CONFORMATIONAL ENERGY CALCULATIONS ON FIVE-MEMBERED RINGS IN PENTACOORDINATE PHOSPHORUS

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# CONFORMATIONAL ENERGY CALCULATIONS ON FIVE-MEMBERED RINGS IN PENTACOORDINATE PHOSPHORUS[1]

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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

I, R = CH₃, F
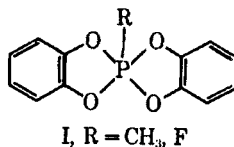
approximating the SP prompts an examination of the conformational requirements of small membered rings in each of the two idealized environments to ascertain if they are sufficiently different to preferentially stabilize the SP form.

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 environment. 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.

In the usual calculation of conformational energies of ring systems, bond distances

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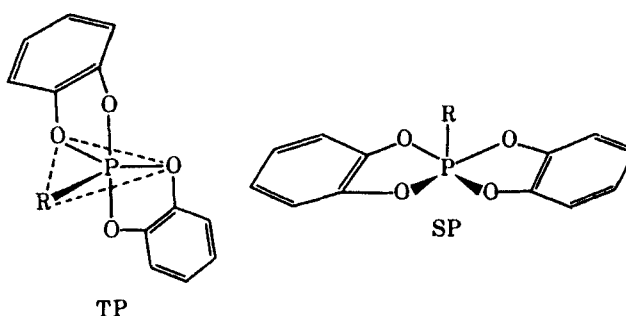
are frequently held constant as a first approximation with energy minima determined by torsional distortions, angle bending, and van der Waals interactions.[14-18] We will see that bond distance variations enter as a more important term for five-coordinate phosphorus containing planar ring systems. This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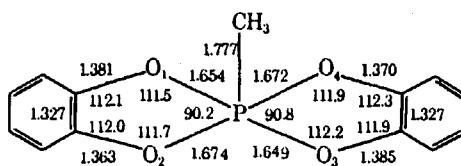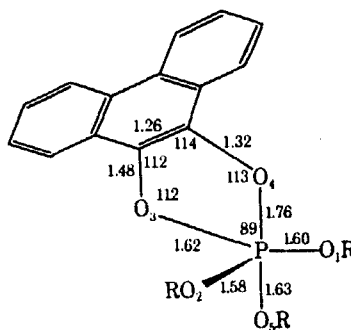
RING STRAIN REQUIREMENTS IN A TP VS. A SP

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 apical-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

CH$_3$

1.777

1.381 O$_1$ 1.654 1.672 O$_4$ 1.370

112.1 111.5   111.9 112.3

1.327   1.327

90.2 P 90.8

112.0 111.7   112.2 111.9

1.363 O$_2$ 1.674 1.649 O$_3$ 1.385

Ia (from ref 12b)

1.26

114 1.32

1.48 112 113 O$_4$

112 1.76

O$_3$

89 1.60

1.62 P O$_1$R

RO$_2$ 1.58 1.63

O$_5$R

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

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]

Examination of the X-ray parameters for the two forms of the oxyphosphorane
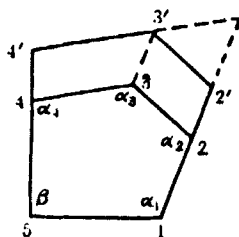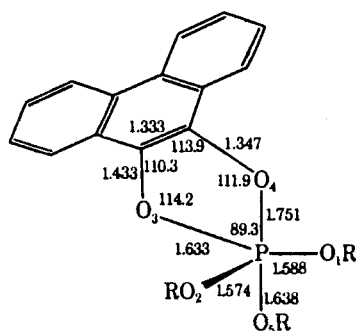
FIGURE 1 The effect of increasing the length of edge 4–5 relative to edge 1–5 on the remaining sides of the pentagon with the length of edge 2–3 held fixed.

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

II^6 shows that the five-membered ring structures largely conform to these geo-
metrical 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.

