

Determination of the nature of the conformational transmission effect in pentacoordinated phosphorus compounds

Citation for published version (APA):

Genderen, van, M. H. P., Koole, L. H., Scheper, olde, B. C. C. M., Ven, van de, L. J. M., & Buck, H. M. (1987). Determination of the nature of the conformational transmission effect in pentacoordinated phosphorus compounds. *Phosphorus and Sulfur and the Related Elements*, 32(1-2), 73-80.
<https://doi.org/10.1080/03086648708080654>

DOI:

[10.1080/03086648708080654](https://doi.org/10.1080/03086648708080654)

Document status and date:

Published: 01/01/1987

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

DETERMINATION OF THE NATURE OF THE CONFORMATIONAL TRANSMISSION EFFECT IN PENTACOORDINATED PHOSPHORUS COMPOUNDS

MARCEL H. P. VAN GENDEREN,* LEO H. KOOLE,
BERND C. C. M. OLDE SCHEPER,‡ LEO J. M. VAN DE VEN and
HENK M. BUCK

*Department of Organic Chemistry, Eindhoven University of Technology, 5600
MB Eindhoven, The Netherlands*

(Received June 30, 1986)

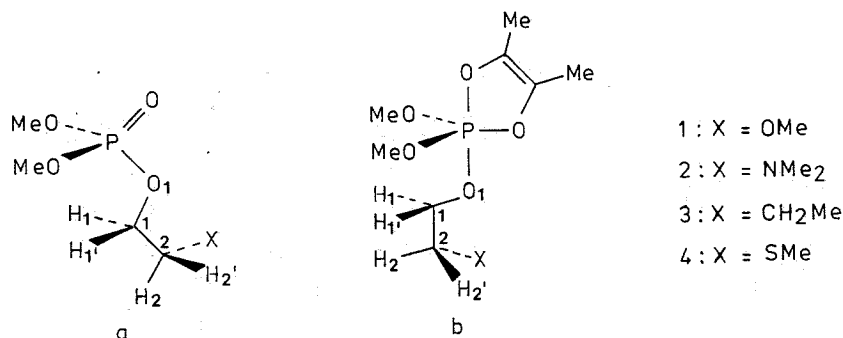
A high resolution $^1\text{H NMR}$ study of several 4- and 5-coordinated (TBP) phosphorus compounds enabled us to determine the nature of the conformational transmission effect, which describes the influence of the phosphorus coordination on the molecular conformation. Of great use was the accurate determination of the J_{POMe} coupling constant, with which the pseudorotational equilibrium around the pentacoordinated phosphorus can be described. It was determined that conformational transmission is purely electrostatic in origin, due to a larger charge density in the axis of the TBP structure. These findings were corroborated with quantumchemical calculations.

INTRODUCTION

Recently, a group of studies has been presented of model systems for nucleotides,¹ phospholipids,² and 6-phosphorylated pyranosides³ that incorporate a pentacoordinated phosphorus (P^{V}) with trigonal bipyramidal geometry (TBP). The P^{V} TBP moiety in these compounds is a stabilized analogue of the transient P^{V} structures that can be formed in phosphate groups by temporary attachment of a fifth ligand (e.g., a solvent molecule). Compared with their P^{IV} counterparts, the P^{V} TBP systems show distinct conformational changes, and it was argued that transient P^{V} formation can therefore have a trigger function for structural changes in e.g. nucleic acids and membranes. The conformational transmission effect on going from P^{IV} to P^{V} TBP in the model systems is based on an increased conformational preference for trans location of the vicinal oxygens in the common $\text{P}-\text{O}-\text{C}-\text{C}-\text{O}$ fragment, leading to the explanation that an enhanced charge repulsion between the oxygens is the cause of this effect. In order to further investigate this idea, we have synthesized compounds **1a,b-4a,b**, and have determined their C_1-C_2 conformations with 300 MHz $^1\text{H NMR}$. These models have substituents with various electronic properties, which allows for the determination of the nature of the conformational transmission effect.

* Author to whom all correspondence should be addressed.

‡ Present address: DSM Research, Geleen, The Netherlands.



