C-N bond strength in nitrobenzene if the experimental heats of formation for nitrobenzene and NO_2 and the MNDO-calculated value for phenyl radical are used. This 70-kcal mol^{-1} value is also in the area of a C-N bond strength according to conventional organic chemistry wisdom. Thus, we feel that a simple C-N bond fission is unlikely as a first step in the thermochemical decomposition of TNT.

Conclusions

cis-1-Nitropropene is a good theoretical model for studying TNT thermochemical decomposition. It reproduces all of the major structural features of a nitro group being ortho to the methyl group in TNT. Of all of the possible reaction steps we considered, only the intramolecular hydrogen transfer changes the aromaticity of the TNT system, making our 1-nitropropene model not quite as good for that case. Even so, we are able to deduce qualitative trends of this effect.

MINDO/3 results do appear to be more reliable than the MNDO results. We cannot explain the abnormally high values of the activation enthalpies that MNDO gives for the oxygen-transfer steps. It is quite feasible that, in spite of repeated attempts, we have still not obtained the transition states for these processes with MNDO. In the other cases, the MINDO/3 and MNDO results are similar.

Our original goal was to draw conclusions about possible first steps of TNT thermochemical decomposition by comparing our theoretical results with the EPR and IDSC results. On an activation energy basis, several processes appear to be likely: both hydrogen transfers, both oxygen transfers, and the nitro–nitrite rearrangement. The fairly large isotope effect, however, is difficult to explain with anything but the two hydrogen-transfer steps, although we are currently calculating deuterium isotope effects for all of these steps. The EPR signals indicate that radicals must be involved, and the spectrum shows two nitrogens and five hydrogens. The intermolecular hydrogen transfer has the attraction that it produces radicals directly, but not with the required two nitrogens. HONO loss from the hydrogen-transfer product does result in a radical with the required two nitrogens and five hydrogens, and further work is in progress to determine the feasibility of these follow-on steps.[15] On the other hand, intramolecular hydrogen transfer followed by OH loss would result in a radical, but with two nitrogens and only four hydrogens.

The intermolecular hydrogen-transfer process is consistent with all of the known experimental facts for TNT thermochemical decomposition. Thus, we feel that it is a major process early in the decomposition. The low activation enthalpies calculated for several other steps, however, make it probable that these other processes go on just as well. Indeed, all of the previous studies on TNT thermochemical decomposition indicate that the system is quite complicated, particularly in light of the multitude of intermediate products. Our calculations certainly indicate the complexity of the system.

Acknowledgment. We thank Ms. Judy Cross and Mrs. Missy Landess for the expert typing of this manuscript. We also acknowledge many helpful discussions with Profesor Michael J. S. Dewar, Professor William R. Carper, Dr. R. Martin Guidry, Professor Michael L. McKee, and others. One of us (A.G.T.) acknowledges the U.S. Air Force Office of Scientific Research for the award of an University Resident Research Professorship.

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(15) Turner, A. G.; Davis, L. P. *J. Energ. Materials*, to be published.

Conformational Transmission in Trigonal-Bipyramidal P^V Compounds. Enhanced Gauche(−) Population around the $C_{4'}$–$C_{5'}$ Linkage in 5′-P^V Phosphorylated Tetrahydrofurfuryl Model Systems

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Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands. *Received January 30, 1984*

Abstract: A 300-MHz ^1H NMR study on a number of 5′-phosphorylated (P^{IV}) tetrahydrofurfuryl model compounds (**1a,b**, **3a,b**, **4a,b**) and their P^V trigonal-bipyramidal (TBP) analogues (**1c,d**, **3c,d**, **4c,d**) has been performed. The results show a significantly greater population of the gauche(−) conformation for axially situated tetrahydrofurfuryl around the $C_{4'}$–$C_{5'}$ bond in the 5′-P^V TBP tetrahydrofurfuryls with respect to their related 5′-P^{IV} compounds which show dominant gauche(+) and gauche(trans) conformations. The conformation analysis of the P^V compounds was hampered by pseudorotation. With model compound **6**, in which both equatorial and axial sites that undergo pseudorotation bear a tetrahydrofurfuryl group, a precise analysis was possible resulting in an excess of gauche(−) for tetrahydrofurfuryl in an axial position (318 K, 61%; 217 K, 80%). The corresponding equatorial location shows a relatively small amount of gauche(−) compared with gauche(+) and gauche(trans) (318 K, 24%; 217 K, 13%). The latter values are similar to the P^{IV} counterpart **5**. This conformational transmission in the $C_{4'}$–$C_{5'}$ bond of tetrahydrofurfuryls agrees with quantum chemical calculations. It is suggested that the enhanced charge repulsion between $O_{5'}$ and $O_{1'}$ in the P^V TBP drives the rotation around the $C_{4'}$–$C_{5'}$ bond. The impact for conformational isomerizations in phosphorylated biomolecules (e.g., DNA) is briefly mentioned.

Recent quantum chemical calculations[1,2] on 5′-phosphorylated tetrahydrofurfuryl give cause for the conclusion that increase in coordination of phosphorus from 5′-P^{IV} to 5′-P^V trigonal-bipyramidal (TBP) with the tetrahydrofurfuryl group in axial position (opposite to the introduced ligand, H_2O, e.g.) results in a specific rotation of this group around the $C_{4'}$–$C_{5'}$ bond. The rotamer population then changes from gauche(+), (g^+) and gauche(trans), (g^t) toward gauche(−), (g^-). It was suggested that the enhanced charge repulsion between the exocyclic oxygen ($O_{5'}$) situated in the axial position of the 5′-P^V TBP and the endocyclic oxygen ($O_{1'}$) triggers the rotation around the $C_{4'}$–$C_{5'}$ bond.[3] Experimental

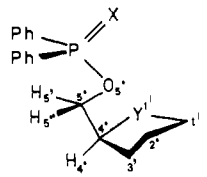
(1) van Lier, J. J. C.; Koole, L. H.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 148.

(2) van Lier, J. J. C.; Smits, M. T.; Buck, H. M. *Eur. J. Biochem.* **1983**, *132*, 55.

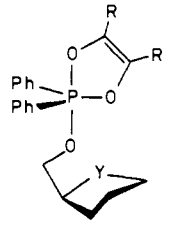
(3) Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 181.

0002-7863/84/1506-5451$01.50/0

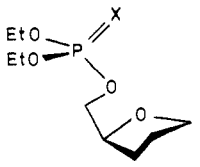
Chart I. Model Compounds Studied in This Work



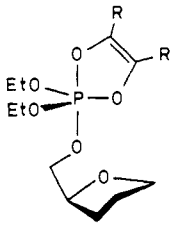
1a : X = O ; Y = O
1b : X = S ; Y = O
2a : X = O ; Y = C(H2)



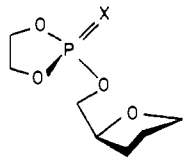
1c : R = Me ; Y = O
1d : R = Ph ; Y = O
2b : R = Me ; Y = C(H2)
2c : R = Ph ; Y = C(H2)



