$RhCl_2(N_2Ph)(PPh_3)_2$; see G. W. Rayner-Canham and D. Sutton, *Can. J. Chem.*, **49**, 3994 (1971).
(47) T. Tsuji and E. M. Kosower, *J. Am. Chem. Soc.*, **92**, 5313 (1970).
(48) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1964).
(49) E. Rahkamaa, *Mol. Phys.*, **19**, 727 (1970); *Z. Naturforsch., Teil A*, **24**, 2004 (1969).
(50) T. Axenrod in "Nitrogen NMR", M. Witanowski and G. A. Webb, Ed., Plenum Press, New York, N.Y., 1973, p 295.
(51) H. J. Yeh, H. Ziffer, D. M. Jerina, and D. K. Boyd, *J. Am. Chem. Soc.*, **95**, 2741 (1973).
(52) J. H. Naggle, J. D. Baldeschweiler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962).
(53) R. Kübler, W. Lütke, and S. Weckherlin, *Z. Electrochem.*, **64**, 650 (1960).
(54) B. L. Haymore, J. A. Ibers, and D. W. Meek, *Inorg. Chem.*, **14**, 541 (1975).
(55) S. Cenini, R. Ugo, and G. LaMonica, *J. Chem. Soc. A*, 3441 (1971).
(56) D. Petredis, A. Burke, and A. L. Balch, *J. Am. Chem. Soc.*, **92**, 428 (1970).

Conformational Energy Calculations on Five-Membered Rings in Pentacoordinate Phosphorus[1]

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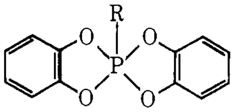
Abstract: It is shown in agreement with X-ray data that the square pyramid (SP) conformation of five-membered ring containing pentacoordinate phosphorus is stabilized relative to the corresponding trigonal bypyramid (TP) when the ring systems are unsaturated and contain highly electronegative heteroatoms directly attached to phosphorus. The primary cause of the stabilization is attributed to ring strain produced by differences in bond lengths which are inherent in the TP form for equatorial vs. apical bonds. For dioxaphospholene compounds examined, ring strain is estimated to be about 3-4 kcal/mol greater in the TP. This enhances the overall stability of the SP conformation relative to the TP form. As the electronegativity of the heteroring atoms is reduced, ring strain effects become less important and the TP appears as the more stable structure in line with structural evidence. The presence of mixed heteroring atoms directly attached to phosphorus and the presence of saturated rings are expected to reduce ring strain differences, thus favoring the formation of the TP, while the presence of four-membered rings will intensify the formation of the SP conformation.

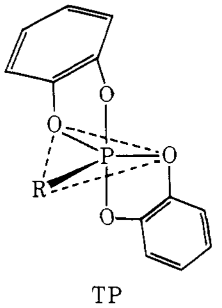
Of the two common isomeric forms for pentacoordinate phosphorus, the trigonal bypyramid (TP) and square pyramid (SP), only the former has been observed for derivatives when simple ligands or monocyclic systems are present.[2-11] The recent appearance of cyclic containing phosphorus compounds, I,[12] bearing structures approximating the SP



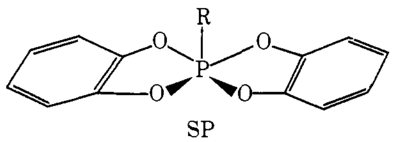
I, R = CH$_3$, F

prompts an examination of the conformational requirements of small membered rings in each of the two idealized environments to ascertain if they are sufficiently different to preferentially stabilize the SP form.

The dominant consideration[1] appears to center on the presence of two sets of bond properties peculiar to pentacoordinate compounds.[13] In the TP, for the particular type of ring system in I, the P-O bonds would differ substantially in character, while this is not the case for the SP envronment. In the TP, apical bonds are longer than equatorial bonds; whereas in the idealized SP, the four basal bonds would have equal character. Other simple coordination polyhedra do not exhibit this characteristic as can be deduced from geometrical requirements.



TP



SP

In the usual calculation of conformational energies of ring systems, bond distances are frequently held constant as a first approximation with energy minima determined by torsional distortions, angle bending, and van der Waals interactions.[14-18] We will see that bond distance variations enter as a more important term for five-coordinate phosphorus containing planar ring systems. This paper will describe strain effects for these small membered rings resulting from the unequal bond properties and provide an estimate of their magnitude.

Ring Strain Requirements in a TP vs. a SP

A comparison of X-ray data[12] on the SP Ia (R = CH$_3$) with that for the related cyclic system IIa,[6] existing in a TP environment, illustrates possible effects of the change in ring conformation between the two structures.

