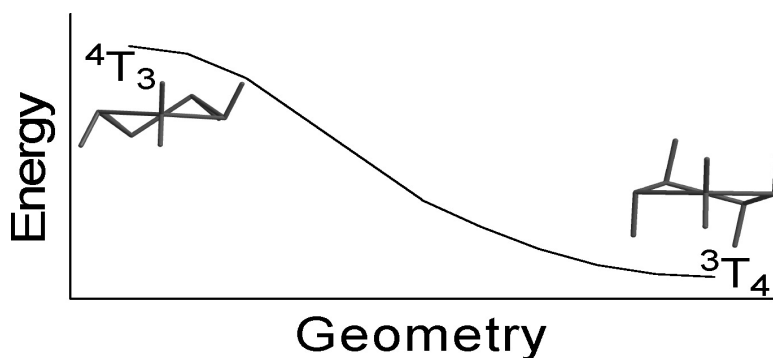


Potential Energy Surfaces for All-*trans* PH and PMe May Be Less Complicated than Anticipated

Qian-Shu Li, Zhifeng Pu, Yaoming Xie, Paul von Rague Schleyer, and Henry F. Schaefer

J. Am. Chem. Soc., **2008**, 130 (29), 9380-9385 • DOI: 10.1021/ja800177p • Publication Date (Web): 25 June 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Potential Energy Surfaces for All-*trans* P₅H₆⁺ and P₅Me₆⁺ May Be Less Complicated than Anticipated

Qian-Shu Li,^{*,†,§} Zhifeng Pu,[†] Yaoming Xie,[‡] Paul von Rague Schleyer,[‡] and Henry F. Schaefer^{*,‡}

Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631, China, School of Chemical Engineering and the Environment, Beijing Institute of Technology, Beijing 100081, China, and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received January 8, 2008; E-mail: qslis@scnu.edu.cn; sch@uga.edu

Abstract: Burford and co-workers recently (2007) investigated the synthesis, structure, and pseudorotation of a family of cyclotetraphosphinophosphonium ions comprehensively. We now report theoretical computations through the CCSD(T) level to study the conformations of the parent model rings, P₅H₆⁺ and P₅Me₆⁺. The all-*trans* conformations on the full pseudorotational cycle for the cyclotetraphosphinophosphonium cation (P₅H₆⁺) and for its methyl-substituted derivative (P₅Me₆⁺) were located systematically on their potential energy surfaces. The potential energy for the pseudorotational circuit of P₅H₆⁺ is smooth and monotonic with only one minimum (³T₄) and one maximum (⁴T₃), but the analogous P₅Me₆⁺ circuit has two minima. The P₅H₆⁺ and P₅Me₆⁺ potential surfaces appear to be qualitatively very different from that for the well investigated tetrahydrofuran. Since the ³T₄ form of P₅H₆⁺ avoids unfavorable eclipsing PH–PH and lone pair–lone pair interactions, it is the global minimum among all possible P₅H₆⁺ configurations and conformations.

Introduction

Numerous theoretical and experimental studies involving pentacyclic molecules have been carried out since the 1940s to elucidate their conformational characteristics.^{1–20} The concept of five-membered ring pseudorotation and phase angle (φ) was introduced by Kilpatrick, Pitzer, and Spitzer in 1947 to describe the ring puckering motions of cyclopentane.³ In 1975, a more

general definition of ring puckering coordinates in terms of phase angle (φ) was proposed by Cremer and Pople to recognize the confirmations of cyclic compounds precisely.¹² Cremer and Pople's second paper¹³ studied the pseudorotation potential surfaces associated with ring puckering in several five-membered ring molecules with *ab initio* methods. On the basis of their analysis, such five-membered rings should have 10 envelope (E) conformations and 10 twist (T) conformations on the full (0–360°) pseudorotational circuit. The E conformations occur when the phase angle (as defined by Cremer and Pople) is even multiples of 18° ($\varphi = 0, 36, 72^\circ, \dots$), whereas the T conformations occur when the phase angle is of odd multiples of 18° ($\varphi = 18, 54, 90^\circ, \dots$).

Dyker, Riegel, Burford, Lumsden, and Decken¹ reported the synthesis of derivatives of the cyclotetraphosphinophosphonium cation in an important recent paper. The parent of these cations is a five-membered ring (P₅H₆⁺), because the hydrogens can be replaced by various substituents, such as methyl, phenyl, cyclohexyl, and tertiary butyl. Burford and co-workers¹ found that the X-ray crystal structures for all their derivatives have all-*trans* configurations, but the most favorable conformations depend on the different substituents. For example, P₅Me₆⁺ was reported¹ to have an E₄ structure ($\varphi = 100^\circ$) and P₅^tBu(C₆H₅)₅⁺ was reported to have a ²T₃ (see next section for notation) structure with $\varphi = 228^\circ$. Figure 1 (which reproduces Figure 9 in their paper) provides an elegant summary of their findings. The present theoretical research aims to establish: (1) the conformations in the pseudorotation circuit which are stationary points and (2) the relative energies of these structures. We

[§] South China Normal University.