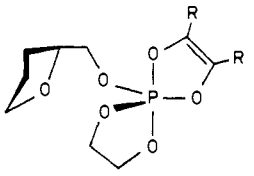
3a : X = O ; 3b : X = S



3c : R = Me ; 3d : R = Ph

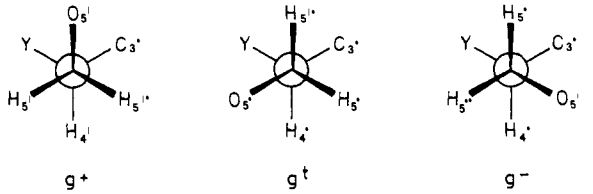


4a : X = O ; 4b : X = S



4c : R = Me ; 4d : R = Ph

evidence for the role of P^V TBP structures in effectuating this specific rotation will be presented in this paper. A set of 5′-P^{IV} and 5′-P^V TBP tetrahydrofurfuryl and cyclopentanemethyl model compounds (Chart I) was synthesized and the $C_{4'}$–$C_{5'}$ conformations were analyzed with 300-MHz ^1H NMR. The results show a significantly greater population of the g^- rotamer (in which $O_{5'}$ is located trans to $O_{1'}$) for the 5′-P^V TBP tetrahydrofurfuryl model compounds compared to their 5′-P^{IV} counterparts. Interestingly, substitution of $O_{1'}$ by $C(H_2)$ gives identical $C_{4'}$–$C_{5'}$ conformations for 5′-P^{IV} and 5′-P^V TBP in which $g^t \equiv g^-$ and dominant with respect to g^+. These experimental findings show a strong coherence with the calculations that predicted an enhanced charge repulsion between $O_{5'}$ and $O_{1'}$ for axial location of the tetrahydrofurfuryl group in the P^V TBP. It should be mentioned, however, that pseudorotation, which involves ligand permutation between the axial and equatorial sites in the TBP, precludes a correct determination of the $C_{4'}$–$C_{5'}$ conformation that corresponds to axial tetrahydrofurfuryl. A *precise* conformational analysis around the $C_{4'}$–$C_{5'}$ bond for axial and equatorial tetrahydrofurfuryl could be obtained from variable-temperature



g+ g^t g−

Figure 1. Newman projections of the rotamers around the $C_{4'}$–$C_{5'}$ bond (Y = O, $C(H_2)$).

Table I. $H_{4'}$–$C_{4'}$–$C_{5'}$–$H_{5'(5'')}$ Torsional Angles (ϕ) in the Rotamers around the $C_{4'}$–$C_{5'}$ Bond and the Corresponding Calculated Proton–Proton Coupling Constants

conformation	$\phi(H_{4'}$–$C_{4'}$–$C_{5'}$–$H_{5'}$), deg	$J_{H_{4'}H_{5'}}$, Hz Y = O	Y = $C(H_2)$	$\phi(H_{4'}$–$C_{4'}$–$C_{5'}$–$H_{5''}$), deg	$J_{H_{4'}H_{5''}}$, Hz Y = O	Y = $C(H_2)$
g^+	−60	2.8	1.9	60	0.9	1.9
g^t	60	3.1	4.1	180	10.7	11.5
g^-	180	10.7	11.5	−60	5.0	4.1

300-MHz ^1H NMR measurements of the P^V TBP model compound **6** (Figure 6) in which both equatorial and axial sites that undergo pseudorotation bear a tetrahydrofurfuryl group. These experimental data unambiguously show the intrinsic bond properties of the equatorial and axial sites in the TBP which are reflected in specific $C_{4'}$–$C_{5'}$ conformational differences between axial and equatorial tetrahydrofurfuryl. Axial location is found to be associated with a marked preference for the g^- rotamer, indicating a pronounced charge repulsion effect between $O_{5'}$ and $O_{1'}$. Equatorial location with excess of g^+ and g^t rotamers closely resembles the $C_{4'}$–$C_{5'}$ conformations for 5′-P^{IV}. *Extrapolating these results to phosphorylated biomolecules, we feel that conformational transmission in nucleic acids may be brought about by activation of the phosphate groups through change in coordination from P^{IV} into P^V TBP* (see also Results and Discussion).

$C_{4'}$–$C_{5'}$ Conformational Analysis

In solution rapid interconversion between the three staggered rotamers g^+, g^t, and g^- (Figure 1) yields weighted time-averaged coupling constants $J_{H_{4'}H_{5'}}$ and $J_{H_{4'}H_{5''}}$, which are related to the individual rotamers and their populations $x(g^+)$, $x(g^t)$, and $x(g^-)$:

$$J_{H_{4'}H_{5'(5'')}} = x(g^+)J_{H_{4'}H_{5'(5'')}}{}^{g^+} + x(g^t)J_{H_{4'}H_{5'(5'')}}{}^{g^t} + x(g^-)J_{H_{4'}H_{5'(5'')}}{}^{g^-}$$

with $x(g^+) + x(g^t) + x(g^-) = 1$. The rotamer populations can be obtained with the help of an empirically generalized Karplus relation developed by Altona et al.,[4,5] from which the coupling constants corresponding to the various rotamers can be calculated. Table I lists the calculated coupling constants and the corresponding proton–proton torsion angles.

In addition a correct assignment of the protons $H_{5'}$ and $H_{5''}$ is required. For the 5′-P^{IV} model compounds $H_{5'}$ and $H_{5''}$ can be distinguished on the basis of a comparison of the $C_{4'}$–$C_{5'}$ conformations in **1a** and **2a**. For **2a** both assignments are equivalent. From $J_{H_{4'}H_{5'}} = J_{H_{4'}H_{5''}} = 6.80$ Hz it follows that $x(g^+) = 0.18$ and $x(g^t) = x(g^-) = 0.41$. Values of 4.26 and 5.78 Hz were found for $J_{H_{4'}H_{5'}}$ and $J_{H_{4'}H_{5''}}$ in **1a**. Assuming that $\delta_{H_{5'}} > \delta_{H_{5''}}$ one arrives at $x(g^+) = 0.40$, $x(g^t) = 0.43$, and $x(g^-) = 0.17$. The reverse assignment yields $x(g^+) = 0.44$, $x(g^t) = 0.19$, and $x(g^-) = 0.37$. These values show that, to a good approximation, inversion of the $H_{5'}/H_{5''}$ assignment has no effect on the estimated g^+ rotamer population.[6,7] However, the populations of g^t and g^- are reversed in both assignments. From the marked increase of $x(g^+)$ upon substitution of cyclopentanemethyl by tetrahydrofurfuryl it can be concluded that $O_{5'}$–$O_{1'}$ gauche orientation represents an energetically more favored state than $O_{5'}$–$C(H_2)$ gauche orientation.[8] This finding applied to the populations of g^t ($O_{5'}$

(4) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

(5) In this generalized equation the standard Karplus relation is extended with a correction term which accounts for the influence of electronegative substituents on $^3J_{HH}$:

$$^3J_{HH} = 13.22\cos^2\phi - 0.99\cos\phi + \sum[0.87 - 2.46\cos^2(\xi_i\phi + 19.9|\Delta\chi_i|)]\Delta\chi_i$$

ϕ is the proton–proton torsion angle, $\Delta\chi_i$ is the difference in electronegativity between the substituent and hydrogen according to the electronegativity scale of Huggins, and ξ_i is a substituent orientation parameter.

(6) Davies, D. B.; Danyluk, S. S. *Biochemistry* **1975**, *14*, 543.

(7) Altona, C. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 413.

