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Ab Initio Study of Cyclenphosphorane: The Molecular Structures of Phosphorus(III) and Phosphorus(V) Tautomers

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Introduction

Since the synthesis of the cyclenphosphorane, (cyclen)PH, was first reported by Richman and Atkins[1] in 1978, many derivatives of (cyclen)PH have been synthesized, and their molecular structures and reactivities have been investigated.[2] It has been known that they could exist as either tricoordinate phosphorus(III) or pentacoordinate phosphorus(V) tautomers. Previous spectral characterizations[1,3] indicate that pentacoordination is rather preferable to tricoordination for the phosphorus atom in (cyclen)PH. It seems that this stabilization of a pentacoordinate tautomer is caused by the constraint of polycyclic tetraamine rings around the phosphorus atom.[3e,4] The tricoordinate tautomer, called the "open form", is isolated only in certain metal complexes.[2f,4a,5] Recently, the isolation of an open form without complexation to a metal, that is, Mes_2B-(cyclen)P, has also been reported.[4b] The structure of pentacoordinate (cyclen)PH, called the "closed form", can have either trigonal bipyramidal (tbp) or square pyramidal (sp) geometry, which is consistent with the previous NMR spectral data.[1a] In addition, the X-ray study[6] of the cyclenfluorophosphorane, (cyclen)PF, shows that its structure is at the midpoint between the ideal sp and tbp geometries for pentacoordinate phosphorus. X-ray crystal and electron diffraction structures of (cyclen)PH have been also determined by Lattmann et al.[3d] Results of both solid state and gas phase structures show that (cyclen)PH has a distorted tbp geometry with the P−N axial bonds longer than the equatorial bonds. However, there is a difference of about 17° in the equatorial N−P−N angle between the X-ray and electron diffraction methods.

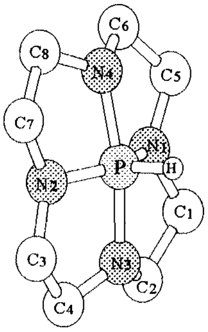

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Figure 1. The structure of the closed form, (cyclen)PH. (Hydrogen atoms bonded to carbon atoms are omitted for clarity.)

In this paper, we investigate the structural properties of (cyclen)PH by an ab initio method. The optimized geometrical parameters are compared with the experimental values. We also perform the conformational studies for the tricoordinate tautomer, H(cyclen)P. Finally, we calculate the molecular energies of pentacoordinate and tricoordinate tautomers in order to discuss the relative stabilities between two tautomeric forms.

Computational Details

Ab initio calculations have been performed using the GAUSSIAN 92 program[7] on a Cray Y-MP supercomputer. The geometries of both tautomers have been fully optimized at the restricted Hartree−Fock (RHF) level by using 6-31G* and 6-311G*. The geometry optimization using the second-order Moeller−Plesset perturbation (MP2) method has been particularly performed with the 6-31G* basis set in order to better understand the electron correlation effects on the conformational nature of the closed form. In the open form, several local minimum points are found while the closed form has only one stable conformer. In order to obtain more reliable energy comparisons for all conformers in the open form on the potential surface, MP2 single-point calculations are performed at the RHF/6-31G* and RHF/6-311G* optimized geometries.

Results and Discussion

Geometry of (cyclen)PH. The structure of the closed from, (cyclen)PH, **1** is shown in Figure 1. The computed geometrical parameters for the closed form **1** are summarized in Table 1 along with the values from X-ray and electron diffraction (ED) data.[3d] The overall geometries at the RHF/6-31G*, RHF/6-311G*, and MP2/6-31G* levels appear to be somewhat distorted tbp with P−N axial bonds longer than equatorial bonds, which is consistent with experimental results. The bond lengths of both axial and equatorial P−N bonds at the RHF/6-31G* and RHF6-311G* levels are in excellent agreement with X-ray values rather than ED values. The equatorial N_1−P−N_2 angle is much closer to the X-ray data, although a significant difference for this angle was reported between X-ray and ED methods. In the previous work,[3d] this difference was thought to be due to a small energy barrier between the tbp and sp geometries with the crystal packing forces, leading to a smaller