[†] Beijing Institute of Technology.

[‡] University of Georgia.

- (1) Dyker, C. A.; Riegel, S. D.; Burford, N.; Lumsden, M. D.; Decken, A. *J. Am. Chem. Soc.* **2007**, *129*, 7464.
- (2) Herzberg, G.; *Infrared and Raman Spectra*; Van Nostrand: New York, 1945.
- (3) Kilpatrick, J. E.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2483.
- (4) Pitzer, K. S.; Donath, W. E. *J. Am. Chem. Soc.* **1959**, *81*, 3213.
- (5) Geise, H. J.; Altona, C.; Romers, C. *Tetrahedron Lett.* **1967**, *15*, 1383.
- (6) Altona, C.; Geise, H. J.; Romers, C. *Tetrahedron* **1968**, *24*, 13.
- (7) Bell, S. *J. Phys. B* **1969**, *2*, 1001.
- (8) Adams, W. J.; Geise, H. J.; Bartell, L. S. *J. Am. Chem. Soc.* **1970**, *92*, 5013.
- (9) Sundaralingam, M. *J. Am. Chem. Soc.* **1971**, *93*, 6644, and references cited.
- (10) Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 8205.
- (11) Dunitz, J. D. *Tetrahedron* **1972**, *28*, 5459.
- (12) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.
- (13) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1358.
- (14) Carreira, L. A.; Lord, R. C.; Malloy, T. B. *Top. Curr. Chem.* **1979**, *82*, 1.
- (15) Strauss, H. L. *Annu. Rev. Phys. Chem.* **1983**, *34*, 301.
- (16) Laane, J. *Pure Appl. Chem.* **1987**, *59*, 1307.
- (17) Allen, W. D.; Csaszar, A. G.; Horner, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 6834.
- (18) Laane, J. *Annu. Rev. Phys. Chem.* **1994**, *45*, 179.

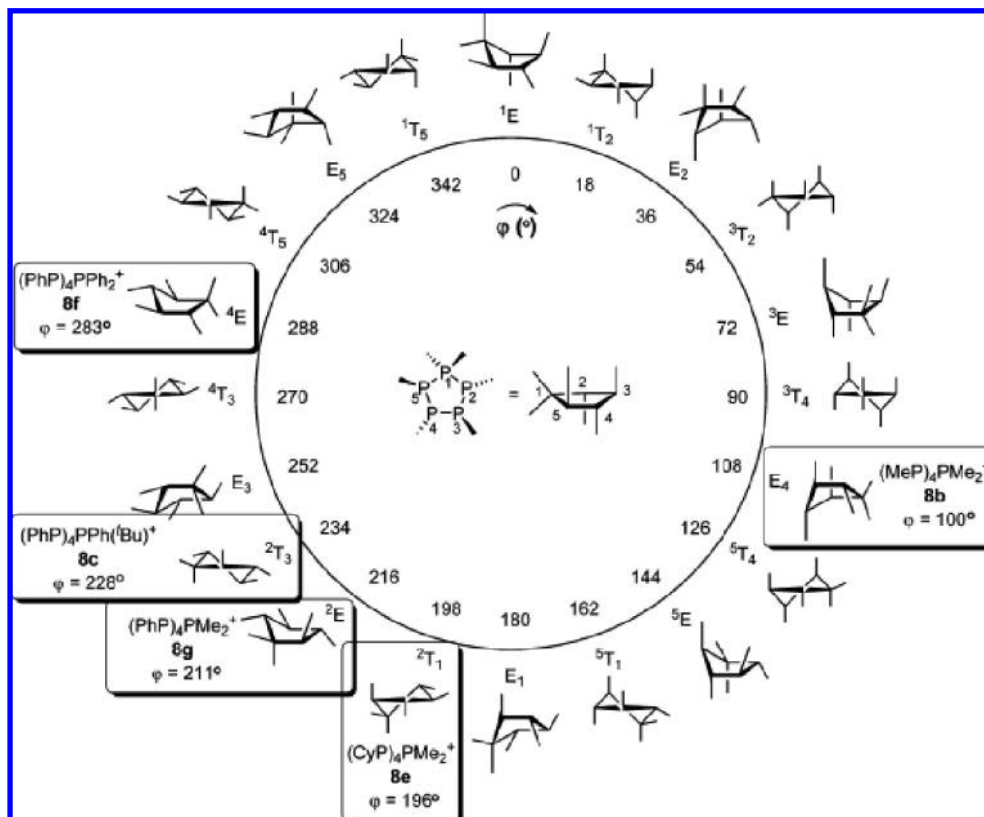


Figure 1. Reproduction of Figure 9 from Burford's paper (ref 1). All-*trans* conformations of P₅R₆⁺ as a function of the phase angle of pseudorotation (φ).

computed the potential energy surface for conformations around the pseudorotation circuit of P₅H₆⁺, which is the simplest model, as well as the permethyl derivative, P₅Me₆⁺, studied experimentally by Burford and co-workers.¹

Theoretical Methods

The geometries of all structures must be optimized to high precision due to the very flat conformational potential energy surfaces. Hartree–Fock (HF) and Møller–Plesset second order perturbation (MP2) methods were used with Dunning's correlation-consistent basis sets, including cc-pVDZ and cc-pVTZ.²¹ There are 388 and 602 basis functions in the aug-cc-pVTZ basis sets for P₅H₆⁺ and cc-pVTZ basis sets for P₅Me₆⁺, respectively.