The differences averaging 0.02 Å between cis PO bond lengths in Ia are evidence of residual TP character as attested by a comparison of the O_1PO_3 and O_2PO_4 angles. These are, respectively, 148.1 and 156.9° showing that oxygen atoms 1 and 3 have some equatorial character while atoms 2 and 4 have some apical character. Likewise, the ring CO bonds have slightly different lengths which bear the same relationship to each other as observed in the TP structure IIa, i.e., a shorter CO bond to an apical oxygen atom compared to the CO bond stemming from an equatorial oxygen. Similar alternations in bond lengths are present in other related systems.[7b,19] With due cognizance of these distortions away from the SP, the oxyphosphorane Ia is highly symmetric relative to the variations in the ring bond lengths seen in the oxyphosphorane IIa. The magnitude of the api-

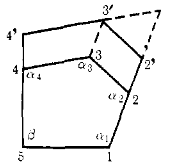
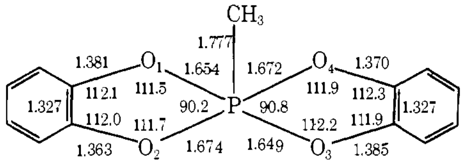
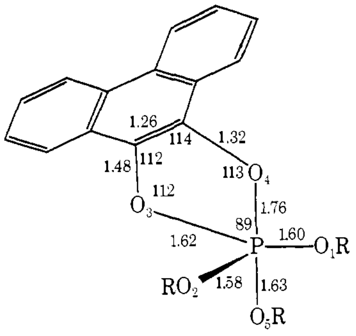


Figure 1. The effect of increasing the length of edge 4-5 relative to edge 1-5 on the remaining sides of the pentagon with the length of edge 2-3 held fixed.



Ia (from ref 12b)



orthorhombic form
IIa (from ref 6a), R = isopropyl
(distances, Å; angles, deg)

cal-equatorial difference in PO bond lengths is comparable to that in the respective CO linkages.

In these structures, the average deviation of the atoms in the five-membered rings is less than 0.06 Å from the respective least-squares plane.[6a,12b] This appears to be a result of the delocalized ring system and the presence of considerable π bonding as may be inferred from a comparison of single bond values (P-O = 1.71 Å;[20] C-O = 1.43 Å[21,22]) with those in the rings, at least for the shorter ring distances. Since the planarity of the heteroring systems is approximately the same in the TP II and SP I, any strain introduced into the ring in the TP as a result of the unequal character of the bonding in the equatorial and apical positions must be minimized by angle bending and bond length changes associated with the various ring atoms. In other words, stabilization due to π bonding is assumed to be greater than the magnitude of ring strain effects such that planarity is maintained. Torsional changes are not of importance here due to the lack of neighbor interactions.

To visualize the geometrical consequence of lengthening an apical bond relative to an equatorial bond in a TP, we start with the pentagon in Figure 1. The latter relative dimensions are designed to approximate those in the SP I. The internal angles α are set by the symmetry given and will be 112.5° with β = 90°. It is apparent that increasing the length of the apical bond 4-5 from 4 to 4′, with the internal angles and the length of the side 2-3 maintained unchanged, will result in a relative increase in the length of side 1-2 (now 1-2′) compared to 3-4 (now 3′-4′).

Another way in which the ring conditions may be satisfied for different ratios of the apical-equatorial bond lengths is to maintain the three lengths 1-2, 2-3, and 3-4 constant but vary the angles. Under these constraints as α_1 and α_3 increase, α_2 and α_4 decrease.[23]

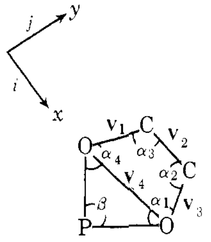
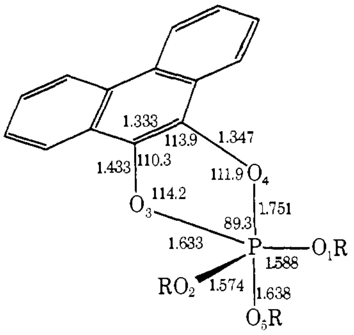


Figure 2. Coordinate description for five-membered phospholene ring system.

Examination of the X-ray parameters for the two forms of the oxyphosphorane II[6] shows that the five-membered ring structures largely conform to these geometrical restrictions. The orthorhombic form IIa is illustrative of the first case described showing a large difference in the bond distances 1-2 and 3-4 with the average α angle equal to 112.8 ± 0.8°. In the monoclinic form IIb the C-O bond distances are considerably closer to each other in value while the α angles vary according to the second case described. The average α angle 112.6 ± 1.5° shows a variation twice that present in the orthorhombic form.



Monoclinic form
IIb (from ref 6b)
(distances Å; angles, deg)

Mathematical Formulation

To obtain specific numerical sets, the following treatment suffices for the planar systems. With reference to Figure 2, the OCCO portion forms a quadrilateral whose sides are the vectors $\mathbf{V}_1$, $\mathbf{V}_2$, and $\mathbf{V}_3$. Their sum is $\mathbf{V}_4$. In terms of unit vector notation $\mathbf{V}_1 = a_1 i + b_1 j$, etc., the conditions prevail

$$a_1 + a_2 + a_3 = |\mathbf{V}_4| \qquad (1)$$

$$b_1 + b_2 + b_3 = 0 \qquad (2)$$

Using the magnitudes of the vectors ($|\mathbf{V}_1| = k$, $|\mathbf{V}_2| = 1$, and $|\mathbf{V}_3| = \mathrm{m}$) we have $a_1^2 + b_1^2 = k^2$, $a_2^2 + b_2^2 = l^2$, and $a_3^2 + b_3^2 = m^2$. If we set the value of l (C-C bond length) equal to 1.33 Å, the resulting three equations in six unknowns may be solved by specifying two lengths and one angle, two angles and one length, etc.