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Table 1. Geometrical Parameters for (cyclen)PH (Closed Form), **1**

bond length, Å	HF/ 6-31G*	HF/ 6-311G*	MP2/ 6-31G*	X-ray[a]	ED[a]
P−H	1.389	1.392	1.413	1.45(7)	1.46(6)
P−N_1	1.696	1.693	1.713	1.698(2)	1.687(2)
P−N_3	1.763	1.760	1.786	1.767(3)	1.775(2)
N_1−C_1	1.438	1.438	1.446		
N_2−C_3	1.439	1.438	1.446	1.436(3)	1.421(3)
N_3−C_4	1.439	1.439	1.451	1.404(4)	1.476(4)
N_4−C_6	1.440	1.439	1.451		
N_4−C_8	1.440	1.439	1.451		
C_3−C_4	1.528	1.526	1.517	1.519(4)	1.523(4)
bond angle, deg	**HF/ 6-31G***	**HF/ 6-311G***	**MP2/ 6-31G***	**X-ray[a]**	**ED[a]**
∠N_1PN_2	142.42	142.57	141.27	137.9(2)	155.3(18)
∠N_3PN_4	165.99	166.10	166.88	170.1(4)	169.0(15)
∠N_1PN_3	87.75	87.78	87.83		
∠N_1PN_4	87.75	87.78	87.83		
∠N_2PN_3	87.75	87.78	87.83	88.2(2)	88.8
∠N_2PH	108.81	108.71	109.37	111.(1)	102.3
∠N_3PH	97.00	96.95	96.56	95.(1)	95.5
∠$C_1N_1C_5$	121.34	121.22	121.99		
∠C_1N_1P	115.08	115.13	114.13		
∠$C_3N_2C_7$	121.32	121.23	121.99	120.5(2)	125.0
∠C_3N_2P	115.06	115.15	114.15	117.6(1)	117.5(5)
∠C_7N_2P	115.06	115.15	114.139		
∠$N_2C_3C_4$	103.86	103.84	103.08	104.6(2)	106.7(11)
∠$C_2N_3C_4$	117.26	117.22	115.56	118.9(5)	111.5
∠$C_3C_4N_3$	105.25	105.20	105.06	110.1(2)	104.5
∠C_2N_3P	114.91	114.94	113.35	114.6(2)	112.7(5)
∠C_4N_3P	114.92	114.94	113.35		
∠C_6N_4P	114.95	114.94	113.35		

[a] Reference 3d.

angle. However, the result of this study shows that the values from the solid state are more reliable than those from the gas phase.

In the geometry optimized at the MP2/6-31G* level, it is shown that values of all bond lengths except for the C_3−C_4 bond are a little longer than those from Hartree−Fock calculations as generally expected. The equatorial N_1−P−N_2 angle is computed to be 141.27°, which is much closer to X-ray data than ED data. Therefore, it is confirmed once again that the equatorial N_1−P−N_2 angle measured in the solid state is more reliable than that in the gas phase, although we take it into consideration that the crystal packing forces can reduce the bond angle to some degree. In addition, the calculated N_2−P−H angle at the MP2/6-31G* level is much closer to the X-ray value rather than the ED value. On the other hand, the N_3−C_4 bond is computed to be 1.451Å at the MP2/6-31G* level, which is rather closer to the ED value than the X-ray value.

Geometry of H(cyclen)P. Possible conformers **2a**−**d** of the open form, H(cyclen)P, are illustrated in Figure 2. In discussing the structure of the open form, we have focused on the open form **2b** only. It is because the geometry of the open form **2b** is most similar to the experimental structure of the (cyclen)P unit in an open form, Mes_2B(cyclen)P, despite the difference of substituents. Table 2 gives the optimized geometrical parameters for the open form **2b** and the X-ray crystal data[4b] for the (cyclen)P unit in Mes_2B(cyclen)P. The conformations of eight-membered rings of four open form conformers are all quite different from one another, while the geometries of two five-membered rings around the P atom are almost the same. These four conformers can be described as a chair-boat form, a crown form, a boat-boat form, and a boat-chair form in **2a**, **2b**, **2c**, and **2d**, respectively.[4a] In the open form conformer **2c**, we can expect that an axial N_4 atom is involved in a transannular interaction with the phosphorus atom through its lone pair electrons.[4a] Since the distance between both atoms is about 2.6 Å at all RHF levels, which is well within the sum of the van der Waals radii, the open form conformer **2c** may not be a genuine tricoordinate tautomer.

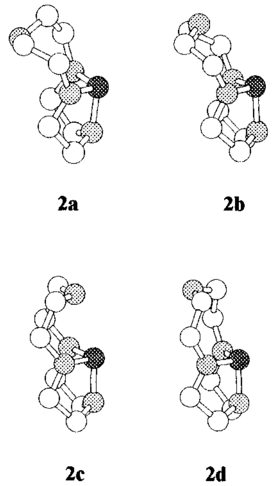

Figure 2. Geometries of possible open form conformers, H(cyclen)P. (All hydrogen atoms are omitted for clarity.)