Because most of the conformations along the full pseudorotation circuit are not stationary points, it is necessary to employ appropriate constraints and partial geometry optimizations. Four sequential P atoms of envelope E-type conformations were required to be coplanar. For example, the P2–P3–P4–P5 dihedral angle was frozen at 0° to study the E₁ conformation. Two equal dihedral angles for the twist T-type conformations were frozen to prevent collapse to an energetically lower-lying E conformation. In the ⁴T₃ conformation, for example, the two dihedral angles P3–P2–P1–P5 and P4–P5–P1–P2 were constrained to be equal throughout the optimization. We adopt the abbreviated nomenclature in Burford's paper.¹ An envelope (E) conformation is defined by four coplanar phosphorus atoms, and a twist (T) conformation by the coplanarity of three phosphorus atoms and the midpoint of the bond opposite. The superscript in each conformation label represents the numbered phosphorus atom above the plane, while the subscript represents

the phosphorus atom below. This nomenclature was defined in 1971 by Sundaralingam.⁹

Harmonic vibrational frequencies of stationary points were obtained (again to high precision) at the same levels of theory by analytically evaluating the second derivatives of the energy with respect to the nuclear coordinates. The computations were carried out with the GAUSSIAN03 program package in Beijing²² and the Q-Chem Program in Georgia.²³ Since the energy differences for different conformations are relatively small, a very tight threshold was set for the self-consistent field (SCF) convergence (10⁻¹⁰ a.u.), as well as for the integral cutoffs (10⁻¹¹ a.u.). Considering that the energy ordering of the conformations of tetrahydrofuran, another five-membered ring system, are very sensitive to the theoretical methods,⁹ we computed further single point energies for the two extreme conformations for P₅H₆⁺ with the MP2 and CCSD(T) methods using a series of basis sets up to aug-cc-pVTZ in order to confirm our theoretical results.

Results and Discussion

It is known that there are 10 envelope (E) and 10 twist (T) all-*trans* conformations along the full pseudorotational (0–360°) circuit for an idealized five-membered ring.¹ However, the conformations in the upper half-circle depicted in Figure 1 are geometrically identical to those in the lower half-circle; thus, only 11 conformations are unique (five E-type structures and six T-type). If the lower half-circle is chosen, these eleven conformations are ⁴T₃ (phase angle $\varphi = 270^\circ$, defined by Cremer and Pople¹²), E₃ (252°), ²T₃ (234°), ²E (216°), ²T₁ (198°), E₁ (180°), ⁵T₁ (162°), ⁵E (144°), ⁵T₄ (126°), E₄ (108°) and ³T₄ (90°).

(19) Laane, J. *J. Phys. Chem. A* **2000**, *104*, 7715.

(20) Fuchs, B. *Top. Stereochem.* **2007**, *10*, 1–94.

(21) (a) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796. (c) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, *98*, 1358.

(22) Frisch, M. J.; et al. *Gaussian 03*, B.04 ed.; Gaussian, Inc.: Pittsburgh, PA, 2003.

(23) Shao, Y. *Phys. Chem. Chem. Phys.* **2008**, . in press.