RESULTS AND DISCUSSION

*C*₁-*C*₂ Conformational Analysis

The conformation around the *C*₁-*C*₂ bond is an equilibrium between the three staggered rotamers, but as two of these rotamers are mirror images and have identical populations, we use a two-state description with a gauche (*g*) and a trans (*t*) state (Figure 1). The population densities x_g and x_t of these states can be determined from the vicinal proton-proton coupling constant J_{12} , which is a mixture of the coupling constants in the two states: $J_{12} = x_g J_g + x_t J_t$, with $x_g + x_t = 1$. The values of J_g and J_t can be calculated with the semi-empirically modified Karplus relation as developed by Haasnoot *et al.*⁴ (Table I). This relation explicitly accounts for electronegativity and orientation of the non-hydrogen substituents.

P^{IV} Compounds **1a-4a**

The *C*₁-*C*₂ conformations⁵ of **1a-4a** (Table II) accurately reflect the properties of the substituents. In **3a**, the *C*₁-*C*₂ bond tends strongly to the sterically favorable trans conformation. Replacement of CH₂Me by OMe or NMe₂ in **1a** resp. **2a** causes a distinct preference for the gauche state, due to the well-known gauche effect.⁶ The electrostatic repulsion between the hetero atoms is fully expressed in **4a**, since it is known that no gauche effect operates between O and S.^{6b} Although sulfur nominally has the same electronegativity as carbon,⁴ there is a charge

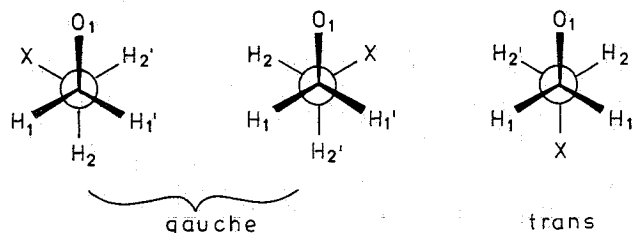


FIGURE 1 Staggered rotamers around the *C*₁-*C*₂ bond.

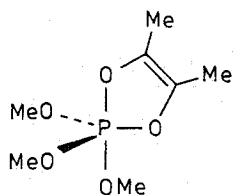
TABLE I
 Calculated coupling constants for 1-4

Compd.	$J_g(\text{Hz})$	$J_t(\text{Hz})$
1 X = OMe	4.13	7.46
2 X = NMe ₂	4.69	7.66
3 X = CH ₂ Me	4.83	7.91
4 X = SMe	4.83	7.91

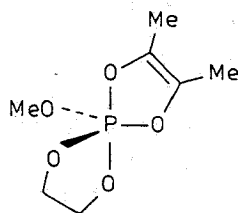
density on sulfur due to the ability of sulfur to use its d-orbitals as polarization functions.⁷ Correspondingly, a strong preference for trans orientation of O₁ and S is found in 4a.

Pseudorotational Analysis

In the P^V TBP compounds rapid pseudorotation⁸ around the pentacoordinated phosphorus obscures the C₁-C₂ conformational analysis, as an average conformation of axial and equatorial OCCX fragments is observed. The axial site in the TBP carries a higher negative charge than the equatorial site,⁹ so it is necessary to separate their contributions to the C₁-C₂ conformation. In earlier work^{1,3} this was accomplished by placing three identical groups on the interchanging positions. We now introduce a method that uses the fact that equatorial or axial location of a methoxy group in a TBP influences the phosphorus-proton coupling constant J_{POMe} .¹⁰ An accurate¹¹ measurement of the J_{POMe} coupling constant in 5 and 6 allowed us to determine the equatorial and axial phosphorus-proton coupling constants J_{eq} and J_{ax} . Taking into account the strain rule for P^V TBP



5



6

systems, stating that five-membered rings preferentially span an axial-equatorial location,¹² one sees that the three methoxy groups in 5 are distributed over two

 TABLE II
 C₁-C₂ Conformations of 1a-4a

Compd.	$J_{12}(\text{Hz})$	x_g	x_t
1a X = OMe	4.6	0.84	0.16
2a X = NMe ₂	5.8	0.61	0.39
3a X = CH ₂ Me	6.5	0.47	0.53
4a X = SMe	6.8	0.37	0.63

