Computational Study of Stability and Pseudorotation of Cyclic Penta-coordinated Phosphorous Compounds

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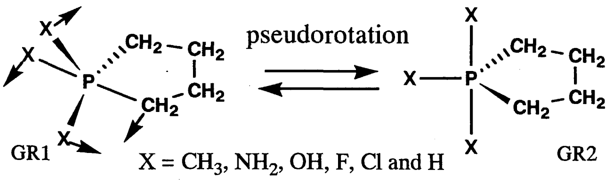
We studied ligand effects to the pseudorotation of cyclic penta-coordinated phosphorous compounds [$PX_3C_4H_8$], X=CH_3, NH_2, OH, F, Cl and H using *ab initio* molecular orbital methods. The most stable structures and the transition states are characterized. These are fundamental data for the control of reaction occurring in this type of compounds.

The cyclic penta-coordinated phosphorous compounds are formed as an intermediate of the hydrolysis reaction of phosphates, for example RNA.[1] Both incoming and leaving groups react along the axial axis of trigonal bipyramid.[1] The intermediates would isomerize with pseudorotation process. For the control of isomerization it is expected to elucidate which position a ligand relatively prefers to occupy in the trigonal bipyramid.[1,2] It is important to study the relative stability of isomers and the character of transition states between them to understand the isomerization of intermediates. There are various studies from this point of view.[1-3] It is frequently explained that the isomer with a ring structure in the equatorial plane is less stable because of the ring distortion.[1] We studied ligand effects to the stability and the pseudorotation of cyclic penta-coordinated phosphorous compounds.

The model of the cyclic penta-coordinated phosphorous compound is shown in the following scheme. GR1 means the isomer in which one end of five-membered ring is in the axial axis and the other end is in the equatorial part. In GR2 both ends of the five-membered ring are in the equatorial plane. TS means the transition state of the pseudorotation between GR1 and GR2. They are treated by *ab initio* molecular orbital methods in this study, and the relative stability between isomers is considered. The pseudorotation reactions between these isomers are also studied. X means CH_3, NH_2, OH, F, Cl and H.



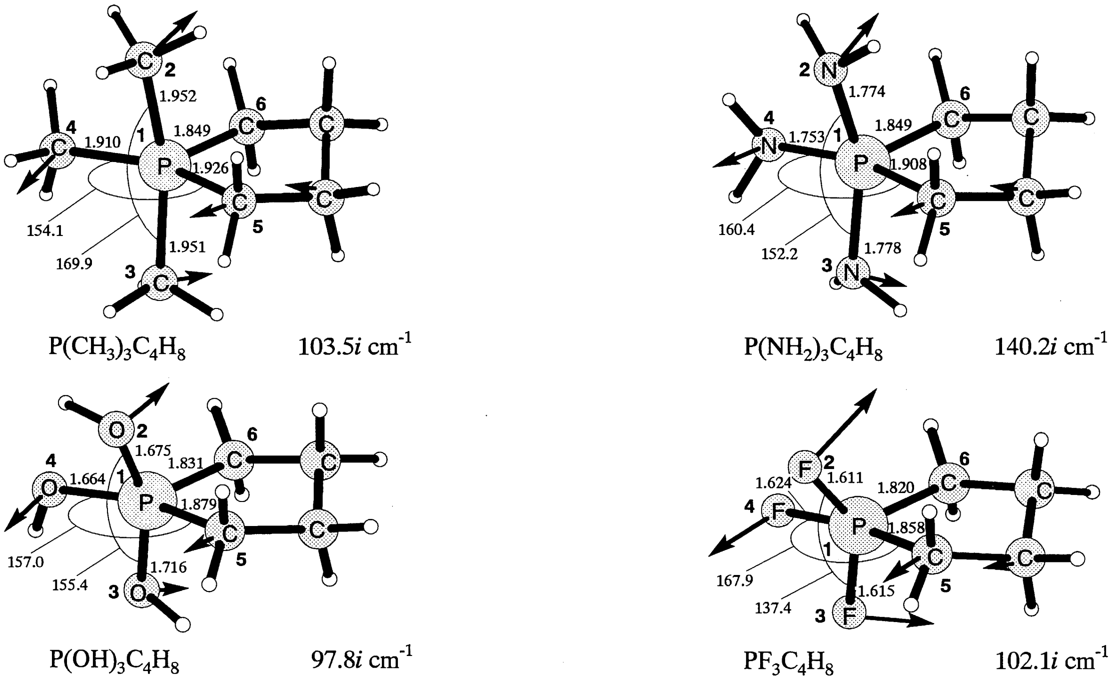
All geometries are fully optimized at RHF level, and vibrational analysis calculations are performed at that geometries to characterize the optimized structures. The basis sets used are Huzinaga-Dunning double-zeta level.[4] Polarization functions are added except for hydrogen atoms which don't connect directly to the phosphorus. The exponents of polarization functions are 0.75 for C, 0.80 for N, 0.85 for O, 0.90 for F, 0.43 for P, 0.6 for Cl and 1.0 for H, respectively. The correlation energies are estimated by MP2 method at RHF optimized geometries. All calculations are carried out using Gaussian 92.[5] The molecular structures and vibrational modes are drawn using MOLCAT.[6]

Total energies calculated with RHF and MP2 are shown on Table 1. GR2 is more stable than GR1 by 0.012665 (a.u.) in RHF and by 0.013711 (a.u.) in MP2 for $PF_3C_4H_8$. In the case of $P(OH)_3C_4H_8$, GR1 is more stable than GR2 by 0.003255 (a.u.) at RHF level. The energy difference between GR1 and GR2 is only 0.001464 (a.u.) in MP2 for this molecule. As the ligand X of the scheme is changed from F to OH, NH_2 and CH_3, the relative stability of GR1 becomes larger. Especially the MP2 energy of TS for $PF_3C_4H_8$ is lower than that of GR1. So we can expect that there is only one energy minimum containing the five-membered ring in the equatorial plane part for $PF_3C_4H_8$.