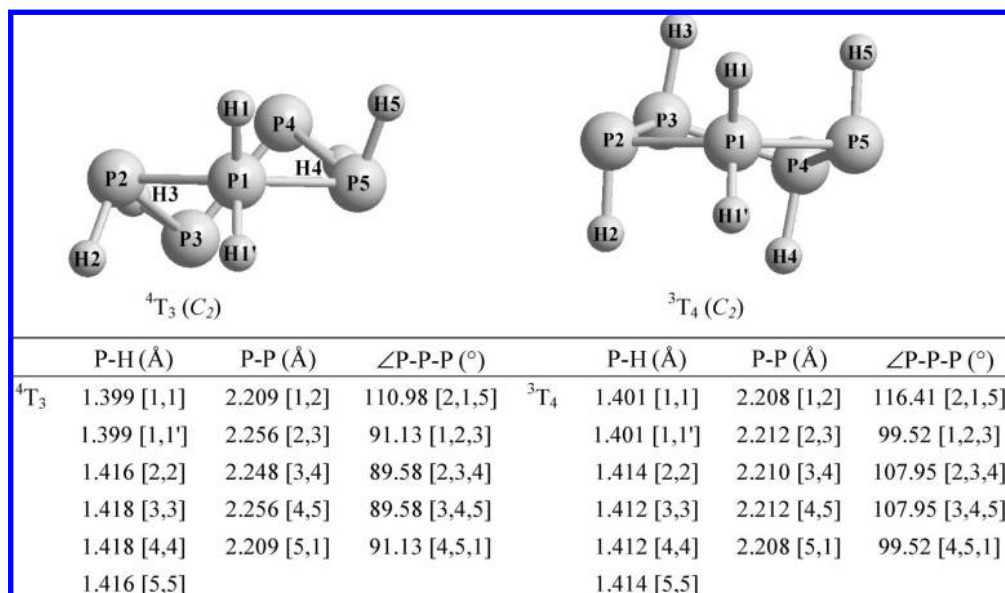


Figure 2. Geometries of two extrema (3T_4 and 4T_3) for $P_5H_6^+$ optimized at the MP2/cc-pVTZ level of theory.

(a) $P_5H_6^+$. The eleven geometry constrained model conformations of $P_5H_6^+$ are optimized at the HF/cc-pVDZ, HF/cc-pVTZ, MP2/cc-pVDZ, and MP2/cc-pVTZ levels of theory. The fully optimized stationary point geometries for the two extrema are reported in Figure 2, whereas the other partially constrained structures appear in the Supporting Information. At the HF/cc-pVTZ level, the 2T_1 ($\varphi = 198^\circ$) conformation collapses to the planar pentagon structure with C_2 symmetry (shown in the center of the circle of Figure 1; Burford's Figure 9), and further collapses to 1T_2 ($\varphi = 18^\circ$). The latter (with a 180° phase angle difference from 2T_1) is identical to 5T_1 ($\varphi = 162^\circ$), due to the same constraints. The MP2 and HF geometries of all the conformers are nearly the same. The MP2 method predicts slightly longer (~ 0.01 Å) P–H bond distances and somewhat shorter (~ 0.01 Å) P–P bond distances.

The theoretical potential energy curves connecting these conformations are shown in Figure 3, which provides a clear description of the relationship between the energies and the phase angles. The theoretical HF and MP2 potential energy surfaces shown in Figures 3 have the same order, ${}^4T_3 > E_3 > {}^2T_3 > {}^2E > {}^2T_1 > E_1 > {}^5T_1 > {}^5E > {}^5T_4 > E_4 > {}^3T_4$; that is, the energies of these conformations decrease monotonously from 4T_3 ($\varphi = 270^\circ$, the far-left side on the pseudorotation circuit) to 3T_4 ($\varphi = 90^\circ$, the far-right side). Our potential curves (Figure 3) follow the lower semicircle of Figure 1, and there is an identical curve along the upper semicircle. Thus, for the model system $P_5H_6^+$, there is only one minimum (3T_4 , with C_2 symmetry and all real vibrational frequencies) and one maximum (4T_3 , a transition structure with C_2 symmetry and one imaginary frequency, $46i$ (HF) or $40i$ (MP2) cm^{-1}) around the full pseudorotation circuit. The energy difference between the maximum 4T_3 and the minimum 3T_4 is 8.29 (HF) or 7.48 (MP2) kcal/mol (Table 1). In contrast, the energy differences between two adjacent conformations (for example, E_4 and 3T_4) can be as small as 0.1 kcal/mol, but it must be noted that some of these were computed with geometrical constraints.

Table 1 also shows the lowest vibrational frequency for each conformation. Some are imaginary, and some are real (but very small). These lowest vibrational frequencies for all conformations are related to the mode of pseudorotation.

Unlike the observed condensed phase derivatives of $P_5H_6^+$, conformations other than the two extrema (3T_4 and 4T_3) are not stationary points in the present theoretical studies, by either the HF method or the MP2 method. To what extent do conclusions based on the simple $P_5H_6^+$ model extend to larger systems, e.g., to $P_5Me_6^+$, which has been observed experimentally to have a stable E_4 conformation?¹

(b) $P_5Me_6^+$. All 11 unique conformations (4T_3 , E_3 , 2T_3 , 2E , 2T_1 , E_1 , 5T_1 , 5E , 5T_4 , E_4 , and 3T_4) for the more realistic model $P_5Me_6^+$ were optimized at the HF/cc-pVDZ, HF/cc-pVTZ, and MP2/cc-pVDZ levels of theory. At the HF/cc-pVTZ level, the 5T_1 conformation collapses to the planar structure, and further to 1T_5 (or 2T_1). Because geometry optimizations at MP2/cc-pVTZ were not practicable, we computed MP2/cc-pVDZ single point energies on the MP2/cc-pVDZ geometries. All the optimized conformations and their geometrical parameters are available in the Supporting Information. Like $P_5H_6^+$, all the conformations have C_1 symmetry except the 4T_3 and 3T_4 structures, which have C_2 symmetry. Also like $P_5H_6^+$, the HF and MP2 geometries are nearly the same. The MP2 P–C bond distances are slightly longer than those at HF. The P–P bond lengths, P–P–P bond angles, and five-membered ring skeletons of $P_5Me_6^+$ are quite close to those predicted for $P_5H_6^+$. The P1–H bond lengths of $P_5H_6^+$ are slightly shorter than the other P–H bond lengths, and the P1–C bond lengths of $P_5Me_6^+$ are similarly slightly shorter than the other P–C bond lengths. For each conformation of $P_5H_6^+$, the P2–P1–P5 bond angle is the largest among all the P–P–P bond angles, and this is also true for the conformations of $P_5Me_6^+$, except for 2E and 2T_1 .