Table II. $J_{H_4'H_{5'(5'')}}$ Values and the Corresponding $C_{4'}$–$C_{5'}$ Rotamer Populations for the 5′-P^{IV} Model Systems at 300 K

compd	$J_{H_4'H_{5'}}$, Hz	$J_{H_4'H_{5''}}$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$
1a	4.26	5.78	0.40	0.43	0.17
1b	4.23	5.82	0.40	0.43	0.17
2a	6.80	6.80	0.18	0.41	0.41
3a	4.08	5.89	0.41	0.44	0.15
3b	4.26	5.76	0.40	0.43	0.17
4a	3.94	5.85	0.42	0.45	0.13
4b	3.84	6.00	0.41	0.47	0.12

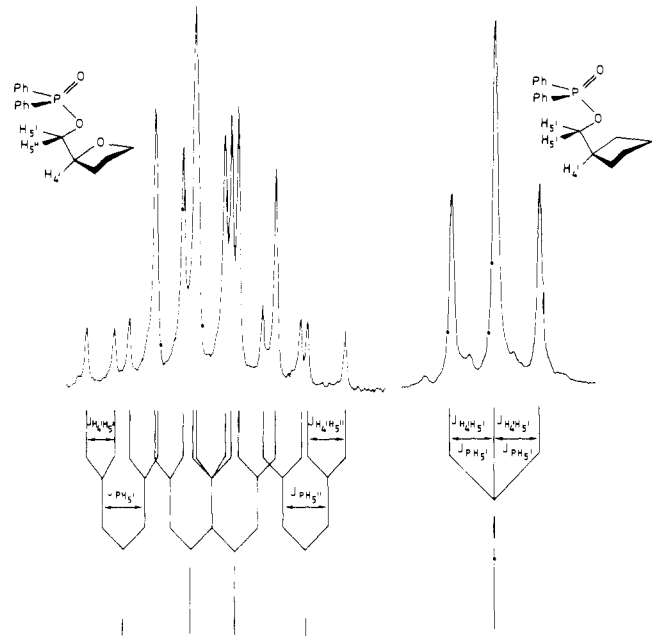


Figure 2. $H_{5'}/H_{5''}$ patterns in the 300-MHz ^1H NMR spectra of **1a** and **2a**.

gauche to $O_{1'}$) and g^- ($O_{5'}$ gauche to $C_{3'}$) yields $x(g^t) > x(g^-)$, or $J_{H_4'H_{5'}} < J_{H_4'H_{5''}}$. This is consistent with the assignment $\delta_{H_{5'}} > \delta_{H_{5''}}$. Variable-temperature 300-MHz ^1H NMR measurements on **1a** revealed that a linear inverse relationship exists between the chemical shift difference δ_{H_5}–$\delta_{H_{5''}}$ and $J_{H_4'H_{5'}} + J_{H_4'H_{5''}}$ (vide infra). Similar linear correlations have been reported for anti-type nucleosides and nucleotides.[9] The linear inverse relationship between δ_{H_5}–$\delta_{H_{5''}}$ and $J_{H_4'H_{5'}} + J_{H_4'H_{5''}}$ is used in this work to arrive at an unequivocal $H_{5'}/H_{5''}$ assignment for each of the 5′-P^V TBP model compounds.

Results and Discussion

In Table II the spectral parameters are given that were obtained from the $H_{5'}/H_{5''}$ patterns of the 5′-P^{IV} model compounds measured in acetone-d_6 at 300 MHz and 300 K.

As typical examples, expansions of the $H_{5'}/H_{5''}$ patterns of **1a** and **2a** are shown in Figure 2. Examination of the data in Table II reveals that the $C_{4'}$–$C_{5'}$ rotamer populations for 5′-P^{IV} tetrahydrofurfuryl are found to be virtually unaffected by the various substituents on phosphorus. Obviously, the $C_{4'}$–$C_{5'}$ conformations of these model systems are dominated by the gauche effect between $O_{5'}$ and $O_{1'}$.[8] The spectral parameters that were found under the same experimental conditions for the P^V TBP model compounds are listed in Table III. The 5′-P^V TBP tetrahydrofurfuryl model

Table III. $J_{H_4'H_{5'(5'')}}$ Values and the Corresponding $C_{4'}$–$C_{5'}$ Rotamer Populations for the 5′-P^V TBP Model Systems at 300 K[a]

compd	$J_{H_4'H_{5'}}$, Hz	$J_{H_4'H_{5''}}$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$
1c	5.45	5.61	0.33	0.35	0.32
1d	5.30	5.69	0.34	0.36	0.30
2b	6.80	6.80	0.18	0.41	0.41
2c	6.80	6.80	0.18	0.41	0.41
3c	5.24	5.57	0.32	0.35	0.33
3d	5.21	5.31	0.38	0.33	0.29
4c	4.74	5.36	0.41	0.36	0.23
4d	4.83	5.21	0.42	0.34	0.24

[a] The rotamer populations are uncorrected for phosphorus pseudorotation.

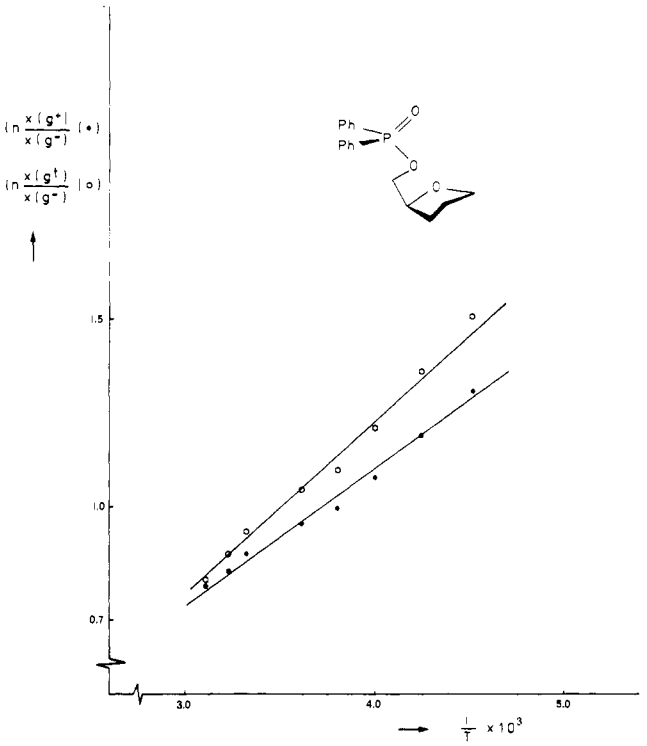


Figure 3. Van 't Hoff plot of **1a** resulting from variable-temperature measurements of $J_{H_4'H_{5'}}$ and $J_{H_4'H_{5''}}$.

compounds **1c**, **1d**, **3c**, and **3d** are characterized by a pronounced g^- population ($x(g^-) = 0.29$–0.33) with respect to their 5′-P^{IV} counterparts ($x(g^-) = 0.15$–0.17). On the other hand, substitution of 5′-P^{IV} by 5′-P^V TBP for the cyclopentanemethyl model compounds leaves the $C_{4'}$–$C_{5'}$ rotamer populations unaffected (compare **2a**, Table II, with **2b** and **2c**, Table III). *These results strongly reflect the effect of enhanced charge repulsion between $O_{5'}$ and $O_{1'}$ by coordination change of phosphorus from four to five.* The $J_{H_4'H_{5'}}$ and $J_{H_4'H_{5''}}$ values listed in Table III are measured under rapid pseudorotation conditions, as is evidenced by the magnetic equivalence of the pseudoaxial and the pseudoequatorial sites in the ^{13}C and ^1H NMR spectra (vide infra). It must be expected that the positional exchange of tetrahydrofurfuryl from an equatorial site (favored by electron-releasing ligands)[10,11] to an axial site (strongly preferred by electron-withdrawing ligands)[10,11] leads to enhanced charge repulsion between $O_{5'}$ and $O_{1'}$. Therefore, the $C_{4'}$–$C_{5'}$ conformations given in Table III must be regarded as time-averaged conformations due to equilibrated axial and equatorial locations of the tetrahydrofurfuryl group. The impact of pseudorotation on the $C_{4'}$–$C_{5'}$ conformation becomes more clear from examination of the rotamer populations of **4c** and **4d**. A decrease in g^- population for **4c** and **4d** ($x(g^-) = 0.23$

(8) The existence of a gauche-effect, i.e., a pronounced preference for gauche over trans geometry in X–C–C–Y fragments in which X and Y represent highly electronegative substituents (N, O, Cl, F), is well-known (Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102). In addition it was pointed out that the conformational behavior of furanoses can be rationalized on the basis of a predominant preference of O–C–C–O bond sequences to adopt gauche rotational arrangements (Olson, W. K. *J. Am. Chem. Soc.* **1982**, *104*, 285 and references cited therein).