Table 1. Total energies (a.u.) of $PF_3C_4H_8$, $P(OH)_3C_4H_8$, $P(NH_2)_3C_4H_8$, $P(CH_3)_3C_4H_8$, $PCl_3C_4H_8$ and $PH_3C_4H_8$

Compounds		E(RHF)	E(MP2)
$PF_3C_4H_8$	GR1	-795.325067	-796.465879
	TS	-795.324326	-796.466697
	GR2	-795.337732	-796.479590
$P(OH)_3C_4H_8$	GR1	-723.272848	-724.446381
	TS	-723.268088	-724.444842
	GR2	-723.269593	-724.444917
$P(NH_2)_3C_4H_8$	GR1	-663.710278	-664.843539
	TS	-663.691997	-664.829200
	GR2	-663.695536	-664.832438
$P(CH_3)_3C_4H_8$	GR1	-615.643749	-616.683155
	TS	-615.626192	-616.669301
	GR2	-615.628323	-616.670581
$PCl_3C_4H_8$	GR1	-1875.298046	-1876.354901
	TS	-1875.296437	-1876.355491
	GR2	-1875.311902	-1876.367059
$PH_3C_4H_8$	GR1	-498.512716	-499.173879
	TS	-498.504622	-499.167218
	GR2	-498.506047	-499.168207

The relative stability of penta-coordinated phosphorous compounds is influenced by the stabilization of the equatorial plane part and the bond stabilization of the axial part.[3] Methyl and methylene groups prefer equatorial position and electronegative group like F prefers axial one. Furthermore F in the equatorial part stabilizes the axial bonds indirectly by lowering the central phosphorus LUMO.[3] This study supports these expectations. For example GR2 of $PF_3C_4H_8$ has a structure where all of equatoriphilic CH_2 groups occupy equatorial positions and the axial bond is most stabilized by two axial Fs and one equatorial F. Results of $PCl_3C_4H_8$ and $PH_3C_4H_8$ are also shown on Table 1. $PCl_3C_4H_8$ has a same



$P(CH_3)_3C_4H_8$ 103.5*i* cm^{-1}

$P(NH_2)_3C_4H_8$ 140.2*i* cm^{-1}

$P(OH)_3C_4H_8$ 97.8*i* cm^{-1}

$PF_3C_4H_8$ 102.1*i* cm^{-1}

Figure 1. The transition state structures of pseudorotation of $PX_3C_4H_8$, where X is CH_3, NH_2, OH and F.

trend of stability as $PF_3C_4H_8$, and $PH_3C_4H_8$ is similar to $P(CH_3)_3C_4H_8$.

We show transition state structures of pseudorotation in Figure 1. The arrow corresponds to the transition vector. The central P and atoms connected directly to P are numbered from 1 to 6. We also show bond lengths around the phosphorus and the bond angles which change remarkably in the isomerization. The unit of length is Å (1Å = 100 pm) and that of angle is degree.

The carbon of No.6 is the pivot of pseudorotation for every molecule. At the transition state the pivot atom stays in the apex position of square pyramid and other ligands (No.2, No.3, No.4 and No.5) form the base of square pyramid. This is very similar to the TS structure of simple compounds such as PF_5.[7] The vibrational frequencies of TS range from 100 *i* to 140 *i* cm^{-1}. These are same level with PF_5's value (137.9 *i* cm^{-1}).[3] It is considered that $PX_3C_4H_8$ series are extension of simple systems by adding a C_4H_8 ring from the view of vibrational modes in TS.

The bond angle ∠2-1-3 shows that the transition state of $P(CH_3)_3C_4H_8$ exists near GR2 where ∠2-1-3 is 175.3°. On the other hand, the transition state of $PF_3C_4H_8$ exists near GR1. If the transition state is complete square pyramidal form, the bond angle ∠2-1-3 is expected to be 150°. This angle is 152.2° for L=NH_2 and 155.4° for L=OH, respectively. So the transition state lies halfway of the above both extremes in the case of $P(NH_2)_3C_4H_8$ and $P(OH)_3C_4H_8$. The same trend is observed for the bond angle ∠4-1-5, too. If we assume GR1 as the initial state and GR2 as final one of the pseudorotation, the transition state of compound having L=F becomes similar to initial state, and approach to final state as the number of less electronegative ligands increases. The arrows of the transition vector mainly appear on No.2, No.3, No.4 and No.5 atoms. The structure of five-membered ring changes fairly small in the pseudorotation.

It is possible to design phosphorous compounds having trigonal bipyramidal structure in the reaction by combining several ligand in different ways using results of this study.

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