The potential energy curve for $P_5Me_6^+$ has an important characteristic similar to that for $P_5H_6^+$, with the 4T_3 conformation ($\varphi = 270^\circ$) higher in energy than the 3T_4 conformation ($\varphi = 90^\circ$) (Table 2 and Figure 4). However, two features of the $P_5Me_6^+$ and the $P_5H_6^+$ PES's differ. First, the $P_5Me_6^+$ HF and MP2 PES's are considerably flatter (Figure 4). The energy difference between the $P_5Me_6^+$ extrema (3T_4 and 4T_3) is less than 2 kcal/mol, and the difference between two neighbors (for example, E_4 and 3T_4) in the pseudorotational circuit can be as small as 0.01 kcal/mol. Second, unlike $P_5H_6^+$, $P_5Me_6^+$ has an additional minimum at conformation 2E at $\varphi = 216^\circ$ (or 2T_1 at

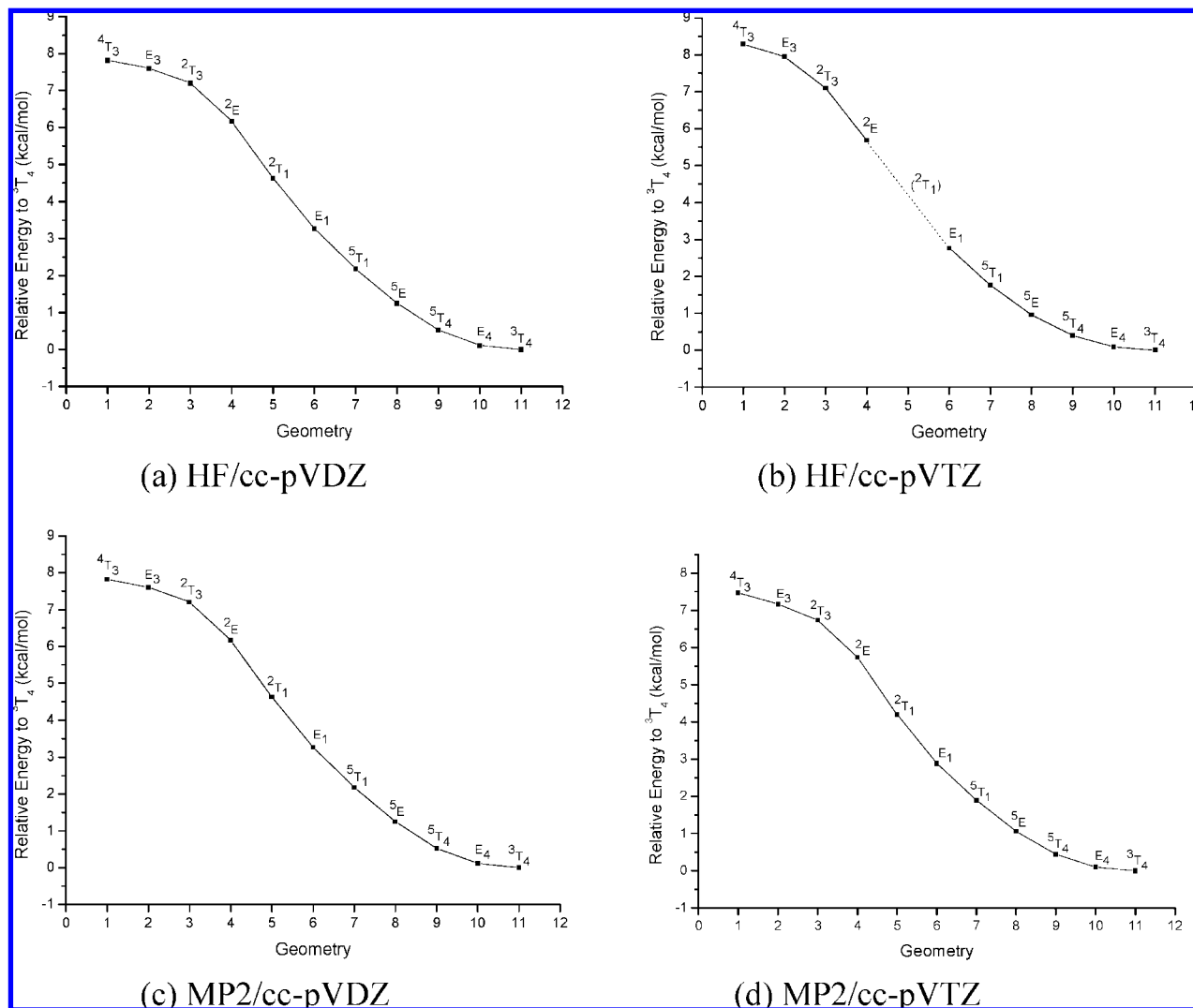


Figure 3. Potential energy curve connecting the all-*trans* conformations of P₅H₆⁺.