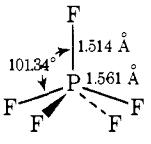
To illustrate, starting with a C-C bond length of 1.33 Å and equal PO bond lengths of 1.65 Å, approximately that observed in the SP Ia, and changing the PO lengths to correspond to those in the TP IIb, results in a change in the two equal CO bond lengths from 1.31 Å ($k = m$) to 1.34 Å (k) and 1.43 Å (m). If three of the angles, α_1 to α_3, which were held constant at 112.5° in the latter calculation, are allowed to vary (α_4 = 111°), the TP structure IIb is closely reproduced, α_3 = 115.5°, α_2 = 109°, and α_1 = 114.5°.

In the subsequent section, energy minimization relative to "normal" parameters in a geometry search will be described to ascertain whether reasonable estimates of TP-SP energy differences are calculable.

Conformational Energy Calculations

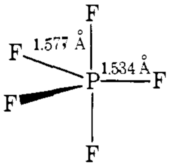
There is no doubt that the PO apical bond lengths in IIa and -b are abnormally long but commonly observed[7,19a] for unsaturated five-membered rings in TP environments. In acyclic MX_5 systems, the bond difference $\Delta(MX_{ap}-MX_{eq})$ rarely exceeds 0.1 Å. In PF_5, having ligands not too different in electronegativity from oxygen atoms, Δ = 0.043 Å. We adopt Δ = 0.065 Å for an acyclic PO_5 TP upon consideration of electron pair repulsion effects of PF relation to PO bonds.

Geometry optimization in an ab initio study of PF_5, performed by Strich and Veillard,[24] gave the following structures for the C_{4v} representation.



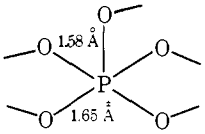
Δ = 0.047 Å

It is noted that the change in bond distances on going to the D_{3h} structure of PF_5, as determined by electron diffraction,[2e] from this C_{4v} representation sums to zero. If we use



Δ = 0.043 Å

the latter criterion with Δ proportionately larger in the SP, than in the TP, for a model PO_5 system III based on the SP

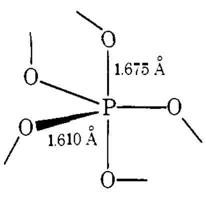


SP

III

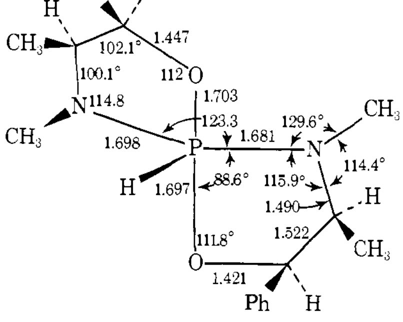
Δ = 0.070 Å

structure I but "adjusted" for residual TP character (and thus giving a PO distance of 1.65 Å), we obtain as the parameterization for the PO_5 TP.



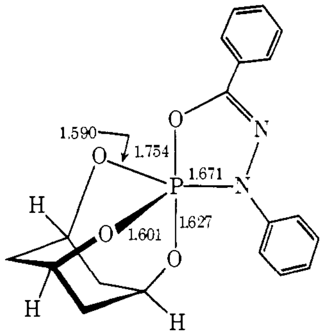
Δ = 0.065 Å

In a recent X-ray structure by Newton et al.[25] on dioxadiazaspirophosphorane IV, representing the first saturated system studied, the PO bond distances, 1.697 and 1.70 Å, provide evidence for the relaxation in strain effects. The ring puckering present in this instance tends to alleviate the ring strain relative to a planar ring system. Most likely some residual strain is present in IV and suggests that the value of 1.675 Å, derived above for the PO apical distance in the acyclic PO_5 moiety, may be a more nearly representative value to use in the absence of steric and electronic factors present in ring systems.



IV

The exocyclic PO distances in IIa and -b which average 1.64 Å (apical) and 1.59 Å (equatorial) are somewhat under the values we suggest as "normal". These lower values, however, are expected. As the PO ring bonds weaken because of ring constraints, electron density concentrates in the remaining PO linkages. This is seen also in the adamantyl derivative[19a] containing a five-membered heterocycle in a distorted TP conformation. The relatively unstrained PO bonds of the adamantyl portion are 1.627 Å (apical) and 1.595 Å (average equatorial) in length.



(distances, Å)

To calculate the ring "strain" energy in the two conformations, bond angle deformations were assumed to follow an elastic potential function

$$E_\alpha = (k/2)(\Delta\alpha)^2$$

A similar expression was assumed for the calculation of the stretching and compression energies required to deform bond lengths from the normal values.

