivatives only at -65° . The greater exchange rate observed when using the ethoxy groups is again expected in that less energy is needed in reaching intermediate B of Figure 1 (higher temperature process), since the alkoxy group should orient axially more easily because of its higher electronegativity compared to the phenyl or methyl groups.

It is apparent that the nmr behavior of these compounds VI and VII may also be interpreted by the exchange process (Figure 2) involving an assumed square pyramidal ground state, since the critical intermediate in determining comparative rates is the same in each mechanism (B in Figure 1). In terms of the square pyramidal geometry, again there is no need for postulating a double intramolecular process.

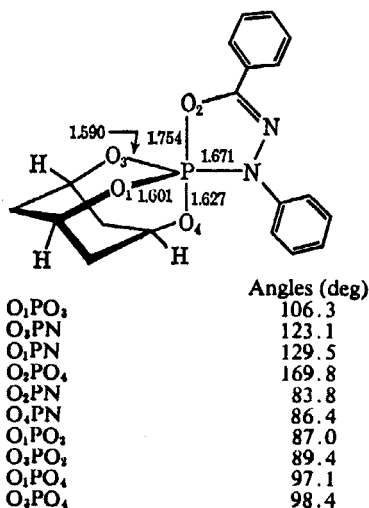
Nmr data indicating exchange of oxyphosphoranes containing both a five-membered ring and a bicyclic moiety have been cited³¹ as support for a turnstile mechanism instead of a Berry pseudorotation.²⁶



The same data may be interpreted by starting with a distorted square pyramidal ground state and following an exchange mechanism similar to that suggested in Figure 2. However, the special geometric constraints imposed by the adamantyl moiety should significantly distort the structure from an idealized representation and render decisions regarding the likelihood of specific exchange mechanisms less useful.



An X-ray structure recently available on a related derivative (PO_4N) ($\text{C}_6\text{H}_5\text{CN}$)(C_6H_5)(C_6H_9) shows a distorted trigonal bipyramidal form.³²



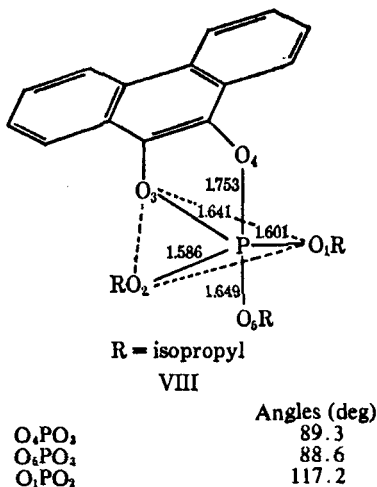
Compared to the pentaoxy cage compound just discussed, distortion toward a trigonal bipyramid is in accord with the presence of the less electronegative nitrogen atom directly bonded to phosphorus, similar to the observation of structural distortion of the thio derivative of the spiro phosphole I (with $\text{R} = \text{CH}_3$) when compared to the corresponding tetraoxy derivative.

DISCUSSION

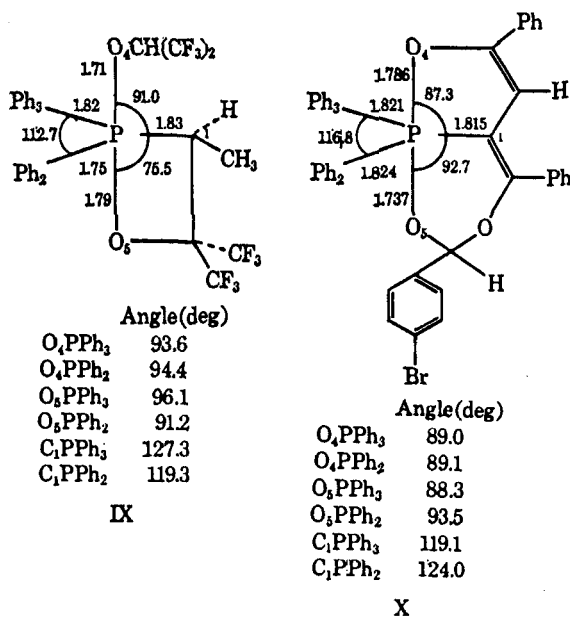
From what has been presented, it is apparent that existing nmr data on spirocyclic oxyphosphoranes support equally well either ground state trigonal bipyramidal or square pyramidal representations, depending on the type of exchange mechanism chosen, all within the framework of established structural principles for these two basic pentacoordinate conformations. Since available X-ray data^{12,14,16} on this class

of compounds support the square pyramid, it appears advantageous to view these oxy spirocyclics on the latter basis and attempt to discern intrinsic structural behavior which by contrast allows monocyclic oxyphosphoranes or pentaorganyl spirocyclic phosphoranes to exist as trigonal bipyramids.