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 V_1, V_2, and V_3. Their sum is V_4. In terms of unit vector
notation $V_1 = a_1 i + b_1 j$, etc., the conditions prevail

$$a_1 + a_2 + a_3 = |V_4| \tag{1}$$

$$b_1 + b_2 + b_3 = 0 \tag{2}$$

Using the magnitudes of the vectors ($|V_1| = k$, $|V_2| = 1$, and $|V_3| = m$) 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
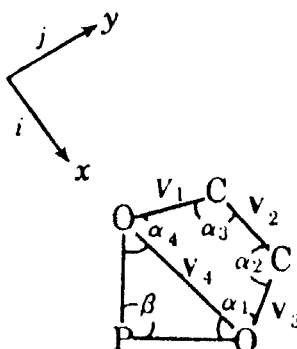

FIGURE 2   Coordinate description for five-membered phospholene ring system.

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 structure for the C_{4v} representation.

$$\Delta = 0.047 \text{ Å}$$
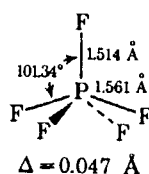
It is noted that the change in bond distances on going to the D_{3h} structure of PF_5, as determined by electron diffraction,[2c] from this C_{4v} representation sums to zero. If we use the latter criterion with Δ proportionately larger in the SP, than in the

$$\Delta = 0.043 \text{ Å}$$
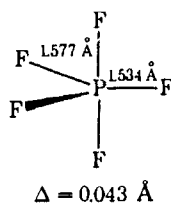
TP, for a model PO_5 system III based on the SP structure I but "adjusted" for residual TP character (and thus giving a PO distance of 1.65 Å), we obtain as the parameterization for the PO_5 TP.

$$\Delta = 0.065 \text{ Å}$$
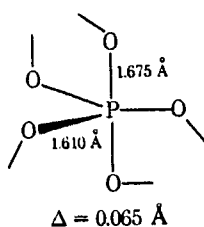
In a recent X-ray structure by Newton *et al.*[25] on dioxadiazaspirophosphorane IV, representing the first saturated system studied, the PO bond distances, 1.697

SP

III

$$\Delta = 0.070 \text{ Å}$$
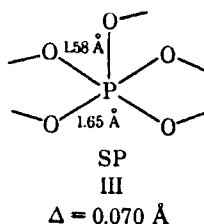
and 1.70 Å, provide evidence for the relaxation in strain effects. The ring puckering present in this instance tends to alleviate the ring strain relative to a planar ring system. Most likely some residual strain is present in IV and suggests that the value of 1.675 Å, derived above for the PO apical 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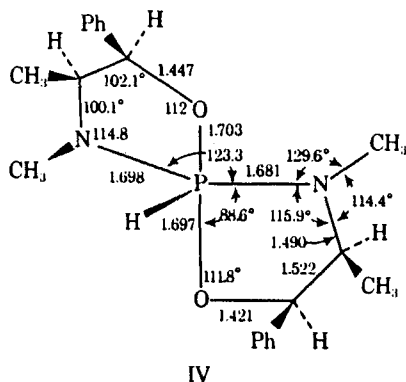 "normal." These lower values, however, are expected. As the PO ring bonds weaken because of ring constraints, electron density concentrates in the remaining PO linkages. This is seen also in the adamantyl derivative[19a] containing a five-membered heterocycle in a distorted TP conformation. The relatively unstrained PO bonds of the adamantyl portion are 1.627 Å (apical) and 1.595 Å (average equatorial) in length.

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.

(distances, Å)
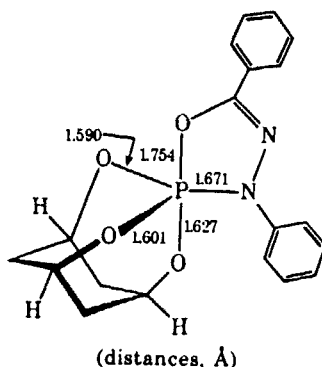
The zero strain angles necessary for the calculation were obtained from data on acyclic compounds. With reference to Figure 1 these are $111.5°^{14}$ for POC ($\alpha_1 = \alpha_4$) and $90°^{26}$ for OPO (β). The value for the CCO angle should approximate $120°$. Some variation seems likely in order 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.
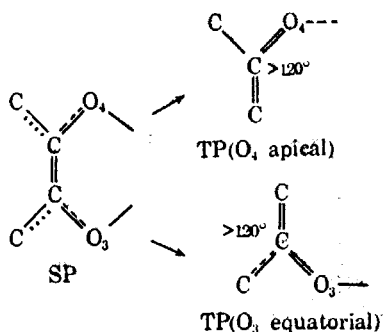