(9) Davies, D. B. In "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsley, J. W., Feeney, J., Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1978; Vol. 12, Part 3, pp 181–184 and references cited therein.

(10) Muetterties, E. L.; Mahler, W.; Schmutzler, R. *Inorg. Chem.* **1963**, *2*, 613.

(11) Holmes, R. R. In "Pentacoordinated Phosphorus"; American Chemical Society: Washington, DC, 1980; Vol. I, II, ACS Monogr. No. 175, 176 and references cited therein.

Table IV. NMR Parameters and $C_{4'}$–$C_{5'}$ Rotamer Populations Obtained by Variable-Temperature ^1H NMR on **1a** and **1c**[a]

1a							1c						
T, K	$J_{H_4'H_5'}$, Hz	$J_{H_4'H_5''}$, Hz	$\Delta\delta$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$	T, K	$J_{H_4'H_5'}$, Hz	$J_{H_4'H_5''}$, Hz	$\Delta\delta$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$
321	4.37	5.70	13.2	0.41	0.41	0.18	320	5.35	5.65	17.7	0.33	0.36	0.31
310	4.31	5.74	13.7	0.40	0.42	0.18	311	5.38	5.64	17.0	0.33	0.35	0.32
300	4.26	5.78	14.0	0.40	0.43	0.17	300	5.45	5.61	15.4	0.33	0.35	0.32
276	4.16	5.86	15.2	0.40	0.44	0.16	270	5.49	5.62	13.6	0.33	0.34	0.33
262	4.11	5.90	16.4	0.40	0.45	0.15	253	5.59	5.58	11.6	0.33	0.33	0.34
249	4.02	5.96	18.3	0.40	0.46	0.14	244	5.66	5.54	10.5	0.32	0.33	0.35
235	3.91	6.06	19.3	0.40	0.48	0.12	237	5.75	5.47	9.8	0.32	0.33	0.36
221	3.80	6.15	19.8	0.40	0.49	0.11	225	5.92	5.39	7.2	0.32	0.30	0.38

[a] No correction is made for phosphorus pseudorotation.

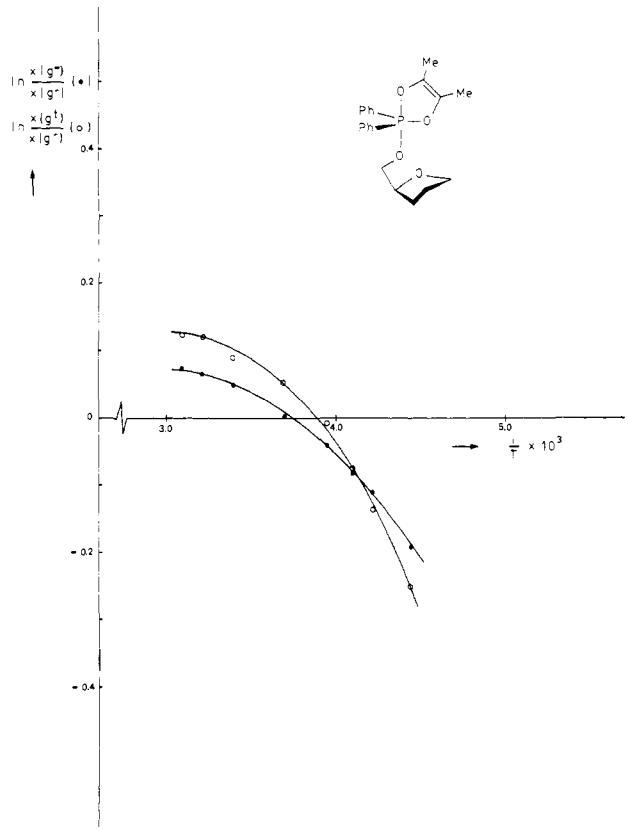


Figure 4. Van 't Hoff plot of **1c** resulting from variable-temperature measurements of $J_{H_4'H_5'}$ and $J_{H_4'H_5''}$.

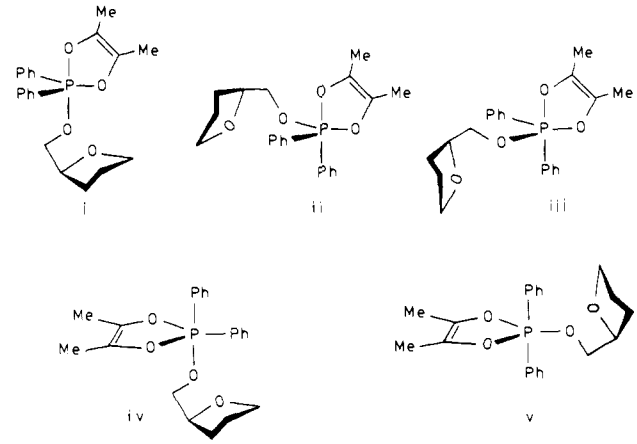
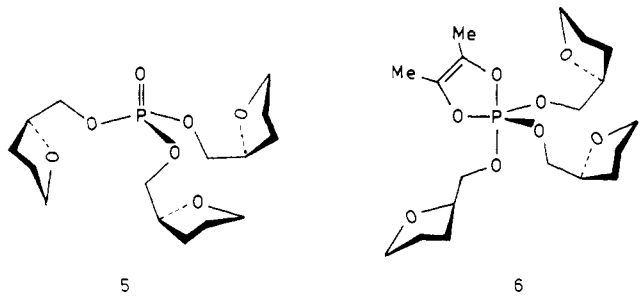


Figure 5. Stereoisomers of **1c**.



5 6

Figure 6. Model compounds **5** and **6**. Dominant $C_{4'}$–$C_{5'}$ rotamers are drawn for the tetrahydrofurfuryl ligands.