Table 2. Geometrical Parameters for H(cyclen)P (Open Form), **2b**

bond length, Å	HF/ 6-31G*	HF/ 6-311G*	exptl data	bond angle, deg	HF/ 6-31G*	HF/ 6-311G*	exptl data
N_4−H	0.996	0.992		∠N_1PN_2	111.10	110.87	111.8(2)
P−N_1	1.714	1.708	1.692(3)	∠N_1PN_3	90.98	91.12	92.0(1)
P−N_2	1.714	1.708	1.712(3)	∠N_2PN_3	90.96	91.14	91.6(1)
P−N_3	1.752	1.747	1.755(3)	∠$C_1N_1C_5$	120.34	120.17	120.3(3)
P−N_4	3.211	3.222	3.61	∠C_1N_1P	114.68	114.77	114.0(2)
N_1−C_1	1.447	1.447	1.485(5)	∠C_5N_1P	123.04	123.27	122.8(2)
N_1−C_5	1.443	1.444	1.456(4)	∠$C_3N_2C_7$	120.35	120.19	118.6(3)
N_2−C_3	1.446	1.447	1.455(5)	∠C_3N_2P	114.68	114.75	114.0(2)
N_2−C_7	1.444	1.443	1.449(4)	∠C_7N_2P	123.05	123.24	121.2(2)
N_3−C_2	1.462	1.462	1.482(5)	∠$C_2N_3C_4$	116.49	116.44	114.7(3)
N_3−C_4	1.462	1.463	1.475(5)	∠C_2N_3P	110.10	110.18	109.0(2)
N_4−C_6	1.450	1.451	1.478(5)	∠C_4N_3P	110.13	110.15	109.1(2)
N_4−C_8	1.451	1.453	1.480(4)	∠$C_6N_4C_8$	121.51	121.30	117.1(3)

[a] X-ray data of Mes_2B(cyclen)P.[4b]

In spite of the difference of substituents between H(cyclen)P and Mes_2B(cyclen)P, the optimized bond lengths and angles of the (cyclen)P unit in H(cyclen)P at the RHF/6-31G* and RHF/6-311G* levels are well matched with the X-ray data obtained from the crystalline Mes_2B(cyclen)P. The bond angles optimized at the RHF levels are in particularly good agreement with the X-ray values. In other words, the optimized geometry of the two five-membered rings around the phosphorus atom is not largely different from the structure of Mes_2B(cyclen)P determined by the X-ray method. However, the X-ray data show that two five-membered rings are unsymmetric. For example, two equivalent bond lengths such as N_1−C_1 and N_2−C_3 are somewhat different compared with those of calculated geometries. It is probably because the solid structure is so highly influenced by steric substituent groups that the geometry of the (cyclen)P unit may be slightly distorted.

The distance between P and axial N_4 atoms in the open form **2b** is computed to be 3.222 Å at the RHF/6-311G* level. Although this value is much larger than that in the open form **2c**, there is some constraint of an eight-membered ring in **2b**. The reason is that the distance between two atoms is within the sum of the van der Waals radii. On the other hand, this distance in Mes_2B(cyclen)P is 3.610 Å, which is longer than the sum of van der Waals radii. The increment of the distance between P and axial N_4 atoms in Mes_2B(cyclen)P results from the steric effect of a bulky Mes_2B group. This Mes_2B group makes the

Table 3. Relative Energies (kcal/mol) for Each Possible Conformer

calculational level	1	2a	2b	2c	2d
PM3	0.0	−6.754	−12.765	−6.546	−6.681
HF/6-31G*	0.0	7.893	4.559	11.147	10.784
HF/6-311G*	0.0	7.110	4.142	10.492	10.279
MP2/6-31G* [a]	0.0	11.160	8.493	12.619	16.037
MP2/6-311G* [b]	0.0	9.068	6.865	10.647	14.734

[a] MP2/6-31G*//6-31G*. [b] MP2/6-311G*//6-311G*.

axial N_4 atom tilt up to a small extent. Nevertheless, the optimized geometry parameters around the phosphorus atom in the open form **2b** are in excellent agreement with experimental data of Mes_2B(cyclen)P. Therefore, the overall geometry around the phosphorus atom of H(cyclen)P can be described as a distorted pyramid rather than a distorted trigonal bipyramid.

