Substituent Effects on Folding in Cyclotetraphosphane[1]

Wolfgang W. Schoeller* and Thilo Busch

Fakultät für Chemie der Universität Bielefeld,
Postfach 8640, W-4800 Bielefeld 1, F.R.G.

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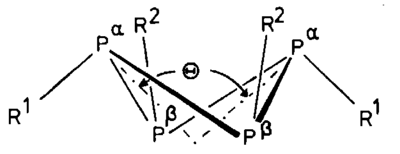
Ab initio quantum chemical calculations evidence a very flat potential hypersurface for folding of parent cyclotetraphosphane. This is in accord with a corresponding vibrational analysis. Electronegative substituents increase folding of the four-membered ring system.

Since the first unequivocal report in 1957 on the synthesis of a cyclotetraphosphane, **1** ($R = CF_3$)[2], meanwhile a plethora of structures have been characterized[3].



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Most noticeable, in these structures the interflap angle Θ in the four-membered ring moiety varies considerably. Pertinent examples of D_{2d} symmetrical structures are collected in Table 1.

Table 1. Folding angle Θ in D_{2d} symmetrically substitued cyclotetraphosphanes

$R^1 = R^2$	Θ [°]	Ref.
C(O)-*tert*-butyl	175.0	4)
tert-butyl	155.5	5)
C_6H_{11}	148.6	6)
C_6F_5	147.8	7)
2-OMe-Ph[a]	143.3	8)
CF_3	146.0	9)
TMP[b]	139.3	3)
$N(TMS)_2$[c]	134.5	3,10)

[a] 2-Methoxyphenyl. — [b] 2,2,6,6-Tetramethylperidyl. — [c] *N*-Bis-(trimethylsilyl).

In this paper we explore the effect of substituents on the geometry of **1** by means of quantum chemical calculations of the double-zeta qualitiy[11]. We will evidence that electronegative substituents at the phosphorus ring atoms induce folding of the four-membered ring moiety. (In the following we analyze vibrations and orbitals according to C_{2v} symmetry.)

For the parent compound **1** ($R = H$), the calculations result in an extremely flat potential hypersurface (Table 2).

Table 2. Potential energy hypersurface of parent cyclotetraphosphane (angles are in degrees, relative energies in kcal/mol)

Θ	*E* (SCF)[a]	*E* (SCF/MP2)[b]
183.7	0.0[c]	0.0[d,e]
130.0	2.67	0.79
150.0	1.11	0.46
190.0	0.08	−0.09
210.0	2.25	0.88

[a] At times optimized at the SCF level. — [b] At the SCF level[a] plus MP2 correction. — [c] *E* = −1365.173732 au. — [d] *E* = −1366.062818 au. — [e] The ring formation from two *trans*-P_2H_2 is exothermic by 40.21 (34.01) kcal/mol at the SCF (SCF/MP2) level.

The ring is almost planar, in contrast to most of the substituted structures (see Table 1). Furthermore, the introduction of electron correlation (at the MP2 level[12]) flattens the obtained electronic hypersurface. We have performed a vibrational analysis within the harmonic approximation[13] on parent compound **1**. The six energy-lowest vibrations can be assigned to the ring moiety, constituted of the phosphorus atoms. They are listed in Table 3[14].

Table 3. Frequencies of ring atoms in parent cyclotetraphosphane

No.	Frequency[a]	Symmetry	Intensity[b]	Type[c]
1	77.3	a_1	0.0	ring deformation, π
2	300.1	a_1	0.1	$P_\alpha P_\beta P_\alpha$ deformation, δ
3	466.1	b_2	1.1	$P_\alpha P_\beta$ stretching, ν
4	466.1	b_1	1.1	$P_\alpha P_\beta$ stretching, ν
5	478.5	a_1	0.0	$P_\alpha P_\beta$ stretching, ν
6	500.9	a_2	0.0[d]	$P_\alpha P_\beta$ stretching, ν

[a] In cm^{-1}. — [b] IR intensity with respect to the most intense (100.0) totally symmetric (a_1) PH vibration. — [c] Nomenclature according to F. Engelke, *Aufbau der Moleküle*, p. 69, B. G. Teubner, Stuttgart 1985. — [d] Vibration is only Raman-active.