and 0.24, respectively) is found in comparison with **1c**, **1d**, **3c**, and **3d**. The apparent explanation lies in the fact that axial location of the tetrahydrofurfuryl group in **4c** and **4d** results in an unfavorable diequatorial arrangement of one of the five-membered ring fragments.[11] In these spirophosphoranes the tetrahydrofurfuryl group is likely to act as the pivot[11,12] which occupies an equatorial position. More detailed information on the TBP-site specificity of the $C_{4'}$–$C_{5'}$ conformation could be obtained by studying the variation in the rotamer populations with temperature for **1c** (5'-P^V TBP) in comparison with **1a** (5'-P^{IV}). The results are given in Table IV. Plots of ln $(x(g^+)/(x(g^-))$ and ln $(x(g^t)/x(g^-))$ vs. $1/T$ yield straight lines (r^2 = 0.997 and 0.998, respectively) for **1a** (Figure 3). The enthalpy and entropy parameters that govern the equilibria $g^- \rightleftarrows g^+$ and $g^- \rightleftarrows g^t$ could be easily abstracted from the corresponding graphs: $\Delta H°(g^-,g^+)$[13] = -3.6 kJ mol^{-1}, $\Delta S°(g^-,g^+)$[14] = -4.3 J mol^{-1} K^{-1}, $\Delta H°(g^-,g^t)$ = -4.4 kJ mol^{-1}, and $\Delta S°(g^-,g^t)$ = -6.8 J mol^{-1} K^{-1}. Entirely different plots are found for **1c** (Figure 4). It is established that **1c** exhibits rapid pseudorotation on the temperature traject 225–320 K. Pseudorotation of **1c** may be regarded as a rapid equilibrium between five stereoisomers (Figure 5) of which i is dominant at low temperatures. The enantiomers ii and iii represent violations of the polarity rule, which states that the axial sites in the TBP are preferentially occupied by electronegative substituents (vide supra). Stereoisomers iv and v represent an unfavorable diequatorial arrangement of the dioxaphospholane ring.[11] It follows that lowering the temperature shifts the pseudorotation equilibrium of **1c** toward i, thereby increasing the time-averaged axial location of the tetrahydrofurfuryl group. It can be derived (Appendix, part A) that the curves in Figure 4 approach straight lines with slopes $-\Delta H°_{ax}(g^-,g^+)R^{-1}$ and $-\Delta H°_{ax}(g^-,g^t)R^{-1}$ on lowering the temperature.[15] A rough estimation of the slopes at 225 K reveals that $\Delta H°_{ax}(g^-,g^+) \approx 5.0$ kJ mol^{-1} and $\Delta H°_{ax}(g^-,g^t) \approx 3.5$ kJ mol^{-1}. This means that axial location of the tetrahydrofurfuryl group is associated with substantial stabilization of the g^- rotamer. Thus, an inversion of the relative stabilities is observed, i.e., g^+ and g^t are dominant for 5'-P^{IV}, whereas g^- is highly preferred for axial location of the tetrahydrofurfuryl group within the P^V TBP. The results allow only a qualitative insight into the TBP-site specificity of the $C_{4'}$–$C_{5'}$ conformations, as the pseudorotation equilibrium constant for axial and equatorial

(12) Luckenbach, R. In "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; Georg Thieme Verlag: Stuttgart, 1973.

(13) $\Delta H°(g^-,g^+)$, and $\Delta H°(g^-,g^t)$ denote the enthalpy differences $H°(g^+) - H°(g^-)$ and $H°(g^t) - H°(g^-)$, respectively.

(14) $\Delta S°(g^-,g^+)$ and $\Delta S°(g^-,g^t)$ denote the entropy differences $S°(g^+) - S°(g^+)$ and $S°(g^t) - S°(g^-)$, respectively.

(15) The subscripts "ax" and "eq" are used with reference to axial and equatorial tetrahydrofurfuryl, respectively.

Table V. NMR Parameters and $C_{4'}$–$C_{5'}$ Rotamer Populations Obtained by Variable-Temperature ^1H NMR on **5** and **6**[a]

5						**6**					
T, K	$J_{H_4'H_5'}$, Hz	$J_{H_4'H_5''}$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$	T, K	$J_{H_4'H_5'}$, Hz	$J_{H_4'H_5''}$, Hz	$x(g^+)$	$x(g^t)$	$x(g^-)$
320	4.16	5.86	0.40	0.44	0.16	318	5.62	5.45	0.33	0.32	0.35
276	4.01	5.92	0.41	0.46	0.13	276	5.66	5.47	0.33	0.32	0.35
249	3.80	6.08	0.41	0.48	0.11	249	5.71	5.50	0.32	0.32	0.36
225	3.62	6.30	0.41	0.51	0.08	217	5.77	5.53	0.32	0.32	0.36

[a] No correction is made for phosphorus pseudorotation.

Table VI. Thermodynamic Parameters of the $C_{4'}$–$C_{5'}$ Conformational Equilibria for Axial and Equatorial Tetrahydrofurfuryl in **6**[a]

ax tetrahydrofurfuryl	eq tetrahydrofurfuryl
$\Delta H°_{ax}(g^-,g^+) = 4.7$ kJ mol^{-1}	$\Delta H°_{eq}(g^-,g^+) = -4.3$ kJ mol^{-1}
$\Delta S°_{ax}(g^-,g^+) = 7.2$ J mol^{-1} K^{-1}	$\Delta S°_{eq}(g^-,g^+) = -9.8$ J mol^{-1} K^{-1}
$\Delta H°_{ax}(g^-,g^t) = 6.1$ kJ mol^{-1}	$\Delta H°_{eq}(g^-,g^t) = -4.0$ kJ mol^{-1}
$\Delta S°_{ax}(g^-,g^t) = 6.9$ J mol^{-1} K^{-1}	$\Delta S°_{eq}(g^-,g^t) = -8.4$ J mol^{-1} K^{-1}

[a] Corrected for phosphorus pseudorotation.

Table VII. $C_{4'}$–$C_{5'}$ Rotamer Populations for Axial and Equatorial Tetrahydrofurfuryl[a]

	ax tetrahydrofurfuryl			eq tetrahydrofurfuryl		
T, K	$x(g^+)$	$x(g^t)$	$x(g^-)$	$x(g^+)$	$x(g^t)$	$x(g^-)$
318	0.25	0.14	0.61	0.37	0.39	0.24
276	0.21	0.11	0.68	0.39	0.41	0.20
249	0.18	0.09	0.73	0.41	0.42	0.17
217	0.14	0.06	0.80	0.43	0.44	0.13

[a] Calculated on the basis of the data in Table VI.