Relative Stability and Tautomerization Energy between (cyclen)PH and H(cyclen)P. In order to discuss the tautomerization between (cyclen)PH and H(cyclen)P, the closed form and possible conformers of the open form are fully optimized at the various RHF levels. In addition, PM3 calculations are carried out to compare these structures with those from ab initio calculations. The vibrational analyses indicate that all the optimized structures are at stationary points corresponding to local minima without imaginary frequencies. In order to compare energy improvement for all conformers on the potential energy surface, MP2/6-31G* and MP2/6-311G* single-point calculations are performed at the RHF/6-31G* and RHF/6-311G* optimized geometries, respectively. Relative energies (kcal/mol) of four possible open form conformers with respect to the closed form are listed in Table 3.

RHF calculations show that the relative stability for the open form conformers is in order **2b** > **2a** > **2d** > **2c**, which is the same as the result of PM3. However, PM3 calculations suggest that the closed form is higher in energy than the open form conformers. This result is not consistent with the previous experimental work. Therefore, one knows that the semiempirical PM3 method is not adequate to predict the relative stability for these particular compounds.

At the RHF/6-31G* and RHF/6-311G* levels, the energy difference between the closed form **1** and the most stable open form **2b** is computed to be about 4 kcal/mol. Among the open form conformers, the energy difference between **2c** and **2d** is computed to be 0.37 kcal/mol and 0.21 kcal/mol at the RHF/6-31G* and RHF/6-311G* levels, respectively. Such a little difference in energy is not enough to determine the order of relative stability between these two conformers. Even though RHF/6-31G* and RHF/6-311G* calculations provide good results for relative stability among conformers, some consideration of electron correlation effects is sometimes required to compare the relative energies more precisely.

When the electron correlation effects are included at the MP2/6-31G* and MP2/6-311G* levels, the stability for the open form conformers is estimated to be in the order **2b** > **2a** > **2c** > **2d**. With electron correlation, the order of stability for **2c** and **2d** is reversed. According to MP2 calculations, the closed form **1** also appears to be the most stable structure, and the energy difference between the closed form and the most stable open form conformer **2b** is computed to be 8.49 kcal/mol and 6.87 kcal/mol at the MP2/6-31G* and MP2/6-311G* levels, respectively. The energy difference between **2c** and **2d**, which is less than 1 kcal/mol at all RHF levels, is computed to be 3.42 and 4.09 kcal/mol at the MP2/6-31G* and MP2/6-311G* levels, respectively. These values are high enough to discuss the relative stability for two conformers. Thus, we can notice that the order of stability among conformers is somewhat influenced by the electron correlation effects. The order of stability in the open form conformers is strongly related to the conformation of an eight-membered ring containing P and axial N_4 atoms. Hence, slighter stability of **2c** over **2d** can be ascribed to the transannular interaction between P and axial N_4 atoms in **2c**. This interaction in **2c** gives more constraint to the macrocyclic tetraamine ring around the phosphorus atom than that interaction in **2d**; this may make **2c** a little more stable. The computed energies of all open conformers are at least about 7 kcal/mol higher than that of (cyclen)PH, **1**, at the MP2/6-311G* level. These energies are good enough to predict that the closed form tautomer is more favorable than the open form tautomer.

In the P(III)−P(V) tautomerism of this compound, the hydrogen atom bonded to the P atom migrates to the axial N_4 atom with P−N bond breaking. This tautomerization may occur between **1** and **2b** although the reaction pathway between both tautomers is not scrutinized. Thus, we suggest that the relative energy of **2b** with respect to the closed form may be considered as the tautomerization energy between (cyclen)PH and H(cyclen)P, and this value is computed to be 8.49 kcal/mol at the MP2/6-31G* level and 6.87 kcal/mol at the MP2/6-311G* level.

Conclusion

We have considered the structures and relative stabilities of (cyclen)PH and H(cyclen)P at various theoretical levels. The optimized geometrical parameters of (cyclen)PH at the RHF/6-31G*, RHF/6-311G*, and MP2/6-31G* levels are in good agreement with the experimental values. On the basis of the computational results, the overall geometry of (cyclen)PH becomes close to tbp rather than sp as the larger polarization basis sets are employed and the correlation effects are incorporated. On the other hand, H(cyclen)P can be classified into four conformers according to the conformation of an eight-membered ring containing P and axial N_4 atoms. Among these conformers, the most stable form corresponding to the conformer **2b** has a distorted pyramidal geometry around the phosphorus atom with an eight-membered ring of the crown form. The greater stability of (cyclen)PH over H(cyclen)P is fairly well established by theoretical calculations; the results of ab initio calculations at higher levels are well consistent with experimental data previously obtained. The effects of polarization functions and electron correlation seem to be more important for studying this tautomerization system, and the availability of polarization functions must definitely favor the closed form tautomer.

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