JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 3
1990

Berry and Turnstyle Processes in the Pseudorotation of Three Phosphoranes

Peng Wang,[a] Dimitris K. Agrafiotis,[a] Andrew Streitwieser,*[a] and Paul von Raqué Schleyer*[b]

[a] *Department of Chemistry, University of California, Berkeley, CA 94720, U.S.A.*
[b] *Institut für Organische Chemie der Friedrich-Alexander-Universitat Erlangen-Nurnberg, D-8520 Erlangen, F.R.G.*

As shown by *ab initio* calculations, the transition states for pseudorotation of PH_5, PH_3F_2, and dioxaphospholene approximate the square pyramidal structures envisaged by Berry in his pseudorotation mechanism, but some of the transition vectors show displacements in accord with a 'turnstyle' process.

Nonrigid five-co-ordinated phosphoranes are subject to stereomutation. Based on analogy with vibrational bending modes for a trigonal bipyramid, Berry described these exchanges as a pseudorotation that involves a rapid rearrangement of ligand positions induced by a concerted axial–equatorial bond-bending motion that takes the structure through a square pyramidal transition state along a low energy pathway.[1] While an alternative 'turnstyle' process has been proposed by Ugi and his co-workers,[2] experimental results have generally been interpreted by the Berry mechanism.[3] Kutzelnigg and Wasilewski, however, have demonstrated that the two processes may be topologically equivalent.[4] To explore these processes further, the stereomutations of PH_5, PH_3F_2, and dioxaphospholene $\overline{\mathrm{PH_3(O{-}CH{=}CH{-}O}})$ shown in Scheme 1 have been chosen for investigation by *ab initio* methods.[5]

The structures (**1**)—(**8**) were fully optimized at the Hartree–Fock level using the 6-31G* basis set within the symmetry constraints shown in Scheme 1. The calculations were performed with the GAUSSIAN 86 suite of programs.[6] Harmonic vibrational frequencies and zero point energies were obtained from analytical second derivatives at the 6-31G* level.[7] Møller–Plesset perturbation theory up to MP4SDTQ (Frozen Core)/6-31G* was employed for the electron correlation correction.[8]