tetrahydrofurfuryl could not be determined. Attempts to retard the pseudorotation of **1c** failed. No decoalescence phenomena were observed in the ^{13}C NMR spectra recorded at 75 MHz down to 173 K. This problem was evaded by studying **6** in comparison with **5** (Figure 6). The enthalpy and entropy parameters concerning the equilibria $g^- \rightleftarrows g^+$ and $g^- \rightleftarrows g^t$ for **5** closely parallel the results for **1a**. It is found that $\Delta H°(g^-,g^+) = -4.0$ kJ mol^{-1}, $\Delta S°(g^-,g^+) = -5.3$ J mol^{-1} K^{-1}, $\Delta H°(g^-,g^t) = -5.2$ kJ mol^{-1}, and $\Delta S°(g^-,g^t) = -8.5$ J mol^{-1} K^{-1}. The $C_{4'}$–$C_{5'}$ rotamer populations for **6** again represent time-averaged values for axial and equatorial location of the tetrahydrofurfuryl groups, which indeed show an enhanced g^- population with respect to **5** (Table V). However, because the three tetrahydrofurfuryl groups which show ligand exchange are distributed over two equatorial and one axial position, one obtains $x^{exp}(i) = {}^1/_3 x_{ax}(i) + {}^2/_3 x_{eq}(i)$, in which $x_{ax}(i)$ and $x_{eq}(i)$ refer to axial and equatorial tetrahydrofurfuryl, respectively, for the rotamers i: g^+, g^t, and g^-. This means that the thermodynamic parameters which govern the $C_{4'}$–$C_{5'}$ conformational equilibria for axial and equatorial tetrahydrofurfuryl can be determined precisely on the basis of $J_{H_4'H_5'}$ and $J_{H_4'H_5''}$ measurements at four different temperatures (Appendix, part B). An iterative numerical procedure was employed which asks for an initial estimation of the set of solutions. As a first approximation the $\Delta H°$ and $\Delta S°$ values of **5** were used as starting values for the equatorially located tetrahydrofurfuryl groups in **6**. Concerning the axial location, starting values of 5 and 3.5 kJ mol^{-1} (according to **1c**, vide supra) were used for $\Delta H°_{ax}(g^-,g^+)$ and $\Delta H°_{ax}(g^-,g^t)$, respectively. The results of the iterative process for **6** at 318, 276, 249, and 217 K are summarized in Table VI. From the thermodynamic parameters given in Table VI the $C_{4'}$–$C_{5'}$ rotamer populations can be calculated for axial and equatorial tetrahydrofurfuryl (Table VII). It is found that a marked preference exists for the g^- rotamer of axial tetrahydrofurfuryl. For 318 K $x_{ax}(g^+) = 0.25$, $x_{ax}(g^t) = 0.14$, and $x_{ax}(g^-) = 0.61$ and for 217 K $x_{ax}(g^+) = 0.14$, $x_{ax}(g^t) = 0.06$, and $x_{ax}(g^-) = 0.80$. Clearly, a pronounced repulsion between $O_{5'}$ and $O_{1'}$ dominates the $C_{4'}$–$C_{5'}$ conformation for axial tetrahydrofurfuryl. The $C_{4'}$–$C_{5'}$ conformation for equatorial tetrahydrofurfuryl resembles the $C_{4'}$–$C_{5'}$ conformation for 5′-P^{IV} tetrahydrofurfuryl. For 318 K $x_{eq}(g^+) = 0.37$, $x_{eq}(g^t) = 0.39$, and $x_{eq}(g^-) = 0.24$ and for 217 K $x_{eq}(g^+) = 0.43$, $x_{eq}(g^t) = 0.44$, and $x_{eq}(g^-) = 0.13$. For **5** (5′-P^{IV}) at 320 K $x(g^+) = 0.40$, $x(g^t) = 0.44$, and $x(g^-) = 0.16$ and at 225 K $x(g^+) = 0.41$, $x(g^t) = 0.49$, and $x(g^-) = 0.08$. From the present results it is clearly established that a change in coordination from P^{IV} to P^V TBP for the various tetrahydrofurfuryl compounds is transmitted into a $C_{4'}$–$C_{5'}$ conformational change when the tetrahydrofurfuryl group is located in the axis of the TBP. On the basis of the experimental and theoretical results, we speculate that conformational changes in DNA can be also achieved by activation of the phosphate via a P^{IV} into P^V TBP transition. This dynamic model has been recently employed by us to give a description of the primary step in the cascade of internal motions for the isomerization of right-handed B DNA into left-handed Z DNA.[1,2,16] Although the model compounds used give only a confined presentation of nucleotides, our preliminary results on 5′-P^V TBP 2′,3′-*O*-isopropylideneuridine show a very pronounced g^- population even without correction on pseudorotation.[17] It seems to us that the extra asymmetry present in nucleotides in comparison with the 5′-phosphorylated tetrahydrofurfuryls will influence the rotamer population around the $C_{4'}$–$C_{5'}$ bond.

Experimental Section

Materials. All solvents and materials were reagent grade and were used as received or purified as required. All reactions were routinely run under an atmosphere of dry nitrogen.

Spectroscopy. ^1H NMR spectra were run in the FT mode on a Bruker CXP-300 spectrometer at 300.1 MHz, 32K data base, 3000-Hz SW, and 5.47-s acquisition time. Coupling constants were taken from expansions of the $H_{5'}/H_{5''}$ patterns and iteratively analyzed with the PANIC program.[18] Chemical shifts were related to the CHD_2COCD_3 quintet, which was set at δ 2.17. ^{31}P and ^{13}C spectra were run at 36.4 and 22.6 MHz, respectively, on a Bruker HX-90R spectrometer with a Digilab FT-NMR-3 pulsing accessory. Chemical shifts are respectively related to 85% H_3PO_4 and Me_4Si as external standards.

Synthesis. (Tetrahydrofurfuryloxy)diphenylphosphine. A solution of chlorodiphenylphosphine (100 mmol, 22.1 g) in 40 mL of anhydrous diethyl ether was added over 30 min to a stirred and cooled (0 °C) solution of tetrahydrofurfuryl alcohol (100 mmol, 10.2 g) and triethylamine (100 mmol, 10.1 g) in 60 mL of anhydrous diethyl ether. After completion of the addition the mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was removed by filtration and washed with 20 mL of anhydrous diethyl ether. After removal of the solvent the oily residue was distilled under reduced pressure to yield (tetrahydrofurfuryloxy)diphenylphosphine as a colorless liquid (80 mmol, 80%), bp 154 °C (0.5 mm), ^{31}P NMR δ 115.5.

(Tetrahydrofurfuryloxy)diphenylphosphine Oxide (1a). An aqueous 12% hydrogen peroxide solution (10 mL) was added dropwise to a cooled (0 °C) solution of (tetrahydrofurfuryloxy)diphenylphosphine (17 mmol, 4.8 g) in 40 mL of acetone. The reaction mixture was refluxed for 3 h, cooled to room temperature, and poured into 60 mL of water. The solution was extracted with diethyl ether. Evaporation of the diethyl ether layer yielded **1a** as a colorless liquid: ^1H NMR δ 1.8–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.8–3.9 (2 H, m, $H_{1'}$), 4.0–4.1 (2 H, m, $H_{5'}$), 4.2–4.3 (1 H, m, $H_{4'}$), 7.5–8.1 (10 H, m, Ar H); ^{31}P NMR δ 35.8; ^{13}C NMR δ 27.1 ($C_{2'}$), 29.1 ($C_{3'}$), 68.4 ($C_{5'}$, $J_{POC} = 6$ Hz), 69.5 ($C_{1'}$), 78.9 ($C_{4'}$, $J_{POCC} = 8$ Hz), 130–134 (m, Ar C).

(Tetrahydrofurfuryloxy)diphenylphosphine Sulfide (1b). S_8 (3 mmol, 0.77 g) was added in small portions to a magnetically stirred solution of 23 mmol (5.8 g) of (tetrahydrofurfuryloxy)diphenylphosphine in 20 mL of dry toluene. After completion of the addition the reaction mixture was refluxed for 1 h. Evaporation of the toluene yielded **1b** as a yellowish viscous oil: ^1H NMR δ 1.5–2.2 (4 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (2 H, m, $H_{1'}$), 4.0–4.2 (2 H, m, $H_{5'}$), 4.3–4.4 (1 H, m, $H_{4'}$), 7.2–8.3 (10 H, m, Ar H);

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(18) PANIC program: Copyright, Bruker Spectrospin AG, Switzerland.

^{31}P NMR δ 82.3; ^{13}C NMR δ 27.2 ($C_{2'}$), 29.1 ($C_{3'}$), 68.2 ($C_{5'}$, J_{POC} = 6 Hz), 69.4 ($C_{1'}$), 78.7 ($C_{4'}$, J_{POCC} = 8 Hz), 129–134 (m, Ar C).

2,2-Diphenyl-2-(tetrahydrofurfuryloxy)-2,2-dihydro-4,5-dimethyl-1,3,2-dioxoasphosphol-4-ene (1c). A cooled (0 °C) solution of (tetrahydrofurfuryloxy)diphenylphosphine (10 mmol, 2.9 g) and butanedione (10 mmol, 0.9 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. The product, which precipitated on standing at −20 °C for several days, was washed with anhydrous acetone to yield white crystals, mp 103–104 °C. Anal. Calcd for $C_{21}H_{25}O_4P$: C, 67.73; H, 6.77. Found: C, 67.57; H, 6.82. ^1H NMR δ 1.7–2.0 (4 H, m, $H_{2'}/H_{3'}$), 2.0 (6 H, s, CH_3), 3.4–3.5 (2 H, m, $H_{1'}$), 3.5–3.6 (2 H, m, $H_{5'}$), 4.0–4.1 (1 H, m, $H_{4'}$), 7.5–8.0 (10 H, m, Ar H); ^{31}P NMR δ −24.4; ^{13}C NMR δ 11.8 (CH_3, J_{POCC} = 9 Hz), 27.1 ($C_{2'}$), 29.8 ($C_{3'}$), 68.0 ($C_{5'}$, J_{POC} = 9 Hz), 69.2 ($C_{1'}$), 80.0 ($C_{4'}$, J_{POCC} = 8 Hz), 128–134 (m, Ar & olefinic C).