Table 1. Relative Energies (ΔE in kcal/mol), Lowest Vibrational Frequencies (ν_1 in cm^{-1}), and Zero Point Vibrational Energy (ZPVE in kcal/mol) for the Different Conformations of P₅H₆⁺^a

conf.	HF/cc- pVTZ			MP2/cc- pVTZ		
	ΔE	ν_1	ZPVE	ΔE	ν_1	ZPVE
⁴ T ₃	8.29	46.0 <i>i</i>	40.5	7.48	40.2 <i>i</i>	38.3
E ₃	7.95	37.5 <i>i</i>	40.6	7.17	1.4	38.4
² T ₃	7.10	45.5 <i>i</i>	40.6	6.74	34.7 <i>i</i>	38.4
² E	5.69	66.9 <i>i</i>	40.7	5.74	58.1 <i>i</i>	38.5
² T ₁	(n/a)			4.20	47.5 <i>i</i>	38.6
E ₁	2.77	36.0 <i>i</i>	40.7	2.89	34.5 <i>i</i>	38.6
⁵ T ₁	1.76	3.8	40.7	1.89	25.9 <i>i</i>	38.6
⁵ E	0.96	32.9	40.7	1.06	16.1	38.6
⁵ T ₄	0.40	48.1	40.7	0.44	44.5	38.6
E ₄	0.09	58.3	40.7	0.10	59.1	38.6
³ T ₄	0.00	61.7	40.7	0.00	63.5	38.6

^a The total energies (in hartree) are available in Supporting Information.

$\varphi = 198^\circ$ with HF/cc-pVTZ). Table 2 also shows that the energies for the two minima (³T₄ and ²E) are very close to each other. The conformation E₄ for P₅Me₆⁺, observed in the condensed phase experiments,¹ may arise from relatively larger crystal packing energies. The E₄ energy is predicted here to be only 0.01 kcal/mol higher than the minimum ³T₄.

Table 2. Relative Energies for the 11 Conformations of P₅Me₆⁺ at Different Levels of Theory

conf.	HF/cc-pVDZ	HF/cc-pVTZ	MP2/cc-pVDZ	MP2/cc-pVTZ// MP2/cc-pVDZ
⁴ T ₃	1.70	1.55	1.92	1.43
E ₃	1.20	1.13	1.27	0.83
² T ₃	0.36	0.38	0.47	0.09
² E	-0.10	-0.07	0.06	-0.25
² T ₁	0.02	-0.10	0.27	-0.03
E ₁	0.18	0.12	0.51	0.37
⁵ T ₁	0.17	(n/a)	0.35	0.33
⁵ E	0.10	0.09	0.16	0.17
⁵ T ₄	0.04	0.04	0.06	0.07
E ₄	0.01	0.01	0.01	0.02
³ T ₄	0.00	0.00	0.00	0.00

(c) Comparison with Tetrahydrofuran. There has been extensive experimental and theoretical research on the pseudorotation of tetrahydrofuran, a common chemical reagent with a five-membered ring.^{24–32} Rayon and Sordo³¹ used several *ab*

(24) Lafferty, W. J.; Robinson, D. W.; Stlouis, R. V.; Russell, J. W.; Strauss, H. L. *J. Chem. Phys.* **1965**, *42*, 2915.

(25) Engerhol, G. G.; Luntz, A. C.; Gwinn, W. D.; Harris, D. O. *J. Chem. Phys.* **1969**, *50*, 2446.

(26) Cadioli, B.; Gallinella, E.; Coulombeau, C.; Jobic, H.; Berthier, G. *J. Phys. Chem.* **1993**, *97*, 7844.