FIGURE 3   Proposed changes in ring π bonding with isomerization from SP to TP for a catechol pentaoxyphosphorane. Increasing bond strength follows the order: --- < ··· < —

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The corresponding force constants[26,28] were 140 kcal/(mol rad^2) for the POC bend and 95 kcal/(mol rad^2) for the CCO deformations. The OPO angle undergoes sufficiently small variations in the two types of structures that this effect is negligble. 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.
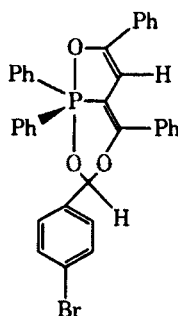
In the saturated derivative IV, for which ring strain should be much reduced, and in the six-membered ring of the bicyclic dioxyphosphorane[7b] the CO distance averages 1.42 Å. Shortening to 1.40 Å was done to account for a small degree of π bonding. In the absence of any other suitable criterion, the 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.

$R = CH_3, C_6H_5$
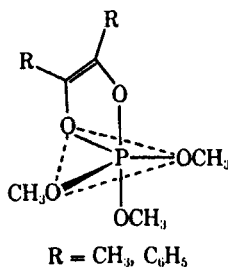
The force constants in Table I for PO bonds were obtained from an analysis of vibrational spectra which we have carried out[29] on TP's closely analogous to II. The skeletal PO stretching vibrations were determined and used in an approximate force constant treatment to obtain the values of k for PO_3 and PO_4. The related PO value for the SP was then estimated by means of Badger's rule.[30] 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]).

TABLE I

Force constants and equilibrium bond distances for the PO_5 system

Bond	Equilibrium distance, Å	Force constant $k/2$, kcal/(mol Å²)
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).

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. This structure compares favorably with ring parameters[6b]

(distances, Å; angles, deg)
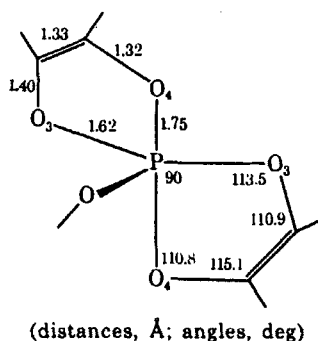
for the X-ray structure IIb. Table II shows some representative structures near the minimum along with the calculated conformational energies except structure C which does represent a minimum. It was obtained without any constraints on bond distances.

TABLE II

Conformational energies (kcal/mol)[a]

	A	B	C	D	E	F[b]
rPO$_4$	(1.750)	(1.75)	1.69	(1.75)	(1.75)	1.66
rPO$_3$	1.622	(1.63)	1.62	(1.63)	(1.63)	1.66
rCO$_4$	1.316	1.34	1.32	1.353	1.36	1.36
rCO$_3$	1.400	1.43	1.40	1.383	1.36	1.36
rCC	1.326	1.33	1.33	1.33	1.33	1.33
$\angle$OPO	(90)	(90)	(90)	(90)	(90)	(90)
$\angle$PO$_4$C	110.5	112.5	112.2	111	110	112.9
$\angle$CCO$_4$	115.1	112.5	114.7	112.6	113.1	112.1
$\angle$CCO$_3$	110.9	112.5	109.5	113.0	112.8	112.1
$\angle$PO$_3$C	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, A; angles, deg. Values in parentheses were held constant during energy minimization. [b] This column contains parameters for the minimum energy SP.

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.

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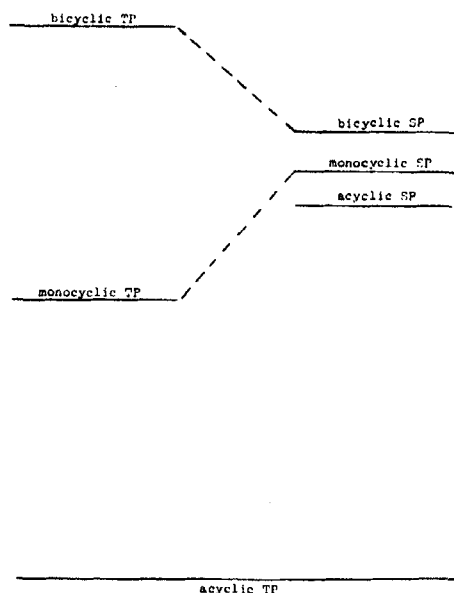
FIGURE 4   The PO_5 system. Values are in kcal/mol and refer to column A of Table II.