2,2,4,5-Tetraphenyl-2-(tetrahydrofurfuryloxy)-2,2-dihydro-1,3,2-dioxaphosphol-4-ene (1d). A cooled (0 °C) solution of (tetrahydrofurfuryloxy)diphenylphosphine (10 mmol, 2.9 g) and diphenylethanedione (10 mmol, 2.1 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **1d** as a viscous oil. ^1H NMR δ 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.7–3.8 (2 H, m, $H_{1'}$), 3.8–3.9 (2 H, m, $H_{5'}$), 4.1–4.2 (1 H, m, $H_{4'}$), 7.3–8.2 (20 H, m, Ar H); ^{31}P NMR δ −28.1; ^{13}C NMR δ 27.1 ($C_{2'}$), 29.8 ($C_{3'}$), 68.4 ($C_{5'}$, J_{POC} = 9 Hz), 69.3 ($C_{1'}$), 79.9 ($C_{4'}$, J_{POCC} = 6 Hz), 128–133 (m, Ar & olefinic C).

(Cyclopentylmethoxy)diphenylphosphine. This compound was prepared from chlorodiphenylphosphine (100 mmol, 22.1 g) and cyclopentylmethanol (100 mmol, 10.0 g) according to the procedure that was described for the preparation of (tetrahydrofurfuryloxy)diphenylphosphine. The product was obtained as a colorless liquid (74 mmol, 74%) bp 162 °C (0.5 mm), ^{31}P NMR δ 111.8.

(Cyclopentylmethoxy)diphenylphosphine Oxide (2a). **2a** was prepared from (cyclopentylmethoxy)diphenylphosphine by the procedure that was described for the preparation of **1a**. The product was obtained as a white crystalline powder, mp 83.5–84.5 °C. Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.99; H, 7.05. Found: C, 71.99; H, 7.16. ^1H NMR δ 1.4–2.0 (8 H, m, cyclopentane H), 2.4 (1 H, m, $H_{4'}$), 4.0 (2 H, t, $H_{5'}$), 7.6–8.0 (10 H, m, Ar H); ^{31}P NMR δ 33.8; ^{13}C NMR δ 26.8 ($C_{1'a}/C_{3'}$), 30.5 ($C_{1'}/C_{2'}$), 41.9 ($C_{4'}$, J_{POCC} = 6 Hz), 69.7 ($C_{5'}$, J_{POC} = 6 Hz), 130–138 (m, Ar C).

2,2-Diphenyl-2-(cyclopentylmethoxy)-2,2-dihydro-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (2b). A cooled (0 °C) solution of (cyclopentylmethoxy)diphenylphosphine (10 mmol, 2.8 g) and butanedione (10 mmol, 0.9 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **2b** as a viscous oil: ^1H NMR δ 1.2–1.8 (8 H, m, cyclopentane H), 2.0 (6 H, s, CH_3), 2.2 (1 H, m, $H_{4'}$), 3.5 (2 H, t, $H_{5'}$), 7.4–8.0 (10 H, m, Ar H); ^{31}P NMR δ −26.1; ^{13}C NMR δ 11.9 (CH_3), 26.9 ($C_{1'a}/C_{3'}$), 30.7 ($C_{1'}/C_{2'}$), 41.7 ($C_{4'}$, J_{POCC} = 6 Hz), 69.9 ($C_{5'}$, J_{POC} = 6 Hz), 129–134 (m, Ar & olefinic C).

2,2,4,5-Tetraphenyl-2-(cyclopentylmethoxy)-2,2-dihydro-1,3,2-dioxaphosphol-4-ene (2c). A cooled (0 °C) solution of (cyclopentylmethoxy)diphenylphosphine (10 mmol, 2.8 g) and diphenylethanedione (10 mmol, 2.1 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **2c** as a viscous oil: ^1H NMR δ 1.3–2.0 (8 H, m, cyclopentane H), 2.3 (1 H, m, $H_{4'}$), 3.6 (2 H, t, $H_{5'}$), 7.3–8.2 (20 H, m, Ar H); ^{31}P NMR δ −22.5; ^{13}C NMR δ 26.9 ($C_{1'a}$, $C_{3'}$), 30.5 ($C_{1'}/C_{2'}$), 42.0 ($C_{4'}$, J_{POCC} = 6 Hz), 69.8 ($C_{5'}$, J_{POC} = 6 Hz), 128–135 (m, Ar & olefinic C).

Tetrahydrofurfuryl Diethyl Phosphite. This compound was prepared from chlorodiethoxyphospine[19] (420 mmol, 52.3 g) and tetrahydrofurfuryl alcohol (420 mmol, 42.8 g), according to the procedure that was described for the preparation of (tetrahydrofurfuryloxy)diphenylphosphine. The product was obtained as a colorless liquid (230 mmol, 55%), bp 65 °C (0.03 mm), ^{31}P NMR δ 138.3.

Tetrahydrofurfuryl Diethyl Phosphate (3a). An ozone–oxygen stream was passed through a solution of tetrahydrofurfuryl diethyl phosphite (45 mmol, 10 g) in 60 ml of dry dichloromethane at −78 °C, until a light blue color of excess ozone was apparent.[20] The reaction mixture was then sparged with dry nitrogen to remove excess ozone. The solution was warmed to room temperature over about 1 h. Evolution of singlet oxygen proceeded smoothly, beginning at −30 °C. Evaporation of the solvent yielded an oily residue, which was distilled under reduced pressure to yield **3a** as a colorless liquid (18 mmol, 40%): bp 79 °C (0.03 mm); ^1H NMR δ 1.4 (6 H, t, CH_3, J_{HH} = 7 Hz), 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (2 H, m, $H_{1'}$), 4.0–4.1 (2 H, m, $H_{5'}$), 4.1–4.3 (5 H, m, $H_{4'}/CH_2$); ^{31}P NMR δ 4.2; ^{13}C NMR δ 17.3 (CH_3, J_{POCC} = 6 Hz), 27.1 ($C_{2'}$), 29.0 ($C_{3'}$), 65.0 (CH_2, J_{POC} = 6 Hz), 69.5 ($C_{1'}$), 70.6 ($C_{5'}$, J_{POC} = 6 Hz), 78.7 ($C_{4'}$, J_{POCC} = 8 Hz).

Tetrahydrofurfuryl Diethyl Thiophosphate (3b). S_8 (8.6 mmol, 2.2 g) was added in small portions to a magnetically stirred solution of 69 mmol (15.3 g) tetrahydrofurfuryl diethyl phosphite in 100 mL of dry toluene. After completion of the addition the reaction mixture was refluxed for 2 h. ^{31}P NMR indicated the reaction to be complete. The product was purified by distillation under reduced pressure to yield **3b** as a slightly colored liquid (31 mmol, 45%): bp 89–90 °C (0.001 mm); ^1H NMR δ 1.5 (6 H, t, CH_3, J_{HH} = 7 Hz), 1.7–2.2 (4 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (2 H, m, $H_{1'}$), 4.0–4.2 (2 H, m, $H_{5'}$), 4.2–4.4 (5 H, m, $H_{4'}/CH_2$); ^{31}P NMR δ 68.0; ^{13}C NMR δ 17.0 (CH_3, J_{POCC} = 8 Hz), 27.1 ($C_{2'}$), 29.2 ($C_{3'}$), 65.5 (CH_2, J_{POC} = 6 Hz), 69.5 ($C_{1'}$), 71.2 ($C_{5'}$, J_{POC} = 7 Hz), 78.5 ($C_{4'}$, J_{POCC} = 7 Hz).