Structural determinations by X-ray diffraction on the monocyclic oxyphosphorane VIII⁵ and mixed oxyorganyl ring containing compounds IX^{6a} and X^{6b} show

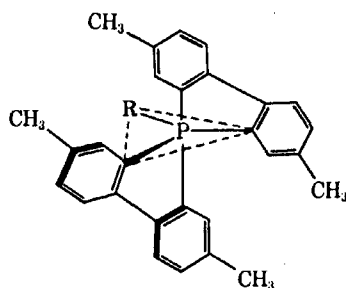


trigonal bipyramidal conformations only moderately distorted from the idealized geometry.



While similar X-ray studies on pentaorganyl derivatives appear to be lacking, the structural inferences from nmr data³³⁻³⁵ are convincing. The fact that spirocyclic

phosphorus carbon compounds derived from XI exhibit a single ^1H nmr methyl signal at 35° and two methyl group signals at -60° is consistent with a trigonal



XI

R = Me, Et, Bz, Ph, and β -Naphthyl

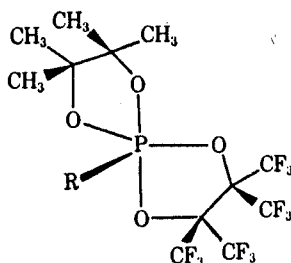
bipyramidal ground state undergoing rapid ligand exchange at higher temperatures and is not consistent with interpretation in terms of a square pyramidal ground state of C_{4v} symmetry. The latter symmetry qualification implies that rotation of R groups about the unique P—C bond must be rapid in the absence of positional exchange. It follows that this rotation must be rapid during positional exchange as well. The presence of rotational hindrance manifests itself in the related derivative XI containing a less symmetric group R = *o*-isopropylphenyl. Here four bitolyl methyl signals are observed³³ at room temperature indicating a static structure. These signals collapse to a single line on warming to 130° . In the more simply substituted derivatives of XI, R = Me and Et, only one methyl signal is expected for a square pyramidal conformation, whether ligand exchange is occurring rapidly or not.

An effective structural correlation may be presented based on two observations. First, the structural data suggest, in line with decreasing electronegativity in the order $\text{O} > \text{S} > \text{C}$, that spirocyclic systems go from square pyramidal toward trigonal bipyramidal. Second, spirocyclic oxyphosphoranes, in contrast to mono- or bicyclic oxyphosphoranes like X, reside in a square pyramidal configuration and suggest the operation of some cooperative effect brought about by the formation of a set of four like bonds compared to two pairs that are possible in the trigonal bipyramidal form.

Electron delocalization, reinforced by the presence of a more extensive basal bonding system present in the square pyramid, is expected to enhance the structural stability of this conformation compared to the trigonal bipyramid. Evidence for the operation of electron delocalization is seen from an examination of P—O bond distance values in the various structures I and VIII—X. The equatorial P—O distance in the ring system of the trigonal bipyramid VIII is similar to the P—O distances in the square pyramid I (R = CH_3 , F, Table I) centered around 1.65 \AA whereas the axial P—O distances in the cyclic components of the trigonal bipyramidal structures VIII—X are considerably longer, centered around 1.76 \AA , even though these axial bonds are at similar angles to neighboring bonds as are found in the square pyramid, each approximating 90° to other P—O linkages (*cf.* VIII and I). Estimates of single bond distances³⁶ for P—O linkages range from 1.76 \AA to 1.83 \AA and support the presence of appreciable multiple bonding as discussed here.

In the argument just presented, there appears to be no reason why monocyclic oxyphosphoranes like VIII should not achieve a similar degree of electron delocalization, with the ring and two OR ligands occupying the four basal positions of the square pyramid. This suggests that the observance of square pyramidal structures for spirocyclic oxyphosphoranes must be dependent on the presence of the spirocyclic system itself, most likely associated with constraints due to ring "strain" effects.

