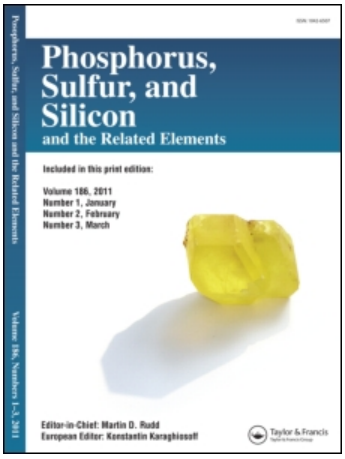

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AB INITIO TREATMENT OF A PHOSPHORUS COORDINATE, TRIGONAL BIPYRAMIDAL TO PENTAFLUORIDE-PYRIDINE REACTION SQUARE PYRAMIDAL TO OCTAHEDRAL

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AB INITIO TREATMENT OF A PHOSPHORUS PENTAFLUORIDE-PYRIDINE REACTION COORDINATE, TRIGONAL BIPYRAMIDAL TO SQUARE PYRAMIDAL TO OCTAHEDRAL[1,*]

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Ab initio calculations of the interaction of pyridine with PF_5 show that the initial trigonal bipyramidal geometry isomerizes to a square pyramid before forming an octahedron as pyridine enters the coordination sphere. The calculated reaction trajectory mimics that found for sulfur donor actions in cyclic pentaoxyphosphoranes where X-ray studies show a range of geometries toward increasing octahedral character from a square pyramid as the P-S interaction increases. It is concluded that inclusion of the donor atom as part of a cyclic system does not control the observed geometrical changes on going from five- to six-coordinate phosphorus.

Keywords: Reaction coordinate; *ab initio*; phosphorus pentafluoride; donor action; hexacoordinate

INTRODUCTION

Recently, we have carried out X-ray studies and demonstrated that sulfur donor atom interaction at phosphorus in cyclic pentaoxyphosphoranes forms a graded series of geometrical changes from a square pyramid to an octahedron as the coordination number increases from five to six,[3-7a,b] Table I. In this series, the P-S distance varies from 3.041(3)Å to 2.362(2)Å in forming the octahedron.[3,7a] For example, in the tris-trifluoroethoxy derivative **1e**[3] the shortest P-S distance of 2.362(2)Å in the series, the structure is estimated to be 69.4% displaced from an ideal square pyramid toward an octahedron. This distance compares with

* Dedicated to Professor Robert Wolf on the occasion of his 70th birthday.

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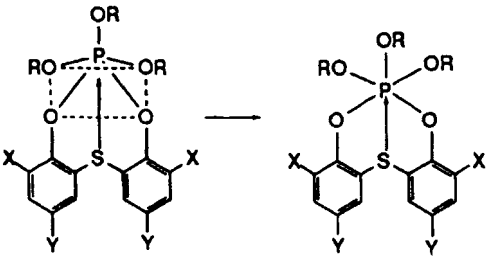
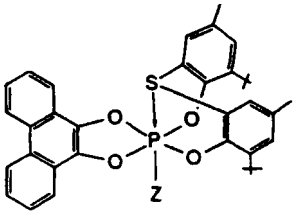
TABLE I Selected Parameters for Pentaoxyphosphoranes with Sulfur and Sulfonyl Containing Eight-Membered Rings



No [a]	*X*	*Y*	*R*	*% octa.* [b]	*P-S, Å*
1a[4]	Me	Me	Ph	44.1	2.880(1)
1b[4]	*t*-Bu	Me	Ph	56.8	2.744(2)
1c[4]	*t*-Bu	*t*-Bu	Ph	60.8	2.640(2)
1d[6]	*t*-Bu	*t*-Bu	CH_2CH_3	64.5	2.504(3)
1e[3]	*t*-Bu	Me	CH_2CF_3	69.4	2.362(2)



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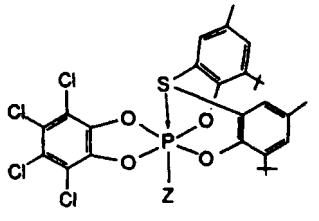