The zero strain angles necessary for the calculation were obtained from data on acyclic compounds. With reference to Figure 1 these are 111.5°[14] for POC ($\alpha_1 = \alpha_4$) and 90°[26] for OPO (β). The value for the CCO angle should approximate 120°. Some variation seems likely in order to reflect the inherent differences in PO bonding in the TP and SP forms. In the SP, the PO σ bonding is intermediate in character between the apical and equatorial positions of a TP. In addition, the presence of a catechol unit leads to a concentration of π bonding in the C=C linkage contained therein. Isomerization of this type of structure to a TP leads to a reduced apical PO bond strength and accompanying enhancement on the equatorial PO bond strength. As a consequence, variations in the CCO network are expected. These are shown schematically in Figure 3.

The resultant CCO angles were chosen as 113° for the SP and 121 and 115° for the apical and equatorial sites of the TP, respectively. The value for the SP was taken to correspond to a tropolone structure[27] having ortho hydroxy groups and which showed similar bond parameters for the various CC and CO linkages as that found in Ia.

One might assign analogous alternatives in the POC bend but this term does not enter in an important way since the angular variations in the different conformations are relatively small.

The corresponding force constants[26,28] were 140 kcal/(mol rad^2) for the POC bend and 95 kcal/(mol rad^2) for

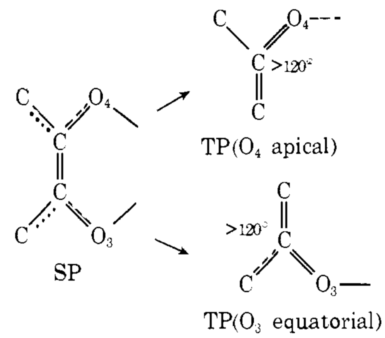
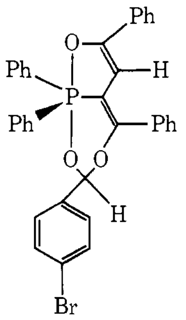


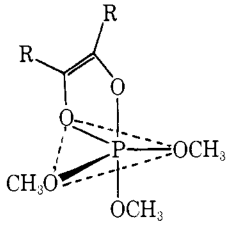
Figure 3. Proposed changes in ring π bonding with isomerization from SP to TP for a catechol pentaoxyphosphorane. Increasing bond strength follows the order: - - - < ··· < —.

the CCO deformations. The OPO angle undergoes sufficiently small variations in the two types of structures that this effect is negligible. The corresponding quantities for bond distance variations following Hooke's law are listed in Table I. The equilibrium PO bond distances assumed have been discussed above. The source of the others are indicated in Table I. The equilibrium ring CO bond distances for the TP, higher (equatorial) and lower (apical) than the SP, are an attempt again to reflect changes expected because of the inherent inequality of equatorial vs. apical bonding in the TP. A normal value of 1.40 Å for a CO linkage in a TP having a low degree of π character (see Figure 3) appears reasonable.

In the saturated derivative IV, for which ring strain should be much reduced, and in the six-membered ring of the bicyclic dioxyphosphorane[7b] the CO distance averages 1.42 Å. Shortening to 1.40 Å was done to account for a small degree of π bonding. In the absence of any other suitable criterion, the sum of the up-down changes from the SP for the CO linkage was taken to be zero. This yielded 1.32 Å for the normal value for the apical CO bond in an unsaturated ring of a TP.



The force constants in Table I for PO bonds were obtained from an analysis of vibrational spectra which we have carried out[29] on TP's closely analogous to II.



R = CH_3, C_6H_5

The skeletal PO stretching vibrations were determined and used in an approximate force constant treatment to obtain the values of k for PO_3 and PO_4. The related PO value for the SP was then estimated by means of Badger's rule.[30]

Table I. Force Constants and Equilibrium Bond Distances for the PO_5 System

Bond	Equilibrium distance, Å	Force constant $k/2$, kcal/(mol Å^2)
PO_3(TP)	1.610	284
PO_4(TP)	1.675	223
PO_1(SP)	1.65	244
PO_2(SP)	1.65	244
CO_4(TP)	1.32[a]	417
CO_3(TP)	1.40[a]	300
CO(SP)	1.36[b]	352
C=C	1.33[b]	692[c]

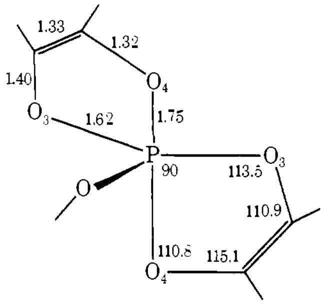
[a] See text. [b] Reference 22 and 27. [c] Based on a frequency assigned[6b] at 1650 cm^{-1} to the five-membered ring C=C bond in IIb (see also ref 15, 16).

Similarly, the force constant for the CO stretch was derived from a characteristic frequency appearing at about 1100 cm^{-1} in a variety of related substances (e.g., cyclic ethers,[22,31] pentacoordinate derivatives,[29,32] and alkoxy phosphates[33]).

Application of Badger's rule,[30] $k(r - c)^3 = 267.7$, provided the variation in k for the different CO distances recorded in Table I. The absolute magnitudes of these force constants are not too important since differences in energy between closely related structures are the quantities of interest in this treatment. Hence, the approximate values listed serve for the present purpose.