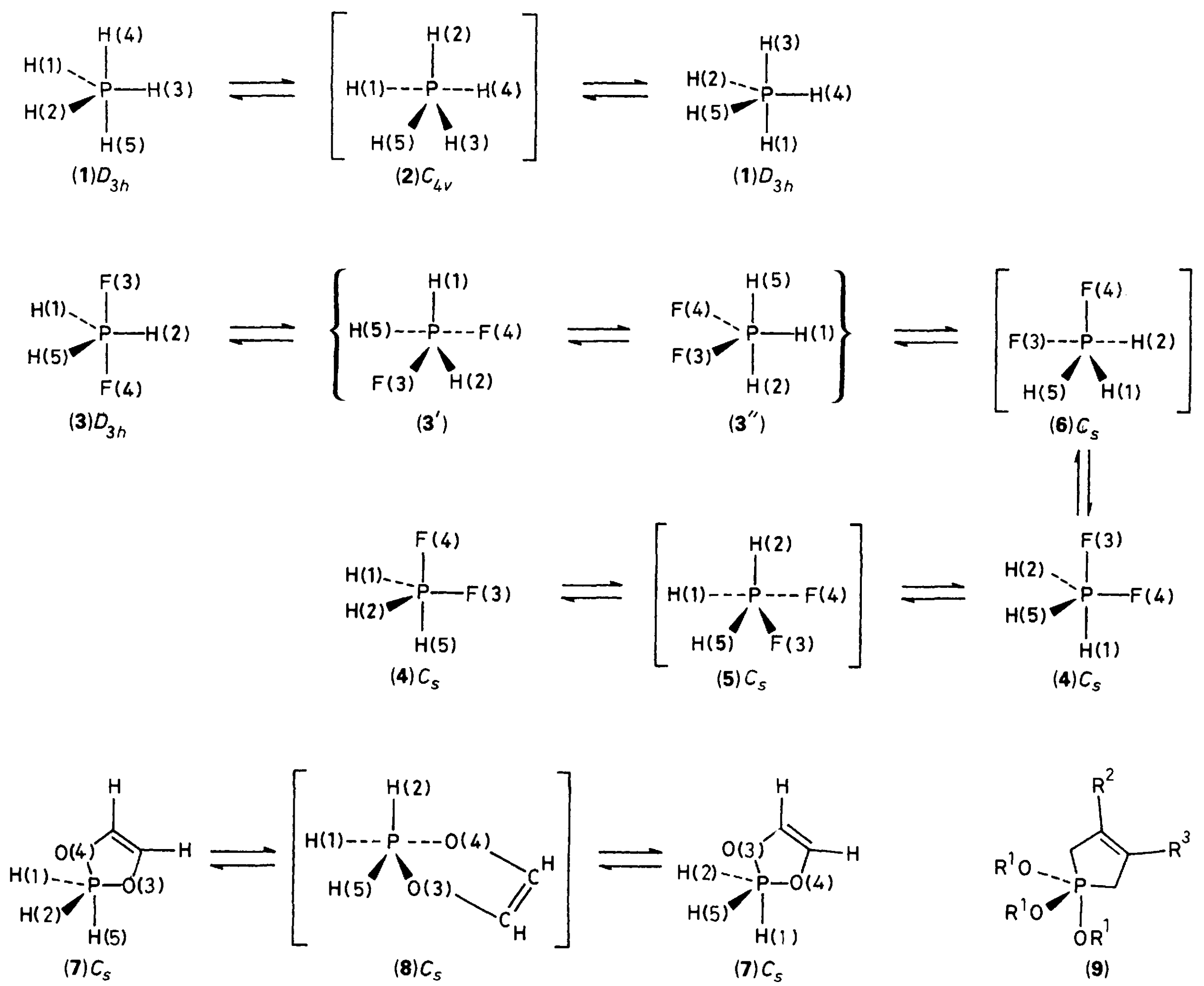
Berry pseudorotation is most simply illustrated by the calculations on the prototype phosphorane, PH_5. The square pyramid (**2**) is the transition state for pseudorotation of the trigonal bipyramidal structure (**1**) (Figure 1). The one imaginary frequency of (**2**) corresponds to displacement of the two opposite basal hydrogens, H(1) and H(3), upwards to form two axial bonds and displacement of the other two, H(4) and H(5), downwards to form two equatorial bonds in (**1**) (Figure 2). The pseudorotation barrier of only 4.7 kJ mol^{-1} at MP4SDTQ/6-31G*//6-31G* + zero point energies (ZPE) agrees well with the configuration interaction (CI) results of Kutzelnigg and Wasilewski (5.0 kJ mol^{-1}).[4] The 'turnstyle' process proceeds on the slope of a valley of the potential energy surface with no stationary transition state.

Difluorophosphorane, PH_3F_2, serves as a model for acyclic

Table 1. Calculated energies.[a]

	6-31G* //6-31G*	MP4SDTQ/ 6-31G* //6-31G*	Zero point energies[b] (ZPE) /kJ mol^{-1}	n[c]	Imaginary frequency /cm^{-1}	Relative energy[e] MP4SDTQ/ 6-31G*//6-31G* + ZPE/kJ mol^{-1}
(**1**)	−343.49988	−343.64586	121.75	0		0.00
(**2**)	−343.49536	−343.64324	119.62	1	458	4.73
(**3**)	−541.34889	−541.83611	91.00	0		0.00
(**4**)	−541.32844	−541.81735	90.29	0		48.57
(**5**)	−541.32350	−541.81376	88.95	1	355	56.65
(**6**)	−541.30890	−541.79894	88.87	1	443	95.50
(**7**)	−569.01482	−569.79451	181.88	0		0.00
(**8**)	−569.01128	−569.79342	181.33	1	294	2.30

[a] Energies are in a.u. [b] Zero point energies are scaled by 0.9. [c] The number of imaginary frequencies calculated at 6-31G*//6-31G*.