3

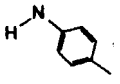
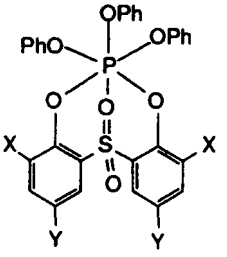
No. [c]	Z	% octa [b]	P–S, Å
2a		23.8	3.041(3)
3a	Me_2N	37.1	2.731(2)
3b		47.4	2.665(2)
2b	Cl	62.9	2.581(2)
3c	Cl	70.8	2.479(2)

TABLE I (continued)



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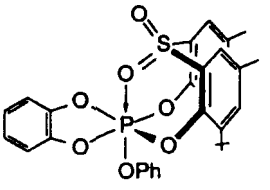


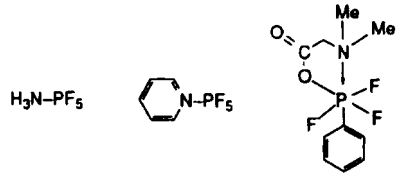
5

No [d]	*X*	*Y*	*% Octa.* [b]	*P-O, Å*
4a	*t*-Bu	*t*-Bu	39.6	2.546(7)
4b	*t*-Bu	Me	44.5	2.487(3)
5	*t*-Bu	Me	55.1	2.607(5)

[a] Reference numbers are shown as superscripts.
[b] Percent displacement from an ideal square pyramid to an octahedron.
[c] The reference for this set of sulfur derivatives is 7a.
[d] The reference for this set of sulfonyl derivatives is 7c.

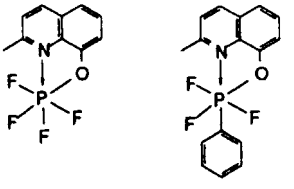
2.14Å for the sum of the covalent radii. In a similar fashion, we have found that the use of a sulfonyl group in place of sulfur induces P-O coordination to give octahedral geometries, Table I. For the three compounds studied by X-ray diffraction,[7c] the P-O donor distances vary from 2.607(5)Å to 2.487(3)Å. This range compares with 1.83Å for the sum of the covalent radii and 3.35Å for the sum of the van der Waals' radii.

The present paper concerns an *ab initio* calculation designed to ascertain whether this type of isomerization coordinate would persist in the absence of ring constraints. The PF_5-pyridine system was chosen as it contains electronegative ligands comparable to those in the phosphorane series whose structures were determined by X-ray crystallography. Although a nitrogen donor atom is present rather than a sulfur atom, energy minimization would allow comparison with the known structure of the PF_5-Py adduct.[8] Pyridine is a good choice from a calculational standpoint as it is a planar rigid entity which results in a reduction in computational time that otherwise might prevail. There also exist some related hexacoordinated phosphorus structures containing P-N bonds involving P-F moieties for comparison. Among these are ammonia-PF_5,[9] 2-(N,N-dimethylamino) acetoxyphenyltrifluorophosphate, $(Me_2NCH_2CO_2)PhPF_3$(6),[10] and the related 2-methyl-8-hydroxyquinoline substituted fluorophosphoranes, $(C_{10}H_8NO)PF_4$ (7)[11a] and $(C_{10}H_8NO)PhPF_3$(8).[11b,12]



P–N, Å 1.842(2) 1.885(4) 2.013(4)

6

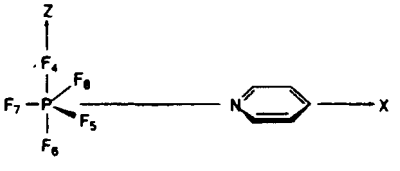


P–N, Å 1.911(4) 1.980(3)

7 **8**

COMPUTATIONAL METHOD

The geometry of each pentacoordinated phosphorus species was fully optimized. Optimization was done as a function of distance as the nitrogen atom of pyridine approached the phosphorus center incrementally along the X axis from beyond the Van der Waals distance to the completely minimized structure.