Energy Minimization

Relative to the equilibrium parameters suggested above, conformational energies were calculated according to the procedure outlined. Both angle and bond distance variations were investigated. With the apical PO bond distance fixed at 1.75 Å, that observed in II, a conformational minimum was obtained for a TP with the following parameters.



(distances, Å; angles, deg)

This structure compares favorably with ring parameters[6b] for the X-ray structure IIb. Table II shows some representative structures near the minimum along with the calculated conformational energies except structure C which does represent a minimum. It was obtained without any constraints on bond distances.

Discussion

The calculations indicate that ring strain in the spirocyclic oxyphospholenes (TP's) exceeds that in the isomeric SP counterparts by approximately 5 kcal/mol. In the absence of ring constraints, however, the TP is inherently more stable than the SP. In PF_5, for example, recent estimates have yielded 3.0–3.9 kcal/mol[34] for this difference. A similar stabilization for the TP PO_5 moiety might be anticipated. In view of the closeness in electronegativity of the oxygen and fluorine ligands, the analogy might not be too far off. If we adopt the lower value to approximate the acyclic (TP − SP) energy difference in the PO_5 case, the graphical display in Figure 4 results.

Table II. Conformational Energies (kcal/mol)[a]

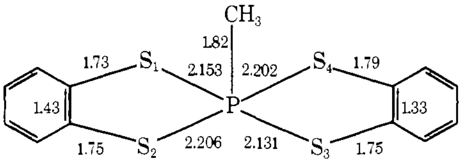
	A	B	C	D	E	F[b]
$r\mathrm{PO}_4$	(1.750)	(1.75)	1.69	(1.75)	(1.75)	1.66
$r\mathrm{PO}_3$	1.622	(1.63)	1.62	(1.63)	(1.63)	1.66
$r\mathrm{CO}_4$	1.316	1.34	1.32	1.353	1.36	1.36
$r\mathrm{CO}_3$	1.400	1.43	1.40	1.383	1.36	1.36
$r\mathrm{CC}$	1.326	1.33	1.33	1.33	1.33	1.33
$\angle\mathrm{OPO}$	(90)	(90)	(90)	(90)	(90)	(90)
$\angle\mathrm{PO_4C}$	110.5	112.5	112.2	111	110	112.9
$\angle\mathrm{CCO_4}$	115.1	112.5	114.7	112.6	113.1	112.1
$\angle\mathrm{CCO_3}$	110.9	112.5	109.5	113.0	112.8	112.1
$\angle\mathrm{PO_3C}$	113.5	112.5	113.7	113.4	114.1	112.9
$\Sigma\alpha$	1.71	2.36	2.25	2.47	2.33	0.22
Σr	2.63	3.61	0.27	3.93	5.03	0.11
E	4.34	5.97	2.52	6.40	7.36	0.33

[a] Distances, Å; angles, deg. Values in parentheses were held constant during energy minimization. [b] This column contains parameters for the minimum energy SP.

The effect of forming one and two rings relative to the acyclic PO_5 system is shown for the TP and SP forms. The energy level scheme indicates, in accord with present knowledge,[2-11] the greater stability of the acyclic and monocyclic TP structure relative to their SP counterparts. When the bicyclic configurations are compared, however, the energy balance is tipped in favor of the SP for the model PO_5 system, again in accord with observations on the structures of I[12a,b] and related members.[12c,35] This conclusion, based on the calculations presented here, largely confirms structural inferences summarized in an earlier paper[1b] about these ring containing derivatives.

Of course, variation in some of the assumed equilibrium parameters shifts the structural minimum so that the lowest energy TP structure may become any one of those listed in Table II. However, if these variations are kept between reasonable limits, the strain energy difference always favors the SP conformation. Most values of this difference lie between 3 and 7 kcal/mol compared to 3-4 kcal/mol we adopt as the "best" range. It is interesting that the rationale resulting in the chosen set of equilibrium parameters led to a minimum energy conformation close to that observed[6] for the dioxaphospholene II. Refinement of the basic parameters will only come as further X-ray structural data are accumulated on related substances. The inclusion of a steric effect associated with the R substituent in I, for example, may well favor the TP.

For PX_5 derivatives containing atoms of reduced electro negativity compared to oxygen, the acyclic SP is predicted[1b] to become less stable relative to the acyclic TP, at least on the basis of a simple repulsion model.[35] The latter is in accord with observations on the structure of the dithiophosphole V.[36] On the basis of the magnitude of the $\mathrm{S_1P\,S_3}$ and $\mathrm{S_2P\,S_4}$ angles, the structure corresponds to about 43% TP character; whereas, the oxaphosphole Ia has 15% TP character.[1b]



angles

$\mathrm{S_1PS_3}$	132.0°
$\mathrm{S_2PS_4}$	158.1
PSC	100.4 (mean)

V

(distances, Å; angles, deg)

However, the ring strain difference between the TP and SP for this case would also be expected to be lowered because of both the presence of longer ring bond distances and reduced force constants for the sulfur linkages. Unfortunately, the necessary structural information is lacking on thio derivatives to allow an estimation of the magnitude of ring strain effects relative to acyclic energy differences for the RPS_4 system similar to that performed on the oxyphosphoranes.