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 electronegativity 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 $S_1P\ S_3$ and $S_2P\ S_4$ angles, the structure corresponds to about 43% TP character; whereas, the oxaphosphole Ia has 15% TP character.[1b]

angles

S_1PS_3 132.0°
S_2PS_4 158.1
$P\overset{\cdot}{S}C$ 100.4 (mean)

V

(distances, Å; angles, deg)
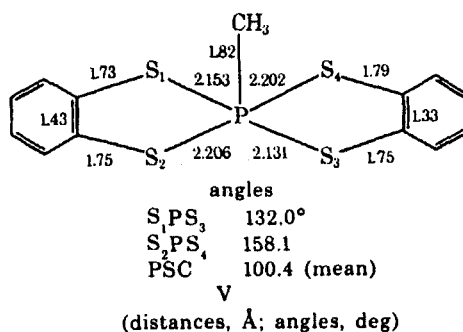
However, the ring strain difference between the TP and SP for this case would also be expected to be lowered because of both the presence of longer ring bond distances and reduced force constants for the sulfur linkages. Unfortunately, the

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.

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
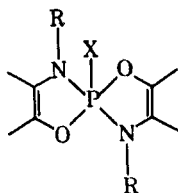

ring strain, favoring the SP, may be largely negated as a result of the presence of two sets of bond properties. In other words, the acyclic energy difference (SP − TP) may increase sufficiently so that ring strain differences become relatively unimportant in determining isomeric conformation. In this 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,
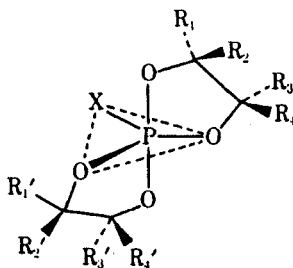
most likely possess strain differences between the TP and SP conformations sufficiently small that the TP will dominate. We have already noted that this is the case for the diazaspirophosphorane IV.[25] For these derivatives, ring puckering provides an additional means of alleviating ring strain which 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.
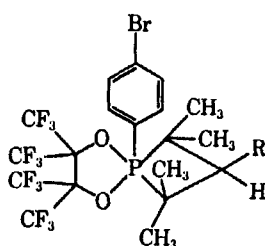
VI, R = H, CH₃

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
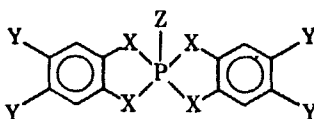
X, Y, electronegative; Z, electropositive

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.
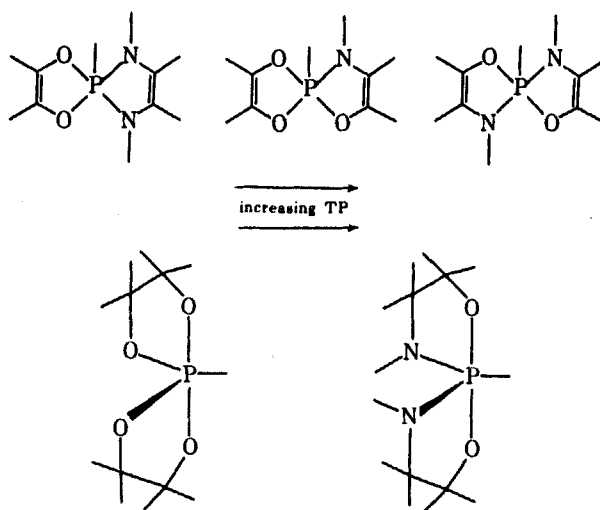

increasing TP

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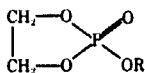
by a reduction in ring strain experienced by the cyclic ester on going to a pentacoordinate transition state with a preferred O—P—O angle of 90°. Consistent with our discussion, these results suggest that the difference in the acyclic TP level and monocyclic TP level shown in Figure 4 becomes compressed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