The ring deformation (ν_1) is extremly low in energy. It refers to the puckering motion in the four membered ring. Hence, the results indicate a highly flexible geometry of the

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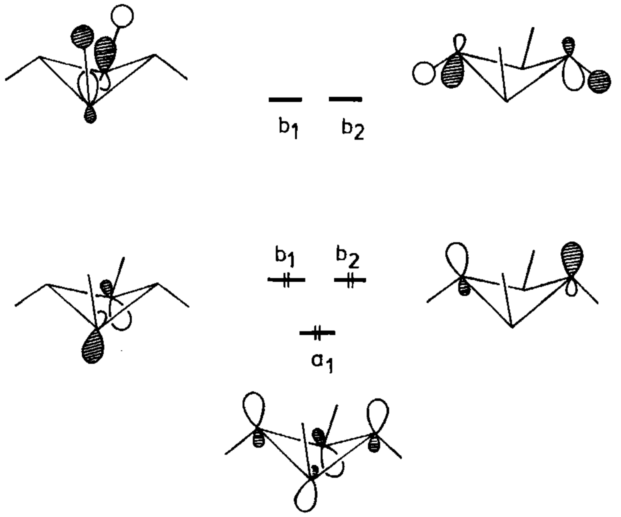
parent cyclotetraphosphane. The calculations predict vibrations of almost negligible IR intensity (ν_6 is not IR-active).

Consider next the replacement of the hydrogens at phosphorus by electronegative groups, e.g. fluorine. In the equilibrium geometry of parent **1** two energetically highest occupied molecular orbitals (HOMOs) refer to a pair of antibonding combinations of lone pairs at phosphorus. The computed orbital energies are −9.1 eV ($8b_1$, $8b_2$) for both orbitals.



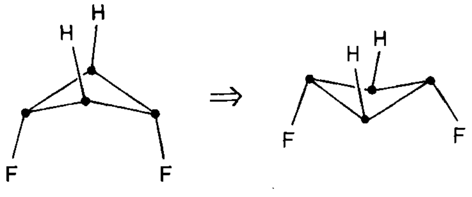
Of lower energy is an orbital, computed to −10.5 eV ($13a_1$). It refers to a combination of lone pairs located at all phosphorus atoms. The corresponding LUMOs are combinations of orbitals which are mainly PH antibonding[15]. The assignment may be compared with the results of detailed photoelectron spectroscopic investigations[16]. The pair of LUMOs bear a coefficient at the hydrogens, in contrast to their counterparts. The replacement of the hydrogens by electronegative substituents lowers the unoccupied molecular orbitals. Consequently, they will mix into the pair of HOMOs. As a consequence, the latter will acquire more s-character and decrease their 1,3-antibonding through-space[17] interaction. It causes a stronger folding of the four-membered ring system, since then the 1,3-bonding (through-space) overlap of lone pair orbitals comes to the fore[18].

In order to put these considerations on firmer ground we have performed corresponding calculations on model-substituted cyclotetraphosphanes. The results for the most important geometrical parameters are summarized in Table 4. For completeness, we have also included the results for the parent compound **1** (R = H). The calculations substantiate the predication that electronegative substituents increase folding of the ring moiety. Of all the various possible conformations only the listed ones are stable entities on the corresponding electronic hypersurfaces, e.g. for the case R^1 = H, R^2 = F two possible conformations are feasible.

Table 4. Geometrical parameters (bond lengths in Å, bond angles in degrees) of various model substituted cyclotetraphosphanes

No.	R^1	R^2	PP	Θ	$P_\beta P_\alpha P_\beta$ ($R^1P_\alpha P_\beta$)	$P_\alpha P_\beta P_\alpha$ ($R^2P_\beta P_\alpha$)
1a[a]	H	H	2.242	183.7	90.0 (95.8)	90.0 (95.8)
1b	H	F	2.230	139.3	87.4 (98.7)	85.4 (100.6)
1c	F	F	2.231	126.8	83.6 (100.9)	83.6 (100.9)
1d	SiH_3[b]	H	2.244	179.9	90.3 (102.1)	89.7 (96.0)
1e	SiH_3[b]	F	2.225	143.3	88.7 (104.3)	85.5 (101.1)

[a] See also H. Schiffer, R. Ahlrichs, M. Häser, *Theor. Chim. Acta* **75** (1989) 1. — [b] SiH_3 staggered to the lone pair at adjacent phosphorus.



a b

In **a** the two nonbonding lone pairs at P(F) are in *trans* orientation and at P(H) in *cis* orientation to each other. In **b** the orientation of lone pairs is opposite. A detailed search on the electronic hypersurface indicates that **a** is not an energy minimum, it readily rearranges without any energy barrier to conformation **b**. This is due to the fact that a geometry is preferred in which the lone pairs with the strongest s-character display the least antibonding through-space interaction. Hence, they adopt *cis* orientation. As a further consequence of electronegative substitution at phosphorus the sum of angles ∢ PPP decreases. The corresponding values (in degrees) are: **1a**: 359.9, **1b**: 345.5, **1c**. 334.5, **1d**: 360.0, **1e**: 348.4.