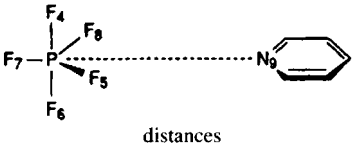
Initially, the axial fluorine atoms, F_4 and F_6, were placed in the XZ plane. They were not fixed but remained there throughout the calculations. It did not matter whether the pyridine ring was held symmetrical about the X-axis or not. However, holding it there reduced computational time. The ring was free to rotate as the P-N distance was shortened. Finally, the P-N distance constraint was removed so that a minimum energy geometry of the adduct could be obtained. Optimization of PF_5 and pyridine was carried out at an infinite P-N distance and also at the P-N distance determined by X-ray crystallography.[8] Calculations were carried out with the program GAUSSIAN 92[13] at the San Diego Supercomputer Center on the Cray C90. The basis set was 6-31G* (split-level valence with

polarization functions on non-hydrogen atoms). Single point calculations (6-31G*) were done at each point of the reaction coordinate to estimate the basis set superposition error, BSSE. At the minimum energy geometry, electron correlation energies were calculated at MP2/6-31G*//6-31G* and at MP3/6-31G*//6-31G* levels.

RESULTS

Table II lists minimum relative energies and bond parameters as a function of the distance of approach between donor and acceptor atoms in the Py-PF_5 system. Figure 1 shows the structural changes encountered along this reaction coordinate. Table III compares the unrestrained minimum energy geometry obtained from the *ab initio* treatment of Py-PF_5 with that from the X-ray study by Sheldrick.[8]

TABLE II Minimum Energies (kcal/mol), Distances (Å), Angles (deg), Atom Charges, and Mulliken Overlap Populations as a Function of P-N Distance (Å) in Py-PF_5.[a]



distances

P–N	∞	*6.000*	*5.000*	*4.000*	*3.000*	*2.500*	*2.200*	*1.937*[d]	*1.885*[e]
P-F_4	1.568	1.568	1.568	1.569	1.564	1.565	1.576	1.590	1.593
P-F_5	1.535	1.534	1.534	1.534	1.551	1.565	1.576	1.590	1.593
P-F_6	1.568	1.568	1.568	1.569	1.564	1.565	1.576	1.590	1.593
P-F_7	1.535	1.536	1.536	1.537	1.531	1.539	1.551	1.564	1.567
P-F_8	1.535	1.534	1.534	1.534	1.551	1.565	1.576	1.590	1.593
				angles					
F_4-P-F_5	90.0	90.0	90.0	89.9	88.3	88.5	89.5	90.0	90.0
F_4-P-F_6	180.0	180.0	180.0	179.6	168.6	162.5	167.8	173.0	174.0
F_4-P-F_7	90.0	90.0	90.0	90.2	95.7	98.8	96.1	93.5	93.0
F_4-P-F_8	90.0	90.0	90.0	89.9	88.3	88.5	89.2	89.6	89.7
F_5-P-F_6	90.0	90.0	90.0	89.9	88.3	88.8	89.2	89.6	89.6
F_5-P-F_7	120.0	119.7	119.5	118.5	107.2	98.7	96.1	93.5	93.0
F_5-P-F_8	120.0	120.5	121.1	123.0	145.6	162.5	167.8	173.0	174.0
F_6-P-F_7	90.0	90.0	90.0	90.2	95.7	98.8	96.1	93.5	93.0
F_6-P-F_8	90.0	90.0	90.0	90.9	88.3	88.8	89.5	90.0	90.0
F_7-P-F_8	120.0	119.7	119.5	118.5	107.2	98.7	96.1	93.5	93.0
dihedral angle [b,c]	---	0.6	80.8	89.9	90.1	45.0	44.9	44.9	44.9

TABLE II Continued[a]

- energies[f]	0.0	*0.3*	*0.7*	*2.4*	*5.0*	*10.3*	*15.7*	*19.7*[g]	*19.4*
BSSE[h]	0.0	0.0	0.0	0.3	1.5	3.0	4.1	5.1	5.3
BSSE[i]	0.0	0.0	0.1	0.5	0.9	1.1	1.4	1.7	1.8
energy corrected for BSSE	0.0	0.3	0.6	1.6	2.6	6.2	10.2	12.9	12.3
					atom charge, q				
P–N	∞	*6.000*	*5.000*	*4.000*	*3.000*	*2.500*	*2.200*	*1.937*[d]	*1.885*[e]
P	1.942	1.943	1.944	1.946	1.977	2.006	2.013	1.985	1.970
F_4, F_6	–0.419	–0.420	–0.420	–0.421	–0.415	–0.418	–0.433	–0.453	–0.457
F_5, F_8	–0.368	–0.367	–0.367	–0.368	–0.394	–0.418	–0.433	–0.453	–0.457
F_7	–0.368	–0.370	–0.372	–0.374	–0.378	–0.387	–0.401	–0.414	–0.417
N_9	–0.515	–0.518	–0.522	–0.533	–0.604	–0.687	–0.731	–0.717	–0.704
					Mulliken overlap population				
P-F_4, P-F_6	0.320	0.319	0.319	0.319	0.323	0.314	0.311	0.307	0.305
P-F_5, P-F_8	0.335	0.336	0.336	0.333	0.317	0.314	0.311	0.307	0.305
P-F_7	0.335	0.335	0.334	0.334	0.344	0.345	0.342	0.340	0.340
P-N_9	---	1.1x 10^{-5}	6.6x 10^{-4}	0.008	0.036	0.067	0.098	0.152	0.171