The square pyramid allows both PO linkages of each ring to assume more or less equal character, depending on the requirements of the attached substituents, in contrast to the substantially different nature of apical and equatorial linkages found for a ring system in a trigonal bipyramid. As a result, residual ring strain should be less in the square pyramid. Thus, the energy balance may be tipped in favor of the square pyramidal configuration compared to the normally more stable trigonal bipyramid when two small-membered rings are present. Introduction of substituents which are different from each other and hence have unequal electronic requirements, whether they be part of the ring system as in V or attached thereto, should be less effective in stabilizing the square pyramidal form. This may be the reason for the appearance of trigonal bipyramidal structures for the spiro oxyphosphoranes XII,¹⁶ which somewhat resemble I in substituent composition but



XII

R = SPh, *p*-OC₆H₄Br

have unequal P—O bond character due to the rather wide difference in electronegativity between the methyl and perfluoromethyl groups.

In the spiro system II containing a four-membered ring, the consequent increase in ring strain effects, if the trigonal bipyramidal structure were adopted, coupled with the presence of a methylene group in an axial site in that configuration apparently provides a sufficient structural advantage to allow the appearance of the square pyramid in this instance.

Obviously, the magnitude of the effects causing preference for one structure over the other need not be large, in view of previous data^{13,19-21} on simple derivatives suggesting that in many cases the two pentacoordinate conformations differ by only a few kilocalories. In the case of the relatively nonrigid trigonal bipyramidal VF₅, an estimate of 1.8 kcal/mol has been given.¹⁹

ACKNOWLEDGEMENT

Grateful appreciation is expressed to Professor R. Schmutzler, Dr. W. Sheldrick, and Dr. M. Fild of Braunschweig University for valuable discussions.

REFERENCES AND NOTES

- (a) E. L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963); (b) E. L. Muetterties, W. Mahler, K. J. Packer and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (c) R. R. Holmes, R. P. Carter, Jr. and G. E. Peterson, *ibid.*, **3**, 1748 (1964); (d) J. E. Griffiths, R. P. Carter, Jr. and R. R. Holmes, *J. Chem. Phys.*, **41**, 863 (1964); (e) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965); (f) L. S. Bartell and K. W. Hansen, *ibid.*, **4**, 1777 (1965); (g) S. B. Pierce and C. D. Cornwell, *J. Chem. Phys.*, **48**, 2118 (1968); (h) W. J. Adams and L. S. Bartell, *J. Mol. Struct.*, **8**, 23 (1971); (i) H. Yow and L. S. Bartell, *ibid.*, **15**, 209 (1973).
- M. J. C. Hewson, R. Schmutzler and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 190 (1973).
- G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 568 (1968).
- P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).
- (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez and C. P. Smith, *J. Amer. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton and J. Ladell, *ibid.*, **89**, 2272 (1967).
- (a) M.-Ul-Haque, C. N. Caughlin, F. Ramirez, J. F. Pilot and C. P. Smith, *J. Amer. Chem. Soc.*, **93**, 5229 (1971); (b) D. D. Swank, C. N. Caughlin, F. Ramirez and J. F. Pilot, *ibid.*, **93**, 5236 (1971).
- J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967).
- A. Almenningen, B. Anderson and E. E. Astrup, *Acta Chem. Scand.*, **23**, 2179 (1969).
- L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).
- H. Hess and D. Frost, *Z. Anorg. Allg. Chem.*, **342**, 240 (1966).
- Extensive reviews of the nmr data are found in the following sources: R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements," Georg Thieme Publishing Co., Stuttgart, 1973; D. Hellwinkel, "Organo Phosphorus Compounds," Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N. Y., 1972, p. 185.
- H. Wunderlich, D. Mootz, R. Schmutzler and M. Wieber, *Z. Naturforsch.*, in press, and personal communication.
- J. Zemmann, *Z. Anorg. Allg. Chem.*, **324**, 241 (1963).
- M. Eisenhut, R. Schmutzler and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973), and personal communication.
- To place structural distortions on a quantitative basis, at least as observed in the solid, an acceptable criterion appears to be to take the sum of the angle differences between the idealized trigonal pyramid (90 and 120°) and that found in a given structure (angles O₁PO₃ and O₂PO₄ in I) compared to the respective sum calculated to exist between the two idealized five-coordinate forms. For the latter purpose, the idealized square pyramid is taken as the one referred to above which has trans basal angles of 150°. Thus, on a scale of 60, structure I (R = CH₃) is nine from the idealized square pyramid, while the corresponding number for structure I (R = F) is 20 and for the sulfur derivative, 26. The percentages of square pyramid then are respectively 85, 67, and 57.
- J. A. Howard, D. R. Russell and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).
- G. O. Doak and R. Schmutzler, *Chem. Commun.*, 476 (1970).
- G. O. Doak and R. Schmutzler, *J. Chem. Soc. A*, 1295 (1971).
- (a) R. R. Holmes, L. S. Couch and C. J. Hora, Jr., *J. Chem. Soc., Chem. Commun.*, 175 (1974); (b) R. R. Holmes, *Accounts Chem. Res.*, **5**, 296 (1972).
- R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).
- (a) R. R. Holmes and R. M. Deiters, *J. Amer. Chem. Soc.*, **90**, 5021 (1968); (b) *Inorg. Chem.*, **7**, 2229 (1968); (c) R. R. Holmes, R. M. Deiters and J. A. Golen, *ibid.*, **8**, 2612 (1969); (d) A. Rauk, L. C. Allen and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972); (e) R. Hoffmann, J. M. Howell and E. Muetterties, *ibid.*, **94**, 3047 (1972); (f) A. Strich and A. Veillard, *ibid.*, **95**, 5574 (1973); (g) P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsois and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971); (h) L. S. Bartell and V. Plato, *J. Amer. Chem. Soc.*, **95**, 3097 (1973).
- (a) P. J. Wheatley, *J. Chem. Soc.*, 3718 (1964); (b) A. L. Beauchamp, M. J. Bennett and F. A. Cotton, *J. Amer. Chem. Soc.*, **90**, 6675 (1968).
- (a) I. R. Beattie, K. M. S. Livingston, G. A. Ozin and R. Sabine, *J. Chem. Soc.*, 784 (1972); (b) G. L. Kok, *Spectrochim. Acta, Part A*, **30**, 961 (1974).
- Bond electron pair repulsions in the case of the trigonal bipyramid should be greater for axial-equatorial pairs at 90° compared to equatorial-equatorial pairs at 120°. In the square pyramidal conformation, bond pair repulsions are greater for basal-basal pairs rather than axial-basal pairs based on the 88 and 105° geometry shown. Thus to equalize repulsions, the axial bonds in the trigonal bipyramid should be longer than the equatorial bonds; whereas, in the square pyramid, the basal bonds should be longer than the axial length. This hypothesis is borne out in the case of the pentachloroindate ion InCl₅²⁻ (D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*,