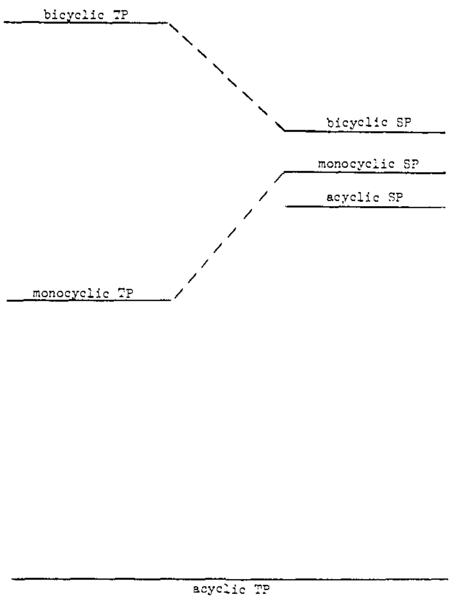
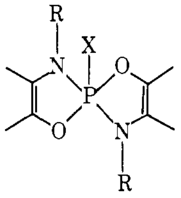


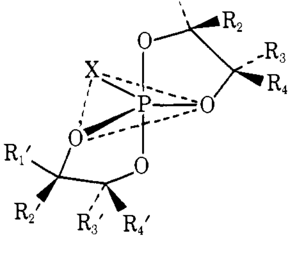
Figure 4. The PO_5 system. Values are in kcal/mol and refer to column A of Table II.

Even for derivatives involving highly electronegative heteroatoms, if these are not identical, for example, in a structure of the type,[37]



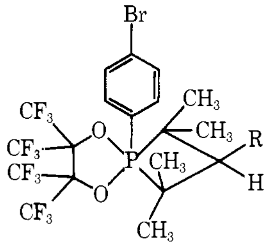
the differential effect of ring strain, favoring the SP, may be largely negated as a result of the presence of two sets of bond properties. In other words, the acyclic energy difference (SP − TP) may increase sufficiently so that ring strain differences become relatively unimportant in determining isomeric conformation. In this respect, the argument is similar to that described for the thio system above. Hence, these structures may closely approximate a TP with the more electronegative atoms apical.

As a further example, derivatives of the type,[37]



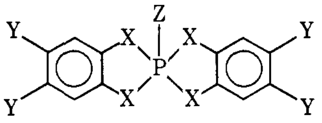
containing saturated ring systems, most likely possess strain differences between the TP and SP conformations sufficiently small that the TP will dominate. We have already noted that this is the case for the diazaspirophosphorane IV.[25] For these derivatives, ring puckering provides an additional means of alleviating ring strain which is considerably less costly in energy than stretching or compressing bonds. In another case, where all four substituents on one ring are methyl groups and all four on the other ring are perfluoromethyl groups, the X-ray structural data are reported[38] to show a TP (X = SPh, p-OC_6H_4Br).[39] Thus, the structural type observed for derivatives containing saturated five-membered rings may be exclusively TP. This tends to correlate with the energy scheme in Figure 4. With saturated rings involving the PO_5 or RPO_4 system, the acyclic SP − TP energy difference is assumed to remain relatively fixed but because of reduced ring constraints, the monocyclic and bicyclic TP levels may easily be lowered below those of the corresponding SP levels.

While attention has been confined to five-coordinate phosphorus derivatives containing two five-membered rings, the presence of four-membered rings should enhance the stabilization experienced by the SP form due to ring strain differences and allow the appearance of the SP for a wider range of ligand electronegativities. Thus the near SP structure[38] of the dioxaphospholane VI is not unexpected.

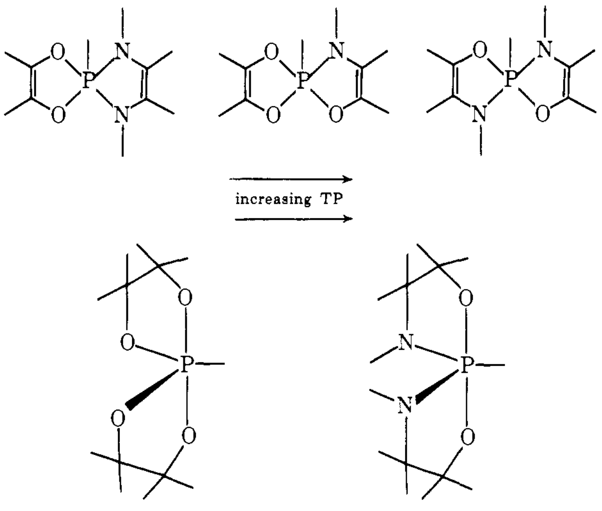


VI, R = H, CH_3

Based on the above, we may summarize the structural consequences of electronic effects and ring constraints in cyclic derivatives of pentacoordinate phosphorus With reference to the general formulation, the SP will be enhanced by electronegative X and Y ligands and electropositive Z groups. Increasing ring saturation and the incorporation of mixed heteroring atoms attached to phosphorus are expected to lend stability to the TP. Similar effects should be encountered with four-membered rings but enhancement of the SP is favored because of amplification of ring strain effects.