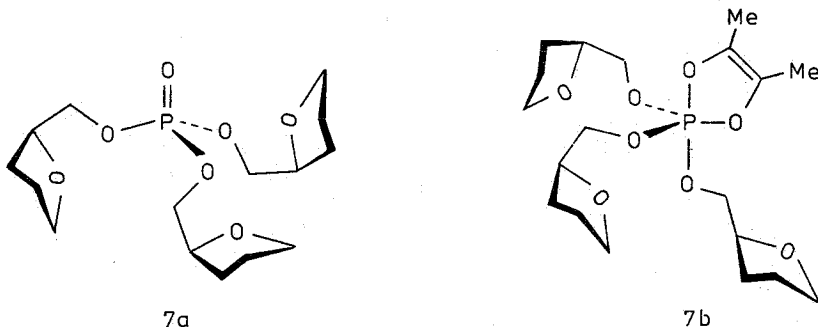
TABLE III
Full C₁-C₂ conformational analysis of **1b** at various temperatures

T(K)	J_{POMe} (Hz)	y	J_{12} (Hz)	x_g^a	x_t^a	$x_{g,\text{eq}}$	$x_{t,\text{eq}}$	$x_{g,\text{ax}}$	$x_{t,\text{ax}}$
295	13.06	0.37	5.03	0.72	0.28	0.86	0.14	0.56	0.44
285	13.06	0.37	5.01	0.74	0.26	0.87	0.13	0.55	0.45
267	13.04	0.36	4.93	0.76	0.24	0.88	0.12	0.53	0.47
249	13.06	0.37	4.84	0.79	0.21	0.90	0.10	0.50	0.50
244	13.04	0.36	4.81	0.80	0.20	0.90	0.10	0.49	0.51

$\Delta H_{\text{eq}}^0 = -4.4 \text{ kJ/mol}$	$\Delta H_{\text{ax}}^0 = 3.3 \text{ kJ/mol}$
$\Delta S_{\text{eq}}^0 = -5.5 \text{ J/mol.K}$	$\Delta S_{\text{ax}}^0 = 7.5 \text{ J/mol.K}$

^a Measured under rapid pseudorotation conditions.

equatorial and one axial site, while in **6** the methoxy group is forced to remain in an equatorial site. From this it follows that $J_{\text{POMe}}(\mathbf{5}) = (J_{\text{ax}} + 2J_{\text{eq}})/3$ and $J_{\text{POMe}}(\mathbf{6}) = J_{\text{eq}}$. As we measured a J_{POMe} coupling constant for **5** and **6** of 13.02 and 13.80 Hz resp., it can be derived that $J_{\text{eq}} = 13.80 \text{ Hz}$ and $J_{\text{ax}} = 11.43 \text{ Hz}$. For the compounds **1b-4b**, we are interested in the equilibrium between axial location of the OCCX fragment ($J_{\text{POMe}} = J_{\text{eq}} = 13.80 \text{ Hz}$) and equatorial location ($J_{\text{POMe}} = (J_{\text{ax}} + J_{\text{eq}})/2 = 12.62 \text{ Hz}$). The fraction y with OCCX axial can be determined from the measured J_{POMe} with: $y = (J_{\text{POMe}} - 12.62)/(13.80 - 12.62)$. As a test of this new method for assessing the pseudorotational equilibrium, we performed a detailed conformational study of **1b**. The results of this study can be compared with earlier work on **7a,b**, which have a highly similar conformation¹ ($x_t(\mathbf{1a}) = 0.16$ and $x_t(\mathbf{7a}) = 0.17$; $x_t(\mathbf{1b}) = 0.28$ and $x_t(\mathbf{7b}) = 0.32$). Using variable temperature experiments, the equatorial and axial conformations were separated (see Appendix). The results (Table III) compare favorably with the axial and equatorial conformations of **7b** ($x_{t,\text{ax}} = 0.65$ and $x_{t,\text{eq}} = 0.27$ at 295 K¹). Only in



the axis of the TBP a change in conformation occurs, while the equatorial site behaves virtually identical to the P^{IV} situation. Therefore the further conformational analysis will be performed with $x_{g/t,\text{eq}} = x_{g/t,\text{P}^{\text{IV}}}$.