[a] Basis set 6-31G*.
[b] Dihedral angle of the pyridine plane to the plane F_4-P-F_6. N_9 and F_7 remain along the bonding axis throughout the calculations.
[c] In the X-ray study of Py-PF_5, this dihedral angle is 49.2°.[8]
[d] This column lists the bond parameters for the minimum energy geometry.
[e] This columns lists the bond parameters for the minimum energy geometry obtained with the P-N distance set equal to the X-ray value.
[f] E(py–PF_5) – E(PF_5) + E(py) where E = E(RHF).
[g] The total energy including the contribution of electron correlation effects was estimated by carrying out the following single point calculations at 1.937Å: MP 2/6-31G*//6/31G* and MP3/6-31G*//6-31G*. These values are –30.1 kcal/mol and –28.8 kcal/mol, respectively.
[h] Single point calculation of PF_5 with pyridine atoms as ghost atoms compared to single point calculation of PF_5 only.
[i] Single point calculation of Py with PF_5 as ghost atoms compared to single point calculation of Py only.

DISCUSSION

As apparent in Figure 1 (top) and Table II, when the nitrogen atom is at an infinite distance from phosphorus, the geometry of PF_5 is that of an unperturbed trigonal bipyramid (TBP). In fact, excellent agreement results on comparing the *ab initio* geometry with that obtained by Hansen and Bartell[14] from an electron diffraction study of PF_5. The P-F_{eq} and P-F_{ax} bond distances from the latter study are 1.534Å and 1.577Å which compares with the calculated values of

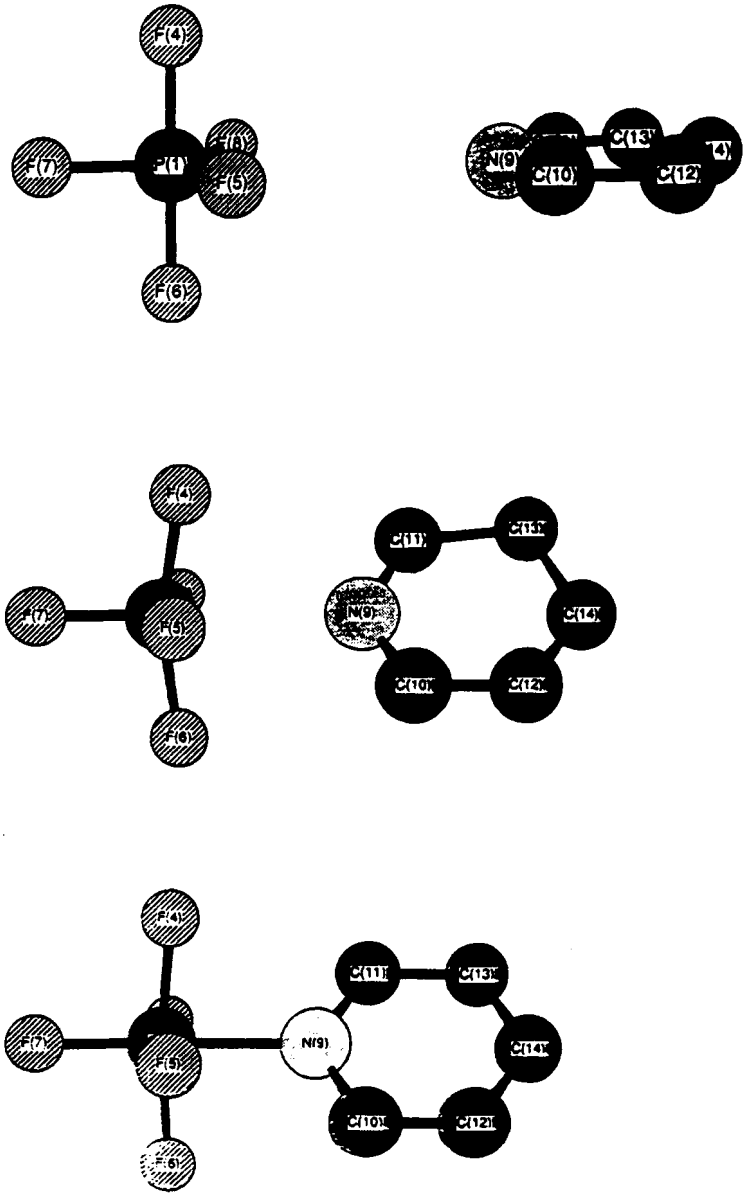
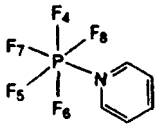