- 8, 14 (1969). Presumably other bond properties will follow this comparative scheme. See also ref 19a and 21d-f.
25. D. Houalla, R. Wolf, D. Gagnaire and J. B. Robert, *Chem. Commun.*, 443 (1969).
 26. R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
 27. M. Sanchez, L. Beslier and R. Wolf, *Bull. Soc. Chim. Fr.*, 2778 (1969).
 28. In this mechanism, the isomeric trigonal bipyramids, structures III and IV, are considered lower in energy than the corresponding intermediates E of Figure 2 and most likely are intraconverting with isomers like D of Figure 2. However, this process does not allow exchange of groups labeled 1 and 2 in Figure 2; it only allows exchange of ring substituents located cis to the nonring ligand.
 29. (a) R. E. Duff, R. K. Oram and S. Trippett, *Chem. Commun.*, 1011 (1971); (b) R. K. Oram and S. Trippett, *J. Chem. Soc. Perkin Trans. I*, 1300 (1973).
 30. B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell and D. W. White, *J. Amer. Chem. Soc.*, **93**, 4004 (1971).
 31. I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie and F. Ramirez, *Accounts Chem. Res.*, **4**, 288 (1971), and references cited therein.
 32. W. C. Hamilton, J. S. Ricci, Jr., F. Ramirez, L. Kramer and P. Stern, *J. Amer. Chem. Soc.*, **95**, 6335 (1973).
 33. G. M. Whitesides and M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).
 34. D. Hellwinkel, *Chemia (Aarau)*, **22**, 488 (1968).
 35. D. Hellwinkel and H. J. Wilfinger, *Tetrahedron Lett.*, 3423 (1969).
 36. (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960; (b) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper & Row, New York, N. Y., 1972; (c) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).