P^V TBP Compounds **1b-4b**

Upon increasing the phosphorus coordination from four to five, a shift in conformational preference toward the trans state is observed for **1**, **2**, and **4**,

TABLE IV
Full C₁-C₂ conformational analysis of **1b-4b** at 300 K

Compd.	J_{POMe} (Hz)	y	J_{12} (Hz)	x_g^a	x_t^a	$x_{g,\text{eq}}$	$x_{t,\text{eq}}$	$x_{g,\text{ax}}$	$x_{t,\text{ax}}$
1b X = OMe	13.05	0.36	5.0	0.72	0.28	0.84	0.16	0.51	0.49
2b X = NMe ₂	13.02	0.34	6.2	0.47	0.53	0.61	0.39	0.21	0.79
3b X = CH ₂ Me	12.93	0.26	6.4	0.48	0.52	0.47	0.53	0.50	0.50
4b X = SMe	13.12	0.42	7.0	0.28	0.72	0.37	0.63	0.17	0.83

^a Measured under rapid pseudorotation conditions.

whereas in **3** no change occurs (Table IV). As the presence of the TBP geometry in **3b** does not affect the C₁-C₂ conformation compared to **3a**, the conformational transmission is not based on steric interactions. A possible influence via a diminished gauche effect in **1b** and **2b** is ruled out by the occurrence of conformational transmission in **4b**. Especially this latter compound demonstrates that only electrostatic repulsion between the hetero atoms can be the cause of the change in conformation. This is consistent with the fact that only in the axis of the TBP (with a higher charge density) conformational transmission is encountered. Furthermore, the thermodynamic parameters that were obtained for **1b** (see Table III) indicate that the effect is enthalpy-controlled, as is expected for an electrostatic repulsion. Comparison of the driving forces of the conformational transmission in **1-4** is possible when we express each C₁-C₂ conformation as the difference in free energy (ΔG^0) between the gauche and trans state (see Appendix). The change in this free energy difference on going from the P^{IV} situation to axial location in the P^V TBP compounds ($\Delta\Delta G^0$) reflects the magnitude of the conformational change. The results (Table V) show indeed a greater change for the more electronegative substituents. In fact, a relation can be found with the charge density on the atom in the X substituent that is vicinal to O₁ (vide infra). This again demonstrates the electrostatic nature of conformational transmission.

Quantumchemical Calculations

Calculations were performed with the MNDO method¹³ on the systems **1a-4a**, and **1b** (with OCCX axial). For **1a** and **1b**, enthalpies of formation (ΔH_f) were obtained after relaxation of the molecular geometry in the gauche and trans states of the C₁-C₂ bond. From these data we could abstract the enthalpy differences

TABLE V
Driving force of the conformational transmission in **1-4**

Compd.	ΔG^0 (kJ/mol) P ^{IV}	ΔG^0 (kJ/mol) P ^V axial	$\Delta\Delta G^0$ (kJ/mol)
1 X = OMe	-2.4	1.6	4.0
2 X = NMe ₂	0.6	5.0	4.4
3 X = CH ₂ Me	2.0	1.7	-0.3
4 X = SMe	3.1	5.7	2.6

TABLE VI
Calculated enthalpies of formation of the states in **1a** and **1b**

		$\Delta H_f(\text{kJ/mol})$	$\Delta H_{gt}(\text{kJ/mol})$
1a	gauche	-851.78	-1.55
	trans	-850.23	0
1b	gauche	-1231.45	2.88
	trans	-1234.33	0

(ΔH_{gt}) for the gauche \rightleftharpoons trans equilibrium (Table VI). It is obvious that the gauche state is more favored in **1a**, while the trans state has the lowest enthalpy in **1b**. As was also found experimentally, there is a reversal in the sign of the enthalpy difference. The magnitude of the enthalpy change between **1a** and **1b** (4.5 kJ/mol) is somewhat smaller than the experimental value (7.7 kJ/mol). On going from P^{IV} to axial location in the P^V TBP, the electron density on O₁ increases from 0.48 e.u. to 0.59 e.u., consistent with the experimental findings (i.e., enhanced repulsion). The electron density on the equatorial oxygen remains 0.48 e.u. The susceptibility of the X substituent for electrostatic interactions is determined by the charge density on the atom that is vicinal to O₁. Calculation of these charge densities in **1a-4a** indeed yields a correspondence with the driving force of the conformational change (see Table V): O, -0.36; N, -0.33; C, -0.02; S, -0.15.