FIGURE 1 Calculated geometries for the pyridine-PF_5 system at 4.0Å (top), 2.5Å (middle), and 1.937Å (bottom)

TABLE III Comparison of Distances (Å) and Angles (deg) for Py-PF_5 from the *Ab Initio* and X-Ray Studies



	distances	
	ab initio	X-ray[a]
P-N	1.937	1.885(4)
P-F_4	1.590	1.586(4)
P-F_5	1.590	1.592(4)
P-F_6	1.590	1.588(4)
P-F_7	1.564	1.582(3)
P-F_8	1.590	1.589(4)
	angles	
F_4-P-F_5	90.0	
F_4-P-F_6	173.0	
F_4-P-F_7	93.5	91.7(2)
F_4-P-F_8	89.6	
F_5-P-F_6	89.6	
F_5-P-F_7	93.5	91.8(2)
F_5-P-F_8	173.0	
F_6-P-F_7	93.5	91.7(2)
F_6-P-F_8	90.0	
F_7-P-F_8	93.5	92.1(2)
F_4-P-N_9	86.5	88.6(2)
F_5-P-N_9	86.5	87.9(2)
F_6-P-N_9	86.5	87.9(2)
F_7-P-N_9	180.0	
F_8-P-N_9	86.5	88.2(2)

[a] Ref. 8.

1.535Å and 1.568Å, respectively, reported in Table II. In line with the longer axial P-F_{ax} bond distance, the overlap population is smaller and the axial fluorine atoms exhibit higher negative charges compared to these quantities for P-F_{eq} bonds (Table II).

Minimal change in geometry is noted until the nitrogen atom is at 3Å from phosphorus, Table II. At this distance, a significant interaction is present which causes an opening of the equatorial angle F_5-P-F_8 to 145.6°and a closing down of the axial angle F_4-P-F_6 to 168.6°. Square pyramidal formation is taking place via

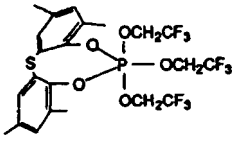
a Berry pseudorotational process[15] commonly invoked for intramolecular ligand exchange phenomena observed by solution NMR data.[16-18] From 5.0Å to 2.5Å, the pyridine molecule moves into the F_5-P-F_8 equatorial plane as seen from the nearly 90° dihedral angle between the pyridine plane and the F_4-P-F_6 axial plane.

More dramatic changes occur at a P-N distance of 2.5Å. Here, the geometry is a perfect square pyramid with the "axial" F_4-P-F_6 and "equatorial" F_5-P-F_8 angles equal to each other at 162.5°. Concurrently, four similar associated basal P-F distances at 1.565Å are present along with a shorter apical P-F distance at 1.539Å, Figure 1 (middle). At this distance, the P-N overlap population experiences a sizeable increase and the nitrogen atom charge becomes more negative. It is interesting to note that use of the semiempirical MNDO/3 method allows equatorial attack of a hydride ion on PH_5 to give a minimum energy path in forming PH_6^- that provides for a slight distortion of the TBP geometry (D_{3h}) towards the square pyramid (C_{2v}) in the early stage of the reaction coordinate (~ 3Å vs a final P-H distance of 1.51).[19] Here, the equatorial angle has opened to 124° while the axial angle has closed to 166°.