Scheme 1

disubstituted phosphoranes. The potential energy surface (PES) of PH_3F_2 was searched carefully at the 6-31G* level. Two energy minima [(**3**) and (**4**)] and two transition states [(**5**) and (**6**)] were found. The diapical structure (**3**) is the global minimum on the PES; the apical–equatorial structure (**4**) is a local minimum, 48.5 kJ mol^{-1} higher in energy than (**3**). From (**3**), the F–P–F angle was decreased in stages with full 6-31G* optimization of all the other parameters until (**4**) was reached. The result is illustrated in Figure 3. The conformations (**3′**) and (**3″**) in Scheme 1, which are assumed in the Berry mechanism, are not stationary points on the PES, structure (**6**) being the only transition state connecting (**3**) and (**4**). In this square pyramidal structure, (**6**), one of the two fluorines is at the apical position and the F–P–F angle is 104.2°. At our highest level, the barrier from (**3**) to (**4**) is 95.4 kJ mol^{-1}. From (**4**), the degenerate interconversion of the two fluorines involves another pseudorotation whose transition structure is (**5**), another square pyramidal conformation. The geometry of (**5**) is shown in Figure 1 along with the transition moments. In (**5**), the H(2)–P–H(1) and H(2)–P–F(3) angles are 101.8 and 103.6°, respectively, close to the 100.5° value of H(2)–P–H(1) in (**2**). The imaginary frequency for the transition state (**5**) is 355i cm^{-1}, less than the value in (**2**). At the transition state, basal hydrogen H(1) moves up to the apical position, while

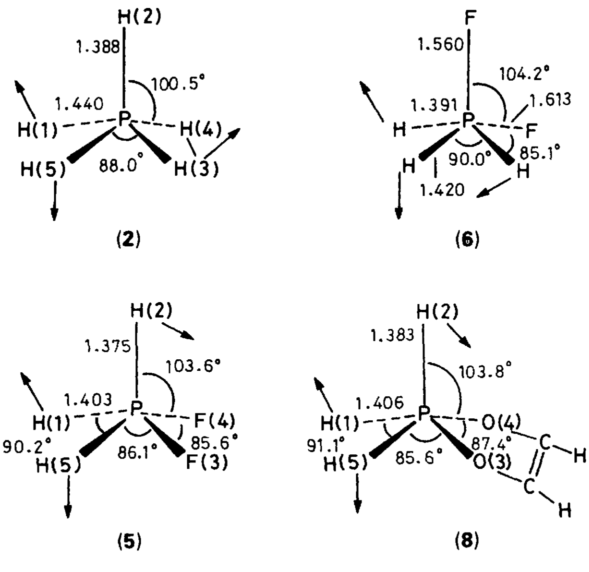


Figure 1. Geometric parameters of transition structures. Bond lengths in Å.

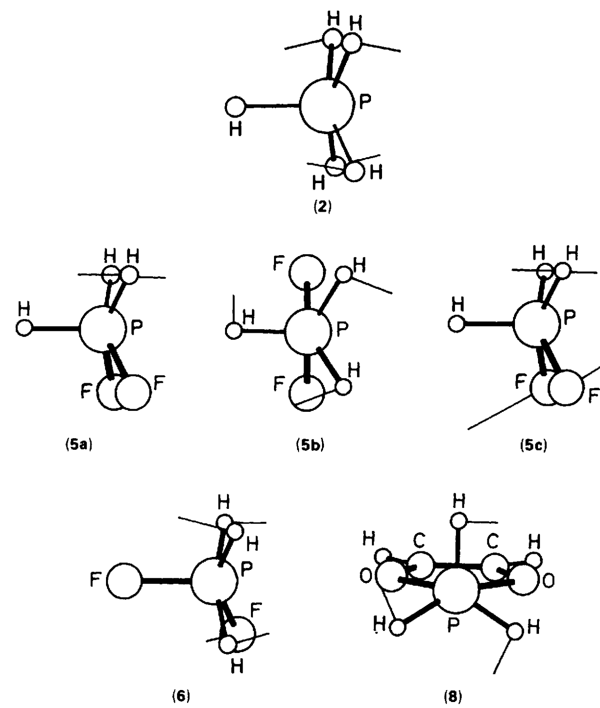


Figure 2. Optimised structures and transition moments.

basal hydrogen H(5) and apical hydrogen H(2) move down to form equatorial bonds in (**4**). The heavier atoms F(3) and F(4) hardly move (Figure 2). The barrier for exchange of the two fluorines in (**4**) is low, only 8.1 kJ mol^{-1} at our highest level.