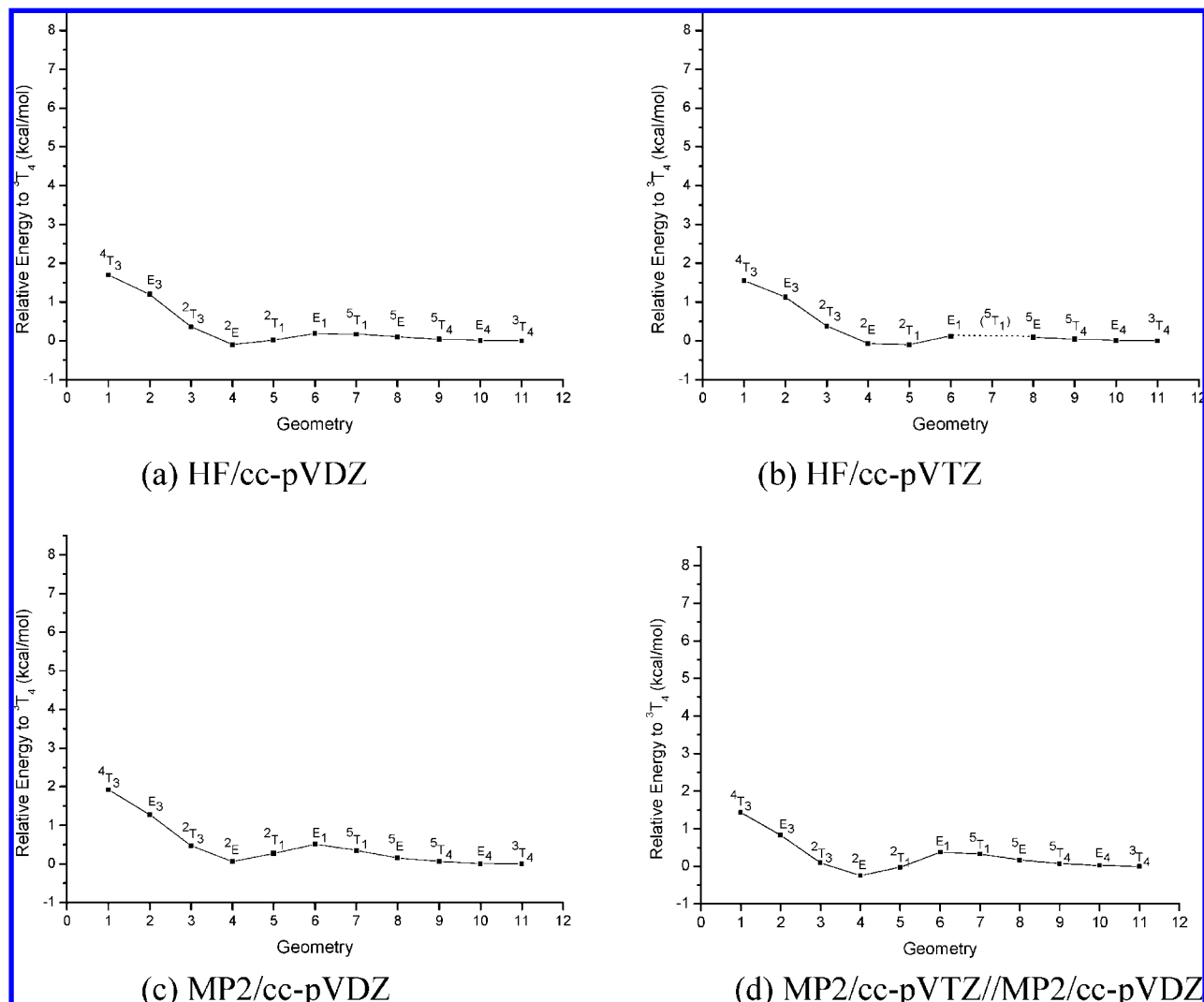


Figure 4. Potential energy curve connecting the all-*trans* conformations of $P_5Me_6^+$.

initio theoretical approaches, including the MP2 and CCSD(T) methods, and found that the pseudorotation potential curve is sensitive to the theoretical methods and basis sets. Even the order of maxima and minima switched at different levels. In contrast, our single point energies for the two extrema (4T_3 and 3T_4) of the $P_5H_6^+$ system at various levels of theory, including the CCSD(T) method, with a series of basis sets up to aug-cc-pVTZ all agree in these respects. The energy of the 4T_3 conformation always is higher than that of 3T_4 (Table 3). Thus, although the PES's for the $P_5H_6^+$ and $P_5Me_6^+$ systems differ qualitatively, both are simpler than that for tetrahydrofuran.

(d) Conformational analysis of $P_5H_6^+$ configurations. The full PES of cyclic $P_5H_6^+$, taking all possible conformations and configurations into account, obviously is more complex. There are six configurations of $PH_2(PH)_4^+$, with many possible

Table 3. Difference of Single-Point Energies of the MP2/cc-pVTZ Geometry (ΔE in kcal/mol) between the Two Extrema (4T_3 and 3T_4) of $P_5H_6^+$ at Various Levels of Theory^a

	ΔE (4T_3 - 3T_4)
MP2/cc-pVDZ	8.02
MP2/cc-pVTZ	7.48
MP2/aug-cc-pVDZ	7.50
MP2/aug-cc-pVTZ	7.51
CCSD/cc-pVDZ	7.55
CCSD/cc-pVTZ	7.58
CCSD/aug-cc-pVDZ	7.28
CCSD/aug-cc-pVTZ	7.35
CCSD(T)/cc-pVDZ	7.63
CCSD(T)/cc-pVTZ	7.55
CCSD(T)/aug-cc-pVDZ	7.27
CCSD(T)/aug-cc-pVTZ	7.13

^a The total energies (in hartree) are available in Supporting Information.

conformations for each. Consider the underlying P_5 ring as being planar. The configuration of the four PH units can either be “up” (U) or “down” (D) with respect to the ring. Thus, there are six possibilities: UDUD, UUUU, UUUD, UUDD, UDDU, and UDUU, each with conformational complexities. These six dispositions correspond to Buford's all-*trans* (TTT), as well as to all-*cis* (CCC), CCT, CTC, TCT, and TTC configurations.