Concluding Remarks

The present conformational study of **1-4** has clearly shown that the conformational transmission effect is due to an electrostatic repulsion, caused by the increased charge on the axial oxygen in the TBP. This explanation is confirmed by quantumchemical calculations. The accurate measurements of the phosphorus-proton coupling constant J_{POMe} has proved to be a useful technique for characterizing the pseudorotation around the pentacoordinated phosphorus.

APPENDIX

Defining $\Delta G^0 = G_t^0 - G_g^0$, we get the Boltzmann distribution $x_g/x_t = 2 \exp(-\Delta G^0/RT)$, or $\Delta G^0 = -RT \ln(x_g/2x_t)$, where the factor two accounts for the two-fold degeneracy of the gauche state. With $x_g + x_t = 1$, we can write:

$$x_g = \frac{\exp(-\Delta G^0/RT)}{\frac{1}{2} + \exp(-\Delta G^0/RT)}$$

Since this equation holds both for the axial and the equatorial conformation, one can deduce with $\Delta G^0 = \Delta H^0 - T\Delta S^0$:

$$x_g = yx_{g,\text{ax}} + (1-y)x_{g,\text{eq}} = y \frac{\exp(-\Delta H_{\text{ax}}^0/RT) \cdot \exp(\Delta S_{\text{ax}}^0/R)}{\frac{1}{2} + \exp(-\Delta H_{\text{ax}}^0/RT) \cdot \exp(\Delta S_{\text{ax}}^0/R)} + (1-y) \frac{\exp(-\Delta H_{\text{eq}}^0/RT) \cdot \exp(\Delta S_{\text{eq}}^0/R)}{\frac{1}{2} + \exp(-\Delta H_{\text{eq}}^0/RT) \cdot \exp(\Delta S_{\text{eq}}^0/R)}$$

As x_g and y are known for each temperature, four unknown quantities remain, allowing a set of four equations based on measurements at four temperatures to be solved.¹⁴

EXPERIMENTAL

Solvents and materials were reagent grade, and were used as received or purified as required. Reactions were run under an atmosphere of dry nitrogen. ¹H NMR spectra were run in the FT mode on a Bruker CXP-300 spectrometer at 300.1 MHz. For more details, see notes 5 and 11. Samples were dissolved in acetone-*d*₆, unless stated otherwise, and chemical shifts were related to TMS ($\delta = 0$). Coupling constants were taken from the expansions, and were simulated with the PANIC program.¹⁵ ³¹P NMR spectra were run at 36.4 MHz on a Bruker HX-90R spectrometer with a Digilab FT-NMR3 pulsing accessory. Chemical shifts were referenced against 85% H₃PO₄ ($\delta = 0$), and were designated positive downfield of this standard. Compounds 5 and 6 were prepared according to Ramirez.¹⁶ Phosphites were prepared as in ref. 1.

2-Methoxyethyl Dimethyl Phosphite. B.p. 68°C/30 mmHg. ³¹P NMR: δ 145.2 ¹H NMR: δ 3.48 (3H, s, OCH₃), 3.63 (6H, d, OCH₃, $J_{\text{POMe}} = 10.6$ Hz), 3.68 (2H, m, H_{2'2'}), 4.05 (2H, m, H_{1'1'}). *N,N-Dimethyl-2-aminoethyl Dimethyl Phosphite*. B.p. 70°C/30 mmHg. ³¹P NMR: δ 145.0. ¹H NMR: δ 2.31 (6H, s, NCH₃), 2.56 (2H, t, H_{2'2'}), 3.57 (6H, d, OCH₃, $J_{\text{POMe}} = 10.4$ Hz), 3.95 (2H, dt, H_{1'1'}). *n-Butyl Dimethyl Phosphite*. B.p. 80°C/40 mmHg. ³¹P NMR: δ 145.0. ¹H NMR: δ 1.02 (3H, t, CH₃), 1.43–1.57 (2H, m, CH₂), 1.62–1.73 (2H, m, H_{2'2'}), 2.55 (6H, d, OCH₃, $J_{\text{POMe}} = 10.4$ Hz), 3.88 (2H, dt, H_{1'1'}). *2-Methylthioethyl Dimethyl Phosphite*. B.p. 72°C/30 mmHg. ³¹P NMR: δ 145.0. ¹H NMR: δ 2.21 (3H, s, SCH₃), 2.79 (2H, t, H_{2'2'}), 3.57 (6H, d, OCH₃, $J_{\text{POMe}} = 10.5$ Hz), 4.02 (2H, dt, H_{1'1'}).