Summary

The present investigations reveal a very flat potential energy surface for the parent cyclotetraphosphane, as indicated by the vibrational analysis and the calculations of various conformations. Electronegative substituents at phosphorus tend to promote puckering of the four-membered ring moiety. On this basis one expects that the large variety in conformations is determined by a combination of electronic and steric effects acting on the ring system.

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CAS Registry Numbers

1a: 132617-16-4 / **1b**: 132513-43-0 / **1c**: 132513-44-1 / **1d**: 132513-45-2 / **1e**: 132539-24-3

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[1] Dedicated to Professor *Ekkehard Fluck* on the occasion of his 60th birthday.

[2] W. Mahler, A. B. Burg, *J. Am. Chem. Soc.* **79** (1957) 251; *ibid.* **80** (1958) 6161.

[3] [3a] M. Nieger, *Dissertation*, University of Bonn, 1989. — [3b] R. Appel, D. Gudat, E. Niecke, M. Nieger, C. Porz, H. Westermann, *Z. Naturforsch.*, submitted for publication.

[4] R. Appel, V. Barth, F. Knoch, unpublished results, cited in ref.[3a].

[5] W. Weigand, A. W. Cordes, P. N. Swepston, *Acta Crystallogr., Sect. B*, **37** (1981) 1631.

[6] J. C. Bart, *Acta Crystallogr., Sect. B*, **25** (1969) 762.

[7] F. Sanz, J. J. Daly, *J. Chem. Soc. A*, **1971**, 1083.

[8] L. Heuer, M. Sell, R. Schmutzler, D. Schomburg, *Polyhedron* **6** (1987) 1295.

[9] G. J. Palenik, J. Donohue, *Acta Crystallogr.* **15** (1962) 564.

[10] E. Niecke, R. Rüger, *Angew. Chem.* **95** (1983) 154; *Angew. Chem., Intern. Ed. Engl.* **22** (1983) 155.

[11] All structures were determined at a (single determinant) SCF level, utilizing the TURBOMOLE program system. [M. Häser, R. Ahlrichs, *J. Comput. Chem.* **10** (1989) 104]. The energy minima were optimized to an accuracy of 10^{-8} au. Thus, we obtained bond lengths (bond angles) to an accuracy of 0.001 Å (0.02 degrees). The basis sets were constructed from Huzinaga bases. S. Huzinaga, *Approximate atomic functions II*, Technical Report, The University of Alberta, Edmonton, Alberta, Canada 1971. They are as follows: F (9s,5p) in the contraction [5, 4 × 1/3, 2 × 1] + 1d (ζ = 1.4); P, Si (11s, 7p) [5, 6 × 1/4, 3 × 1] + 1d (0.5; 0.4); H (4s) [3, 1] + 1p (0.65).

[12] A. Szabo, N. S. Ostlund, *Modern Quantum Chemistry*, McGraw-Hill, Inc., New York, 1989.

[13] The IR intensitites were determined by an analysis of the dipol moment operator.

[14] The vibrations ν_7 to ν_{18} are (IR intensities and symmetries in parentheses, with respect to C_{2v} symmetry): 678.8 (13.5, a_1); 687.8 (1.1, b_2); 687.8 (1.1, b_2); 735.6 (a_2, IR-inactive); 894.9 (0.0, a_1); 988.4 (0.7, b_1); 988.4 (0.7, b_2); 1046.9 (a_2, IR-inactive); 2533.6 (0.0, a_1); 2541.5 (5.6, b_1); 2541.5 (5.6, b_2); 2553.4 (100.0, a_1).

[15] In more detail, by interaction with the degenerate set of peripheral Walsh ring orbitals [see R. Hoffmann, R. B. Davidson, *J. Am. Chem. Soc.* **93** (1971) 5699] one obtains two degenerate set of molecular orbitals. For a detailed discussion see ref.[16]).

[16] R. Gleiter, M. C. Böhm, M. Baudler, *Chem. Ber.* **114** (1981) 1004. – A. H. Cowley, M. J. S. Dewar, M. Lattman, J. L. Mills, M. McKee, *J. Am. Chem. Soc.* **100** (1978) 3349.

[17] For the distinction between through-space and through-bond interaction see R. Hoffmann, *Acc. Chem. Res.* **4** (1971) 1. – R. Gleiter, *Angew. Chem.* **86** (1974) 770; *Angew. Chem., Intern. Ed. Engl.* **13** (1974) 696.

[18] The four lone pairs at the phosphorus atoms form in addition two combinations of lone pairs[16]. They are 1,3-bonding through-space. Hence puckering of the four-membered ring systems is the result of a detailed balance of two 1,3-bonding (a_1) and two 1,3-antibonding (b_1, b_2) interactions. For a detailed pictorial representation see ref.[16].

[11/91]