- (27) Meyer, R.; Lopez, J. C.; Alonso, J. L.; Melandri, S.; Favero, P. G.; Caminati, W. *J. Chem. Phys.* **1999**, *111*, 7871.
 (28) Mamleev, A. H.; Gunderova, L. N.; Gallev, R. V. *J. Struct. Chem.* **2001**, *42*, 365.
 (29) Melnik, D. G.; Gopalakrishnan, S.; Miller, T. A.; De Lucia, F. C. *J. Chem. Phys.* **2003**, *118*, 3589.
 (30) Wu, A.; Cremer, D. *Int. J. Mol. Sci.* **2003**, *4*, 158.
 (31) Rayón, V. M.; Sordo, J. A. *J. Chem. Phys.* **2005**, *122*, 204303.
 (32) Yang, T. C.; Su, G. L.; Ning, C. G.; Deng, J. K.; Wang, F.; Zhang, S. F.; Ren, X. G.; Huang, Y. R. *J. Phys. Chem. A* **2007**, *111*, 4927.

Interconversion does not take place, as the inversion barriers at phosphorus are known to be very high (e.g., ca. 37 kcal/mol for PH_3).³³ However, the Buford's best all-axial conformation of the TTT form is confirmed here to be the global $PH_2(PH)_4^+$ minimum. The lowest energy geometries of the CCC, CCT, CTC, TCT, and TTC configurations are computed (at the B3LYP/6-311+G** level) to be at least 3.5 kcal/mol less stable than the 3T_4 TTT form.

Although the greater stability of the 3T_4 than 4T_3 conformation of $P_5H_6^+$ is easily explained in terms of reduced eclipsing interactions of the vicinal P–H bonds, the problem is more complicated if configurations other than the all *trans*-TTT form are considered. The energy of cisoid C_{2v} P_2H_4 , which has two eclipsed PH bonds as well as eclipsed lone pairs, is about 3.5 kcal/mol higher in energy than a transoid C_2 model conformation, which has one eclipsed and one anti vicinal PH pair and reduced vicinal lone pair repulsion. The 3T_4 global minimum is ideal, because all the PH conformations are axial and transoid. Its ring is closer to being planar. In contrast, the high energy all-equatorial 4T_3 TTT alternative has more nearly eclipsed cisoid conformations, and puckers to reduce these unfavorable interactions. Note that the energy differences between 4T_3 and 3T_4 given in Table 3 are approximately 3×3.5 kcal/mol. Also the 4T_3 TTT form is about 3.5 kcal/mol most stable than the best conformations of the CTT and TCT configurations, each of which has one cisoid C_{2v} P_2H_4 type arrangement.

Summary

Several $P_5R_6^+$ five-membered phosphorus ring derivatives have been synthesized and shown to have all-*trans* conforma-

tions by X-ray analysis.¹ The present computational studies of cyclic $P_5H_6^+$ and $P_5Me_6^+$ transversed the full ($0^\circ - 360^\circ$) pseudorotational circuit. The geometries were optimized, and the energies were obtained at high precision with HF and MP2 levels. (Higher level theoretical methods, e.g., CCSD(T), support the conclusions.)

The potential curves along the pseudorotational circle (Figure 1) for both $P_5H_6^+$ and $P_5Me_6^+$ were explored, in part by using some geometrical constraints. $P_5H_6^+$ has only one true minimum (3T_4) and one transition state (4T_3), whereas that for $P_5Me_6^+$ has two minima (3T_4 and 2E) along with the TS. The energy difference between the maximum and the minimum is 8.3 (HF) or 7.5 (MP2) kcal/mol for $P_5H_6^+$ and smaller, only 1.6 (HF) or 1.9 (MP2) kcal/mol for $P_5Me_6^+$. The energy differences between two neighboring conformations (such as E_4 and 3T_4 , not necessarily stationary points) along the pseudorotational circuit for $P_5Me_6^+$ may be as small as 0.01 kcal/mol. A conformational analysis of all possible $P_5H_6^+$ configurations confirms that the 3T_4 form to be the global minimum, since it avoids unfavorable eclipsing of PH–PH and lone pair–lone pair interactions. Consequently, all the geometrical possibilities boil down to a single conformation of a single configuration.

Acknowledgment. We are indebted to the 111 Project (B07012) in China and the U.S. National Science Foundation (Grants CHE-0749868 and CHE-0716718) for support of this work.

Supporting Information Available: Optimized geometries and total energies at different levels of theory. Complete refs 22–23. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA800177P

(33) See, R. F.; Dutoi, A. D.; McConnell, K. W.; Naylor, R. M. *J. Am. Chem. Soc.* **2001**, *123*, 2839.