Phosphates. All phosphates were obtained by oxidation of the corresponding phosphite. An ozone-oxygen stream was passed at -78°C through an NMR sample tube containing a solution of phosphite in dry dichloromethane, until a blue color appeared due to excess ozone. The reaction mixture was then sparged with oxygen, and allowed to warm to room temperature. The dichloromethane was evaporated by passing dry nitrogen through the tube, after which a deuterated solvent was added. Completion of the reaction was confirmed by ³¹P NMR.

2-Methoxyethyl Dimethyl Phosphate (1a). ³¹P NMR: δ 6.5. ¹H NMR: δ 3.43 (3H, s, OCH₃), 3.57 (2H, m, H_{2'2'}), 3.71 (6H, d, OCH₃, $J_{\text{POMe}} = 11.1$ Hz), 4.20 (2H, m, H_{1'1'}). *N,N-Dimethyl-2-aminoethyl Dimethyl Phosphate (2a)*. ³¹P NMR: δ 6.6. ¹H NMR: δ 2.37 (6H, s, NCH₃), 2.79 (2H, t, H_{2'2'}), 3.81 (6H, d, OCH₃, $J_{\text{POMe}} = 11.0$ Hz), 4.33 (2H, dt, H_{1'1'}). *n-Butyl Dimethyl Phosphate (3a)*. ³¹P NMR: δ 6.6. ¹H NMR: δ 1.04 (3H, t, CH₃), 1.47–1.58 (2H, m, CH₂), 1.70–1.80 (2H, m, H_{2'2'}), 3.81 (6H, d, OCH₃, $J_{\text{POMe}} = 12.0$ Hz), 4.13 (2H, dt, H_{1'1'}). *2-Methylthioethyl Dimethyl Phosphate (4a)*. ³¹P NMR: δ 6.2. ¹H NMR: δ 2.02 (3H, s, SCH₃), 2.87 (2H, t, H_{2'2'}), 3.88 (6H, d, OCH₃, $J_{\text{POMe}} = 12.0$ Hz), 4.40 (2H, dt, H_{1'1'}).

Phosphoranes. All phosphoranes were obtained by adding an equimolar amount of 2,3-butanedione at 0°C to a solution of the corresponding phosphite in a deuterated solvent. After standing for 30 min at 0°C, formation of the phosphorane was ascertained with ³¹P NMR.

2,2-Dimethoxy-2-(2-methoxyethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (1b). ³¹P NMR: δ -43.9. ¹H NMR: δ 1.89 (6H, s, CH₃ dioxalene ring), 3.40 (3H, s, OCH₃), 3.57 (2H, m, H_{2'2'}), 3.62 (6H, d, OCH₃, $J_{\text{POMe}} = 13.0$ Hz), 4.03 (2H, m, H_{1'1'}). *2,2-Dimethoxy-2-(N,N-dimethyl-2-aminoethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (2b)*. ³¹P NMR: δ -44.0. ¹H NMR: δ 1.71 (6H, s, CH₃ dioxalene ring), 2.37 (6H, s, NCH₃), 2.51 (2H, t, H_{2'2'}), 3.60 (6H, d, OCH₃, $J_{\text{POMe}} = 13.0$ Hz), 4.00 (2H, dt, H_{1'1'}). *2,2-Dimethoxy-2-(n-butoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (3b)*. ³¹P NMR: δ -43.9. ¹H NMR: δ 1.01 (3H, t, CH₃), 1.50 (2H, m, CH₂), 1.62 (2H, m, H_{2'2'}), 1.89 (6H, s, CH₃ dioxalene ring), 3.60 (6H, d, OCH₃, $J_{\text{POMe}} = 12.9$ Hz), 3.95 (2H, dt, H_{1'1'}). *2,2-Dimethoxy-2-(2-methylthioethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (4b)*. ³¹P NMR: δ -43.9. ¹H NMR: δ 1.90 (6H, s, CH₃ dioxalene ring), 2.21 (3H, s, SCH₃), 2.74 (2H, t, H_{2'2'}), 3.62 (6H, d, OCH₃, $J_{\text{POMe}} = 13.1$ Hz), 4.07 (2H, dt, H_{1'1'}).