The equivalence of the Berry and 'turnstyle' processes is shown very nicely by three different representations, (**a**), (**b**), and (**c**), for the transition structure (**5**) (Figure 2). In (**a**), the hydrogens appear to move in opposite directions relative to the heavy atoms which remain nearly fixed in the square pyramid. This conforms to the Berry model. In representation (**c**), where the displacement vectors associated with the fluorine atoms are arbitrarily magnified by a factor of 10 to reveal the direction of their motion, the analogy between (**2**) and (**5**) becomes apparent. However, in representation (**b**), seen along the F–P–F disector, the transition moments reveal a 'turnstyle' hydrogen motion and the system resembles remarkably the transition structure with the local symmetry properties envisaged by Ugi.[2]

Dioxaphospholene (**7**) is chosen as a general model for cyclic phosphoranes. Calculations show that the trigonal bipyramidal structure (**7**) is an energy minimum, with C_s symmetry, that undergoes degenerate pseudorotation *via* the square pyramidal transition state (**8**) (Figure 2). The structure and displacement vectors associated with the imaginary frequency (294i cm^{-1}) show close similarities with the acyclic transition structure (**5**); the set of three hydrogens bonded to phosphorus move in the same 'turnstyle' fashion as in (**5**) while the heavier atoms hardly move at all, and the H(2)–P–O and H(2)–P–H(5) angles are 107.8 and 100.9°, respectively (Figure 1), quite close to the corresponding values in (**5**). Transition state (**8**) is only 2.3 kJ mol^{-1} above the ground state (**7**). This result is totally consistent with experimental data. The ^{1}H NMR spectra of a series of phospholenes[9] (**9**) show only one doublet (spin coupling with phosphorus) in the methoxy region even at −100 °C, suggesting rapid positional exchange between equatorial and apical sites.

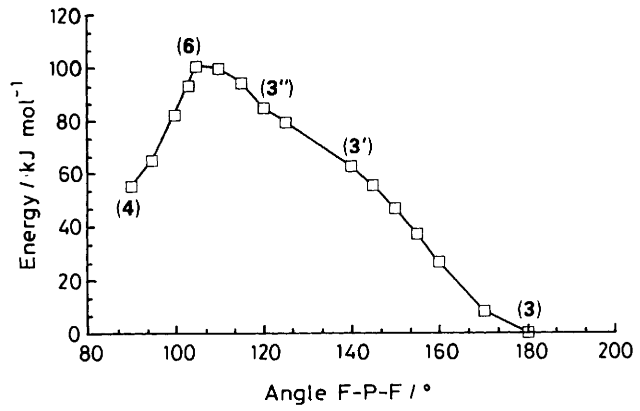


Figure 3. Relative energy (in kJ mol^{-1}) *vs.* the F–P–F angle in PH_3F_2.

We appreciate support from NSF, DFG, and a NATO grant. D. K. A. thanks the A. Onassis Foundation for financial support.

Received, 28th September 1989; Com. 9/04164H

References

1 R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.
2 I. Ugi, D. Marquarding, H. Klusacek, G. Gokel, and P. Gillespie, *Angew. Chem.*, 1970, **82**, 741; I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Acc. Chem. Res.*, 1971, **4**, 288.
3 R. R. Holmes, 'Pentacoordinated Phosphorus,' American Chemical Society, Washington, DC, 1980, vol. I, ch. 3; vol. II, ch. 2; for recent reviews, see R. R. Holmes, *Prog. Inorg. Chem.*, 1984, **32**, 119; P. Lemmen, R. Banmgartner, I. Ugi, and F. Ramirez, *Chem. Ser.*, 1988, **28**, 451; T. P. E. Auf der Heyde and H.-B. Bürgi, *Inorg. Chem.*, 1989, **28**, 3982.
4 W. Kutzelnigg and J. Wasilewski, *J. Am. Chem. Soc.*, 1982, **104**, 954; see also J. A. Altmann, K. Yates, and I. G. Csizmadia, *ibid.*, 1976, **98**, 1450.
5 For theoretical work on pentavalent phosphorus, see P. Wang, Y. Zhang, R. Glaser, A. E. Reed, P. v. R. Schleyer, and A. Streitwieser, *J. Am. Chem. Soc.*, submitted.
6 M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. M. Fleuder, and J. A. Pople, 'Gaussian 86,' Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
7 J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symp.*, 1976, **10**, 1; J. S. Binkley and J. A. Pople, *ibid.*, 1975, **9**, 229.
8 J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quantum Chem. Symp.*, 1981, **15**, 269; D. J. DeFrees and A. D. McLean, *J. Chem. Phys.*, 1985, **82**, 33.
9 D. Hellwinkel, 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, New York, vol. 3, 1972, p. 185.
10 D. K. Agrafiotis, A. Streitwieser, and H. S. Rzepa, MOLECULE, Quantum Chemistry Program Exchange Bulletin, **9**, 1989, Program 583.