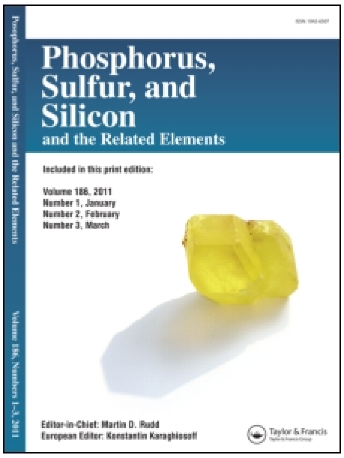

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DETERMINATION OF THE NATURE OF THE CONFORMATIONAL TRANSMISSION EFFECT IN PENTACOORDINATED PHOSPHORUS COMPOUNDS

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

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A high resolution ^{1}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 pyranosides[3] 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 P—O—C—C—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}H NMR. These models have substituents with various electronic properties, which allows for the determination of the nature of the conformational transmission effect.

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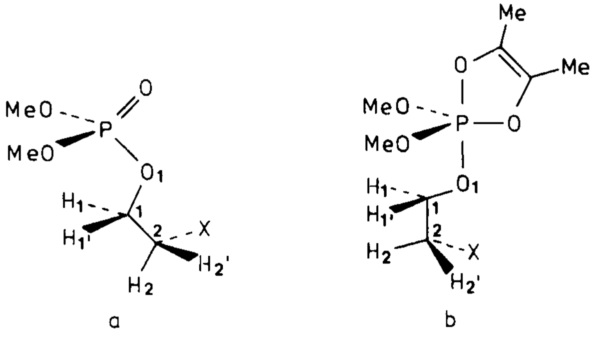


1 : X = OMe
2 : X = NMe_2
3 : X = CH_2Me
4 : X = SMe

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 explicitely accounts for electronegativity and orientation of the non-hydrogen substituents.

P^{IV} *Compounds* **1a–4a**

The C_1–C_2 conformations[5] 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 CH_2Me by OMe or NMe_2 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

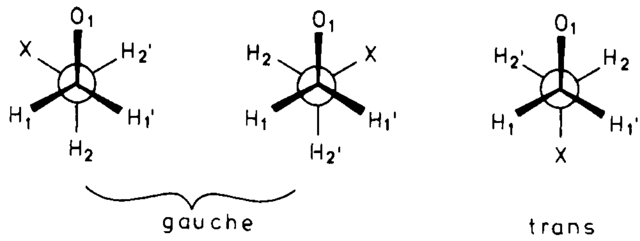


FIGURE 1 Staggered rotamers around the C_1–C_2 bond.

TABLE I

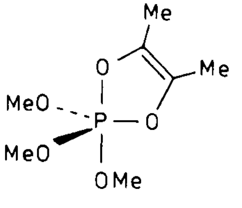
Calculated coupling constants for **1–4**

Compd.	J_g(Hz)	J_t(Hz)
1 X = OMe	4.13	7.46
2 X = NMe_2	4.69	7.66
3 X = CH_2Me	4.83	7.91
4 X = SMe	4.83	7.91

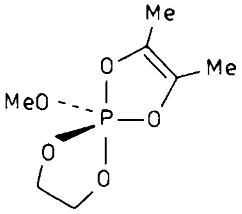
density on sulfur due to the ability of sulfur to use its d-orbitals as polarization functions.[7] Correspondingly, a strong preference for trans orientation of O_1 and S is found in **4a**.