Proceeding to the unconstrained energy minimization, which occurs at a P-N distance of 1.937Å, the geometry becomes nearly octahedral with an increase in all P-F distances from the geometry at a P-N distance of 2.5Å, Figure 1 (bottom). The F_4-P-F_6 and F_5-P-F_8 angles, formerly the axial and equatorial angles in the initial TBP, are equal at 173.0°. The average P-F bond distance has increased from 1.548Å in the TBP to 1.585Å for the minimum energy octahedron in line with an increase in coordination number. Reflecting this bond distance increase, all P-F overlap populations decrease as the octahedron is formed. During this geometrical transformation, all fluorine atom charges have become more negative while the atom charge for the phosphorus atom becomes more positive compared to the initial trigonal bipyramid. N_9 experiences its greatest change near 3.0Å. It undergoes an overall increase from -0.515 in the isolated pyridine molecule (P-N = ∞) to -0.704 in the minimum energy octahedron. It is apparent from energies corrected for BSSE, reported in Table II, that the basis set superposition error is not the major influence in determining geometries along the reaction trajectory. There is also a close comparison between calculated and X-ray[8] bond parameters for Py-PF_5 as seen in Table III. The bond distances agree to within ±0.013Å on average and the bond angles to within ±1.7°. The largest deviation in bond length between the *ab initio* values and the X-ray values occurs in the P-N bond distance. However, from the energy calculated at d(P-N) = 1.885Å (P-N bond distance from X-ray structure[8]) compared to the energy at d(P-N) = 1.937Å, it can be seen that a 0.05Å change in d(P-N) near the optimum value results in an energy change of only 0.3 kcal/mol. Thus the geometry as a function of the P-N bond distance apparently has a broad minimum.

The order of increasing P-N bond lengths, H_3N-PF_5[9] < Py-PF_5[8] < $(C_{10}H_8NO)PF_4$(**7**)[11] < $(C_{10}H_8NO)PhPF_3$ (**8**)[12] < $(Me_2NCH_2CO_2)PhPF_3$ (**6**)[10], reflects that expected for the most part based on the donor-acceptor interaction. Pyridine is a weaker donor than ammonia. Replacement of a fluorine atom with the less electronegative oxygen atom on going from the PF_5 complexes to the cyclic tetrafluorophosphorane **7** causes a further increase in the P-N distance. In **6-8**, the oxygen atom bonded to phosphorus also is capable of P-O π bonding[20] which accenuates the build up of electron density at phosphorus and thus reduces its acceptor character. Similarly, in the phenyltrifluorophosphorus complex **8**, the phenyl substitution in place of a fluorine atom of **7** causes a further reduction in the phosphorus acceptor ability. It is not apparent what is the cause of the small increase in the P-N distance on going from **8** to **6**. The values in this series in general trend above the sum of the covalent radii for P-N, 1.85Å.

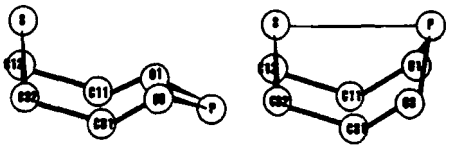
The series of structural changes encountered as pyridine approaches the trigonal bipyramidal PF_5 molecule parallels that observed by X-ray diffraction studies[3-7a,b]mentioned in the Introduction where varying sulfur-phosphorus and sulfonyl-phosphorus[7c] donor action is encountered with cyclic pentaoxyphosphoranes. In the series involving P-S donor coordination, the P-S distance decreases from 3.041(3)Å to 2.362(2)Å as the geometry at phosphorus orients more toward an octahedron from an initial square pyramid, from 44% to 70.8%, respectively. The same ring system with methyl substituents, **10**,[6] has a TBP geometry with a P-S distance of 3.504(3)Å. This distance is approaching the Van der Waals' sum of 3.75Å.



10

The conformation of the ring is that of a boat form for the pentaoxyphosphoranes whose geometries are between square pyramidal and octahedral,[3-6] while that for the trigonal bipyramidal molecule **1d**,[6] the eight-membered ring is in a chair-like conformation. Shown here is the ring geometry of **10** compared with that of **1d**.