ACKNOWLEDGEMENTS

This investigation has been supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank Dr. J.W. de Haan for valuable discussions.

REFERENCES AND NOTES

1. L. H. Koole, E. J. Lanfers and H. M. Buck, *J. Am. Chem. Soc.*, **106**, 5451 (1984).
2. G. H. W. M. Meulendijks, W. van Es, J. W. de Haan and H. M. Buck, *Eur. J. Biochem.*, **157**, 421 (1986).
3. N. K. de Vries and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **105**, 150 (1986).
4. C. A. G. Haasnoot, F. A. A. M. de Leeuw and C. Altona, *Tetrahedron*, **36**, 2783 (1980). The equation used is:

$$J_{\text{HH}} = 13.89 \cos^2 \phi - 0.98 \cos \phi + \sum_i \Delta\chi_i \{1.02 - 3.40 \cos^2(\xi_i \phi + 14.9|\Delta\chi_i|)\},$$

where $\Delta\chi_i = \Delta\chi_i - 0.24 \sum_j \Delta\chi_j$ is the group electronegativity corrected for β -substituents. ϕ is the proton-proton torsion angle (taken as $\pm 60^\circ$ or 180°), and ξ_i is a substituent orientation parameter. The electronegativity of the elements relative to hydrogen has been derived from the Huggins scale: $\Delta\chi_o = 1.30$, $\Delta\chi_N = 0.85$, and $\Delta\chi_S = \Delta\chi_C = 0.40$. As the coordination of phosphorus is an effect in γ -substituents only, it does not affect the calculated coupling constants, which can therefore be used for both P^{IV} and P^{V} TBP compounds.

5. Using 32K points and a spectral window of 3000 Hz, one obtains an accuracy of 0.09 Hz in coupling constants, resulting in population fractions with an accuracy of ca. 0.02. For the variable temperature experiments described later, 16K points were used with a spectral window of 300 Hz, yielding an accuracy of 0.018 Hz in coupling constants and 0.005 in population fractions.
6. (a) S. Wolfe, *Acc. Chem. Res.*, **5**, 102 (1972); (b) A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen* (Springer Verlag, Berlin, 1983), p. 32-36.
7. (a) M. M. E. Scheffers-Sap and H. M. Buck, *J. Am. Chem. Soc.*, **102**, 6422 (1980); (b) H. S. Aldrich, L. A. Alworth and N. R. Clement, *J. Am. Chem. Soc.*, **100**, 2362 (1978); (c) J.-M. Lehn and G. Wipff, *J. Am. Chem. Soc.*, **98**, 7498 (1976).
8. R. Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements* (Georg Thieme Verlag, Stuttgart, 1973), p. 3-5.
9. *ibid.*, p. 10-11.
10. See for instance: (a) F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968); (b) D. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **92**, 634 (1970).
11. Measurements of J_{POMe} were performed with 32K points and a spectral window of 100 Hz, giving an accuracy of 0.003 Hz in coupling constants. Repeated measurements showed the coupling constants to be reproducible within 0.01 Hz.
12. Reference 8, p. 43-46 and 50-51.
13. Although the MNDO method does not include d-orbitals for phosphorus in its parametrization, a fifth bond can be accommodated because the program uses four bonding MOs and the first antibonding MO. In the latter MO, the AO of phosphorus has the same symmetry as the necessary d-orbital. This is shown by MNDO calculations on PH_5 , and is confirmed by earlier ab initio work on the same molecule: R. A. J. Janssen, G. J. Visser and H. M. Buck, *J. Am. Chem. Soc.*, **106**, 3429 (1984).
14. M. J. D. Powell, *A FORTRAN Subroutine for Solving Systems of Non-linear Algebraic Equations*, Harvell Report, AERE-R5947, H.M.S.O., 1968.
15. PANIC program, copyright Bruker Spectrospin AG, Switzerland.
16. F. Ramirez, *Bull. Soc. Chim. Fr.*, **1**, 2443 (1966).