Pseudorotational Analysis

In the P^V TBP compounds rapid pseudorotation[8] around the pentacoordinated phosphorus obscures the C_1–C_2 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 C_1–C_2 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 accurate[11] 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 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



5



6

TABLE II

C_1–C_2 Conformations of **1a–4a**

Compd.	J_{12}(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_2Me	6.5	0.47	0.53
4a X = SMe	6.8	0.37	0.63

TABLE III

Full C_1–C_2 conformational analysis of **1b** at various temperatures

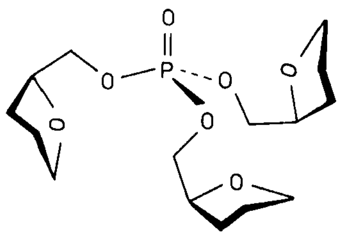
T(K)	J_{POMe}(Hz)	y	J_{12}(Hz)	x_g[a]	x_t[a]	$x_{g,eq}$	$x_{t,eq}$	$x_{g,ax}$	$x_{t,ax}$
295	13.06	0.37	5.03	0.72	0.28	0.86	0.14	0.56	0.44
285	13.06	0.37	5.01	0.74	0.26	0.87	0.13	0.55	0.45
267	13.04	0.36	4.93	0.76	0.24	0.88	0.12	0.53	0.47
249	13.06	0.37	4.84	0.79	0.21	0.90	0.10	0.50	0.50
244	13.04	0.36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

$\Delta H^0_{eq} = -4.4$ kJ/mol $\quad \Delta H^0_{ax} = 3.3$ kJ/mol

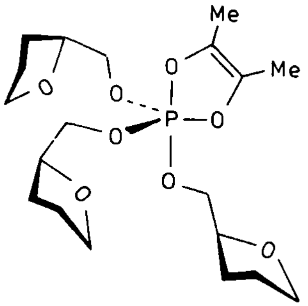
$\Delta S^0_{eq} = -5.5$ J/mol.K $\quad \Delta S^0_{ax} = 7.5$ J/mol.K

[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 $J_{POMe}(\mathbf{5}) = (J_{ax} + 2J_{eq})/3$ and $J_{POMe}(\mathbf{6}) = J_{eq}$. 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 $J_{eq} = 13.80$ Hz and $J_{ax} = 11.43$ Hz. For the compounds **1b**–**4b**, we are interested in the equilibrium between axial location of the OCCX fragment ($J_{POMe} = J_{eq} = 13.80$ Hz) and equatorial location ($J_{POMe} = (J_{ax} + J_{eq})/2 = 12.62$ Hz). The fraction y with OCCX axial can be determined from the measured J_{POMe} with: $y = (J_{POMe} - 12.62)/(13.80 - 12.62)$. 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 conformation[1] ($x_t(\mathbf{1a}) = 0.16$ 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** ($x_{t,ax} = 0.65$ and $x_{t,eq} = 0.27$ at 295 K[1]). Only in



7a



7b

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 $x_{g/t,eq} = x_{g/t,P^{IV}}$.

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 C_1–C_2 conformational analysis of **1b**–**4b** at 300 K

Compd.	J_{POMe}(Hz)	y	J_{12}(Hz)	x_g[a]	x_t[a]	$x_{g,eq}$	$x_{t,eq}$	$x_{g,ax}$	$x_{t,ax}$
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_2Me	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 C_1–C_2 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 C_1–C_2 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 O_1 (vide infra). This again demonstrates the electrostatic nature of conformational transmission.

Quantumchemical Calculations

Calculations were performed with the MNDO method[13] 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 C_1–C_2 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_2Me	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**

		ΔH_f(kJ/mol)	ΔH_{gt}(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 $\rightleftarrows$ 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 O_1 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 O_1. 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 $\Delta G^0 = \Delta H^0 - T\Delta S^0$:

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

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. ^{1}H 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] ^{31}P 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% H_3PO_4 ($\delta = 0$), 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. ^{31}P NMR: δ 145.2 ^{1}H NMR: δ 3.48 (3H, s, OCH_3), 3.63 (6H, d, OCH_3, J_{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. ^{31}P NMR: δ 145.0. ^{1}H NMR: δ 2.31 (6H, s, NCH_3), 2.56 (2H, t, $H_{2/2'}$), 3.57 (6H, d, OCH_3, J_{POMe} = 10.4 Hz), 3.95 (2H, dt, $H_{1/1'}$). *n-Butyl Dimethyl Phosphite.* B.p. 80°C/40 mmHg. ^{31}P NMR: δ 145.0. ^{1}H NMR: δ 1.02 (3H, t, CH_3), 1.43–1.57 (2H, m, CH_2), 1.62–1.73 (2H, m, $H_{2/2'}$), 2.55 (6H, d, OCH_3, J_{POMe} = 10.4 Hz), 3.88 (2H, dt, $H_{1/1'}$). *2-Methylthioethyl Dimethyl Phosphite.* B.p. 72°C/30 mmHg. ^{31}P NMR: δ 145.0. ^{1}H NMR: δ 2.21 (3H, s, SCH_3), 2.79 (2H, t, $H_{2/2'}$), 3.57 (6H, d, OCH_3, J_{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 ^{31}P NMR.

2-Methoxyethyl Dimethyl Phosphate (**1a**). ^{31}P NMR: δ 6.5. ^{1}H NMR: δ 3.43 (3H, s, OCH_3), 3.57 (2H, m, $H_{2/2'}$), 3.71 (6H, d, OCH_3, J_{POMe} = 11.1 Hz), 4.20 (2H, m, $H_{1/1'}$). *N,N-Dimethyl-2-aminoethyl Dimethyl Phosphate* (**2a**). ^{31}P NMR: δ 6.6. ^{1}H NMR: δ 2.37 (6H, s, NCH_3), 2.79 (2H, t, $H_{2/2'}$), 3.81 (6H, d, OCH_3, J_{POMe} = 11.0 Hz, 4.33 (2H, dt, $H_{1/1'}$). *n-Butyl Dimethyl Phosphate* (**3a**). ^{31}P NMR: δ 6.6. ^{1}H NMR: δ 1.04 (3H, t, CH_3), 1.47–1.58 (2H, m, CH_2), 1.70–1.80 (2H, m, $H_{2/2'}$), 3.81 (6H, d, OCH_3, J_{POMe} = 12.0 Hz), 4.13 (2H, dt, $H_{1/1'}$). *2-Methylthioethyl Dimethyl Phosphate* (**4a**). ^{31}P NMR: δ 6.2. ^{1}H NMR: 2.02 (3H, s, SCH_3), 2.87 (2H, t, $H_{2/2'}$), 3.88 (6H, d, OCH_3, J_{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 ^{31}P NMR.

2,2-Dimethoxy-2-(2-methoxyethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (**1b**). ^{31}P NMR: δ −43.9. ^{1}H NMR: δ 1.89 (6H, s, CH_3 dioxalene ring), 3.40 (3H, s, OCH_3), 3.57 (2H, m, $H_{2/2'}$), 3.62 (6H, d, OCH_3, J_{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**). ^{31}P NMR: δ −44.0. ^{1}H NMR: δ 1.71 (6H, s, CH_3 dioxalene ring), 2.37 (6H, s, NCH_3), 2.51 (2H, t, $H_{2/2'}$), 3.60 (6H, d, OCH_3, J_{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**). ^{31}P NMR: δ −43.9. ^{1}H NMR: δ 1.01 (3H, t, CH_3), 1.50 (2H, m, CH_2), 1.62 (2H, m, $H_{2/2'}$), 1.89 (6H, s, CH_3 dioxalene ring), 3.60 (6H, d, OCH_3, J_{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**). ^{31}P NMR: δ −43.9. ^{1}H NMR: δ 1.90 (6H, s, CH_3 dioxalene ring), 2.21 (3H, s, SCH_3), 2.74 (2H, t, $H_{2/2'}$), 3.62 (6H, d, OCH_3, J_{POMe} = 13.1 Hz), 4.07 (2H, dt, $H_{1/1'}$).

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

   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 ±60° 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.
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