The verification by *ab initio* calculations on the Py-PF_5 system that the same type of geometrical transformation takes place in the absence of ring constraints as that found by X-ray studies[3-7] on cyclic pentaoxyphosphoranes suggests that inclusion of the donor atom as part of the cyclic system does not appreciably alter the reaction pathway.



P–S distance = 3.504(3)Å P–S distance = 2.504(3)Å

Ring conformation for 10 Ring conformation for 1d

In view of the ease with which phosphorus assumes the higher coordinate octahedral geometry by simple donor atom coordination, *e.g.*, O, S, N, serious consideration should be given to addressing this possibility at active site interactions of phosphoryl transfer enzymes.[12a] The donor action causing increased coordination are just the ones that may be encountered with active site residues. At present, phosphorus pentacoordination has only been considered primarily via trigonal bipyramidal geometries as activated states in in-line nucleophilic displacements.[12a,21] In our recent work, we have studied the reactivity of pentaoxyphosphorane members of Table I which exhibit hexacoordination and find they exhibit high reactivity in nucleophilic displacement reactions with catechol molecules via an associative process.[7c,22]

CONCLUSION

The agreement in geometrical changes determined from theoretical and experimental studies involving nitrogen and sulfur donor action at phosphorus on phosphorus pentafluoride and pentaoxyphosphoranes, respectively, suggests that this geometrical sequence may serve as a reaction coordinate in nucleophilic displacements at pentacoordinated phosphorus.[12a,21] Further, proposed pentaoxyphosphorane formulations at enzyme active sites, e.g., at ribonuclease and staphylococcal nuclease,[21]may undergo donor action with nearby nitrogen containing amino acid residues, thus inducing hexacoordination, a feature not previously explored in constructing reaction mechanisms for phosphoryl transfer enzymes.[12a]

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References

[1] (a) Pentacoordinated Molecules. 112. (b) Part 111: Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996,** *35,* 6552-6560.

[2] Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

[3] Holmes, R. R.; Prakasha, T. K.; Day, R. R. *Inorg. Chem.* **1993,** *32,* 4360-4367.

[4] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993,** *115,* 2690-2695.

[5] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992,** *31,* 3391-3397.

[6] Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992,** *31,* 1913-1920.

[7] (a) Sherlock, D.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997,** *119,* 1317-1322. (b) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Phosphorus, Sulfur, and Silicon* **1993,** *75,* 249- 252. (c) Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997,** *119,* 11434-11441.

[8] Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974,** 1402.

[9] Storzer, W.; Schomburg, D.; Röschenthaler, G.-V.; Schmutzler, R. *Chem. Ber.* **1983,** *116,* 367.

[10] Krebs, R.; Schmutzler, R.; Schomburg, D. *Polyhedron* **1989,** *8,* 731.

[11] (a) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974,** 1841. (b) John, K.-P.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1974,** 2466.

[12] Also see (a) Holmes, R. R. *Chem. Rev.* **1996,** *96,* 927-950, and (b) Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev.* **1996,** *96,* 1917-1951 for an extensive coverage of hexacoordinate phosphorus.

[13] Gaussian 92, Revision A: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

[14] Hansen, K. W.; Bartell, L. S. *Inorg. Chem.* **1965,** *4,* 1775.

[15] Berry, R. S. *J. Chem. Phys.* **1960,** *32,* 933.

[16] Holmes, R. R. *Pentacoordinated Phosphorus - Structure and Spectroscopy,* Volume I, ACS Monograph 175, American Chemical Society, Washington, D.C., 1980, 479 pp.

[17] Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977,** *99,* 3318-3326.

[18] Holmes, R. R. *Chem. Rev.* **1990,** *90,* 17-31.

[19] Minyaev, R. M.; Minkin, V. I. *Zh. Strukturnoi Khim.* **1979,** *20,* 842-853.

[20] Trippett, S. *Pure Appl. Chem.* **1974,** *40,* 595.

[21] Holmes, R. R. *Pentacoordinated Phosphorus - Reaction Mechanisms,* Volume II, ACS Monograph 176, American Chemical Society, Washington, D.C., 1980, 237 pp, and references cited therein.

[22] Holmes, R. R.; Chandrasekaran, A.; Day, R. O. Presented in part at the 211th American Chemical Society National Meeting, New Orleans, LA, March, 1996.