X, Y, electronegative; Z, electropositive



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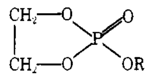
References and Notes

(1) (a) Presented in part at the 168th National Meeting of the American Chemical Society, Division of Inorganic Chemistry, Atlantic City, N.J., Sept 1974, INOR 65; (b) Pentacoordinated Molecules. XX. Previous paper in this series. R. R. Holmes, *J. Am. Chem. Soc.*, **96**, 4143 (1974).
(2) (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).
(3) M. J. C. Hewson, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 190 (1973).
(4) G. Chioccola and J. J. Daly, *J. Chem. Soc. A*, 568 (1968).
(5) P. J. Wheatley, *J. Chem. Soc.*, 2206 (1964).
(6) (a) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967); (b) R. D. Spratley, W. C. Hamilton, and J. Ladell, *ibid.*, **89**, 2272 (1967).
(7) (a) M.-Ul.-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Am. Chem. Soc.*, **93**, 5229 (1971); (b) D. D. Swank, C. N. Caughlin, F. Ramirez, and J. F. Pilot, *ibid.*, **93**, 5236 (1971).
(8) J. W. Cox and E. R. Corey, *Chem. Commun.*, 123 (1967).
(9) A. Almenningen, B. Anderson, and E. E. Astrup, *Acta Chem. Scand.*, **23**, 2179 (1969).
(10) L. G. Hoard and R. A. Jacobson, *J. Chem. Soc. A*, 1203 (1966).
(11) H. Hess and D. Frost, *Z. Anorg. Allg. Chem.*, **342**, 240 (1966).
(12) (a) H. Wunderlich, D. Mootz, R. Schmutzler, and M. Wieber, *Z. Naturforsch., Teil B*, **29**, 32 (1974); (b) H. Wunderlich, *Acta Crystallogr., Sect B*, **30**, 939 (1974); (c) H. Wunderlich and D. Mootz, *Ibid.*, **30**, 935 (1974).
(13) For a recent review on pentacoordination see R. R. Holmes, *Acc. Chem. Res.*, **5**, 296 (1972).
(14) G. E. Wilson, Jr., *J. Am. Chem. Soc.*, **96**, 2426 (1974).
(15) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, p 433.
(16) F. H. Westheimer in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, p 523.
(17) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).
(18) N. L. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *J. Am. Chem. Soc.*, **89**, 4345 (1967).
(19) (a) W. C. Hamilton, J. S. Ricci, Jr., F. Ramirez, L. Kramer, and P. Stern, *J. Am. Chem. Soc.*, **95**, 6335 (1973); (b) F. P. Boer, J. J. Flynn, and J. W. Turley, *ibid.*, **90**, 6973 (1968); (c) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *ibid.*, **91**, 6301 (1969).
(20) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).
(21) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
(22) O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, Ed., "Molecular Structures and Dimensions", Vol. A1, International Union of Crystallography, 1972.
(23) If the edge 1–5 is called the apical bond of the TP, then the argument just presented yields the effect on shortening the apical bond relative to the equatorial bond. The latter case is sometimes observed in transition metal pentacoordination. See J. S. Wood, *Prog. Inorg. Chem.*, **16**, 227 (1972), for a recent review of these complexes.
(24) A. Strich and A. Veillard, *J. Am. Chem. Soc.*, **95**, 5574 (1973).
(25) M. G. Newton, J. E. Collier, and R. Wolf, *J. Am. Chem. Soc.*, **96**, 6888 (1974).
(26) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 2320 (1965).
(27) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London, 1958, and Supplement, 1965.
(28) T. Shimanouchi, M. Tsuboi, and Y. Kyogoku, *Adv. Chem. Phys.*, **7**, 435 (1964).
(29) R. R. Holmes and L. S. Couch, unpublished work.
(30) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).
(31) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, N.Y., 1962, p 119.
(32) L. C. Thomas, "Interpretation of the Infrared Spectra of Organophosphorus Compounds", Heyden and Son, New York, N.Y., 1974.
(33) J. R. Durig and J. W. Clark, *J. Chem. Phys.*, **50**, 107 (1969).
(34) (a) R. R. Holmes, L. S. Couch, and C. J. Hora, Jr., *J. Chem. Soc., Chem. Commun.*, 175 (1974); (b) L. S. Bernstein, J. J. Kim, K. S. Pitzer, S. Abramowitz, and I. W. Levin, Thirtieth Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June, 1975, Abstract TA6, and private communication.
(35) R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *Can. J. Chem.*, **38**, 818 (1960); *J. Chem. Educ.*, **40**, 295 (1963).
(36) M. Eisenhut, R. Schmutzler, and W. S. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 144 (1973).

(37) (a) D. Hellwinkel, "Organo Phosphorus Compounds", Vol. 3, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, p 185; (b) R. Luckenbach, "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements", Georg Thieme Publishing Co., Stuttgart, 1973.

(38) J. A. Howard, D. R. Russell, and S. Trippett, *J. Chem. Soc., Chem. Commun.*, 856 (1973).

(39) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 2320 (1965), showed that the rapid hydrolysis of the monocyclic ester,



relative to its acyclic analog is explicable largely by a reduction in ring strain experienced by the cyclic ester on going to a pentacoordinate transition state with a preferred O–P–O angle of 90°. Consistent with our discussion, these results suggest that the difference in the acyclic TP level and monocyclic TP level shown in Figure 4 becomes compressed when dealing with saturated ring systems.

Effect of Extraplanar Ligands on the Redox Properties and the Site of Oxidation in Iron, Ruthenium, and Osmium Porphyrin Complexes

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Abstract: The redox properties of the complex Os(OEP)(CO)(py) (OEP^{2-} is the octaethylporphyrin dianion and py is pyridine) and related complexes of iron have been investigated in dichloromethane using electrochemical techniques. The osmium complex undergoes two electrochemically reversible oxidations. From spectral studies, the site of the first oxidation is at the osmium ion in contrast to related complexes of ruthenium where the first oxidation is at the porphyrin ring. Oxidation of the complex Fe(Etio I)(CO)(Im) (Etio I^{2-} is the etioporphyrin I dianion and Im is imidazole), which was prepared in situ, occurs at a potential ~0.6 V higher than for oxidation of the analogous bisimidazole complex. Oxidation of Fe(Etio I)(CO)(Im) apparently also occurs at the central metal ion. The effect of CO as an extraplanar ligand in the iron, ruthenium, and osmium porphyrin complexes is discussed in terms of strong back-bonding with metal orbitals of dπ symmetry. In agreement with available crystallographic evidence, it is concluded that in the carbonyl complexes there is a significant tetragonal distortion. The variable site of oxidation in the porphyrin complexes is an example of an oxidation state isomerism in which the isomers differ with regard to the site of oxidation. Possible implications of the redox properties of the synthetic porphyrin–CO complexes for heme-based redox processes are discussed.

There have been few systematic studies of the effects of extraplanar ligands on the redox properties of metalloporphyrins.[1-3] We recently reported that changes in the extraplanar ligands can change not only reduction potentials but also the site of oxidation in ruthenium(II) porphyrins.[4] When pyridine occupies the extraplanar sites, oxidation occurs at the ruthenium ion. If CO is one of the extraplanar ligands, the site of oxidation is at the porphyrin ring.

The change in the site of oxidation with change in the extraplanar ligand is an interesting chemical problem. Qualitatively, the change has been explained in the ruthenium porphyrin complexes by stronger back-bonding to CO compared to pyridine. With strong back-bonding, the metal orbitals of dπ symmetry are lowered in energy below the porphyrin π levels which then become the valence MO's of the system.

It is a question of some interest in the metalloporphyrins as to whether or not the site of oxidation can be varied in a systematic way by synthetic modifications. In addition to variations in the extraplanar ligands it is possible to vary the central metal ion. The preparation of carbonyl complexes of osmium(II) octaethylporphyrin has been described by Buchler and coworkers,[5] and related complexes of iron have been characterized in solution. In the present paper we compare the redox properties of several iron, ruthenium, and osmium porphyrins with different ligands in the fifth and sixth coordination sites.

Experimental Section[6]

Measurements. Ultraviolet-visible spectra were obtained on a Cary Model 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. All electrochemical measurements were vs. the saturated sodium chloride calomel electrode (SSCE) at 25 ± 2° and are uncorrected for junction potentials. Electrochemical measurements were made on an instrument previously described,[7] or a PAR Model 173 potentiostat was used for potential control with PAR Model 175 Universal Programmer as a sweep generator for voltammetric experiments. Values of n, where n is the total number of electrons transferred in exhaustive electrolyses at constant potential, were calculated after measuring the total areas under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen below 1% of its initial value. All voltammetric measurements were carried out at platinum electrodes. Electrochemical reversibility was determined, where possible, from plots of log $(i_l - i)/i$ vs. E from stirred solution voltammetry. In some cases reversibility was determined by cyclic voltammetry. In a cyclic voltammetry experiment, reversibility was based on the ratio of anodic to cathodic peak currents (i_c/i_a) and the potential separation of the peaks (ΔE_p). The ratio i_c/i_a was usually ~1.0, but ΔE_p (~70 mV) was higher than the theoretical value of 59 mV. The higher values most likely arise because of uncompensated solution resistance. Couples like ferrocene-ferricennium, which are known to be reversible, gave similar ΔE_p values in the same medium indicating that the $E_{1/2}$ values cited here are an accurate measurement of reduction potentials except for a usually negligible term involving the ratio of diffusion coefficients.

Materials. Tetra(n-butyl)ammonium hexafluorophosphate was prepared by standard techniques,[8] recrystallized three times from hot ethanol-water mixtures, and vacuum dried at 80° for 12 hr. A sample of Os^{II}(OEP)(CO)(py) was kindly provided by Professor J. W. Buchler. Fe^{III}(Etio I)Cl was prepared by the method of Adler et al.[9] from FeCl$_2 \cdot n$H$_2$O and etioporphyrin I.[10] Dichloromethane (Fisher "Spectroanalyzed") was used without further purification. Imidazole (Aldrich) was recrystallized from dichlomethane and

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