2,2-Diethoxy-2-(tetrahydrofurfuryloxy)-2,2-dihydro-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (3c). A cooled (0 °C) solution of tetrahydrofurfuryl diethyl phosphite (10 mmol, 2.2 g) and butanedione (10 mmol, 0.9 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **3c** as a viscous oil: ^1H NMR δ 1.3 (6 H, t, CH_3, J_{HH} = 7 Hz), 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 1.9 (6 H, s, CH_3), 3.7–3.9 (2 H, m, $H_{1'}$), 3.8–3.9 (2 H, m, $H_{5'}$), 4.0–4.1 (4 H, m, CH_2), 4.1–4.3 (1 H, m, $H_{4'}$); ^{31}P NMR δ −45.8; ^{13}C NMR δ 10.9 (CH_3), 16.9 (CH_3, J_{POCC} = 6 Hz), 26.1 ($C_{2'}$), 28.8 ($C_{3'}$), 64.1 (CH_2, J_{POC} = 11 Hz), 68.7 ($C_{1'}$), 69.9 ($C_{5'}$, J_{POC} = 11 Hz), 78.2 ($C_{4'}$, J_{POCC} = 9 Hz), 129.4 (olefinic C, J_{POC} = 2 Hz).

2,2-Diethoxy-2-(tetrahydrofurfuryloxy)-2,2-dihydro-4,5-diphenyl-1,3,2-dioxaphosphol-4-ene (3d). A cooled (0 °C) solution of tetrahydrofurfuryl diethyl phosphite (10 mmol, 2.2 g) and diphenylethanedione (10 mmol, 2.1 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **3c** as a viscous oil: ^1H NMR δ 1.4 (6 H, t, CH_3, J_{HH} = 7 Hz), 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.7–4.0 (2 H, m, $H_{1'}$), 4.0–4.1 (2 H, m, $H_{5'}$), 4.1–4.3 (5 H, m, $H_{4'}/CH_2$), 7.4–8.3 (10 H, m, Ar H); ^{31}P NMR δ −46.6; ^{13}C NMR δ 17.8 (CH_3, J_{POCC} = 8 Hz), 27.1 ($C_{2'}$), 29.6 ($C_{3'}$), 65.3 (CH_2, J_{POC} = 12 Hz), 69.5 ($C_{1'}$), 71.0 ($C_{5'}$, J_{POC} = 11 Hz), 79.5 ($C_{4'}$, J_{POCC} = 11 Hz), 128–137 (Ar & olefinic C).

2-(Tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane. This compound was prepared from 2-chloro-1,3,2-dioxaphospholane[21] (474 mmol, 60.0 g) and tetrahydrofurfuryl alcohol (474 mmol, 48.3 g) according to the procedure that was described for the preparation of (tetrahydrofurfuryloxy)diphenylphosphine. The product was obtained as a colorless oil (298 mmol, 63%), bp 75–76 °C (0.05 mm), ^{31}P NMR δ 138.3.

2-(Tetrahydrofurfuryloxy)-2-oxo-1,3,2-dioxaphospholane (4a). This compound was prepared from 2-(tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane according to the procedure that was described for the preparation of **3a**. The product was obtained as a colorless oil: bp 128 °C (0.05 mm); ^1H NMR δ 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (2 H, m, $H_{1'}$), 4.1–4.2 (3 H, m, $H_{4'}/H_{5'}$), 4.5–4.6 (4 H, d, CH_2); ^{31}P NMR δ 22.2; ^{13}C NMR δ 27.1 ($C_{2'}$), 29.0 ($C_{3'}$), 68.0 (CH_2, J_{POC} = 2 Hz), 69.5 ($C_{1'}$), 71.5 ($C_{5'}$, J_{POC} = 6 Hz), 78.7 ($C_{4'}$, J_{POCC} = 8 Hz).

2-(Tetrahydrofurfuryloxy)-2-thioxo-1,3,2-dioxaphospholane (4b). S_8 (8.6 mmol, 2.2 g) was added in small portions to a magnetically stirred solution of 69 mmol (13.2 g) of 2-(tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane in 100 mL of dry toluene. After completion of the addition the reaction mixture was refluxed for 3 h. ^{31}P NMR indicated the reaction to be complete. The product was purified by distillation under reduced pressure to yield **4b** as a slightly colored liquid (17 mmol, 25%): bp 182–185 °C (0.02 mm); ^1H NMR δ 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (2 H, m, $H_{1'}$), 4.0–4.1 (2 H, m, $H_{5'}$), 4.1–4.2 (1 H, m, $H_{4'}$), 4.4–4.6 (4 H, d, CH_2); ^{31}P NMR δ 84.3; ^{13}C NMR δ 27.0 ($C_{2'}$), 29.2 ($C_{3'}$), 67.5 (CH_2, J_{POC} = 2 Hz), 69.3 ($C_{1'}$), 70.8 ($C_{5'}$, J_{POC} = 8 Hz), 78.6 ($C_{4'}$, J_{POCC} = 9 Hz).

2,3-Dimethyl-5-(tetrahydrofurfuryloxy)-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]non-2-ene (4c). A cooled (0 °C) solution of 2-(tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane (10 mmol, 1.9 g) and butanedione (10 mmol, 0.9 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **4c** as a colorless viscous oil: ^1H NMR δ 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 2.4 (6 H, s, CH_3), 3.7–4.0 (2 H, m, $H_{5'}$), 3.9–4.1 (2 H, m, $H_{1'}$), 4.0–4.2 (1 H, m, $H_{4'}$), 4.3–4.4 (4 H, d, CH_2); ^{31}P NMR δ −22.8; ^{13}C NMR δ 11.5 (CH_3), 27.0 ($C_{2'}$), 29.2 ($C_{3'}$), 61.3 (CH_2, J_{POC} = 5 Hz), 69.4 ($C_{1'}$), 70.7 ($C_{5'}$, J_{POC} = 10 Hz), 79.0 ($C_{4'}$, J_{POCC} = 9 Hz), 130.7 (olefinic C, J_{POC} = 5 Hz).

2,3-Diphenyl-5-(tetrahydrofurfuryloxy)-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]non-2-ene (4d). A cooled (0 °C) solution of 2-(tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane (10 mmol, 1.9 g) and diphenylethanedione (10 mmol, 2.1 g) in 5 mL of anhydrous diethyl ether was stirred for 3 h. Evaporation of the solvent yielded **4d** as a viscous oil: ^1H NMR δ 1.7–2.1 (4 H, m, $H_{2'}/H_{3'}$), 3.7–4.0 (2 H, m, $H_{5'}$), 4.0–4.1 (2 H, m, $H_{1'}$), 4.1–4.2 (1 H, m, $H_{4'}$), 4.3–4.4 (4 H, d, CH_2), 7.5–8.4 (10 H, m, Ar H); ^{31}P NMR δ −23.2; ^{13}C NMR δ 27.2 ($C_{2'}$), 29.4 ($C_{3'}$), 61.2 (CH_2, J_{POC} = 4 Hz), 69.5 ($C_{1'}$), 70.7 ($C_{5'}$, J_{POC} = 9 Hz), 79.5 ($C_{4'}$, J_{POCC}

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= 8 Hz), 128–136 (Ar & olefinic C).

Tri(tetrahydrofurfuryl) Phosphite. A solution of PCl_3 (300 mmol, 41.3 g) in 100 mL of anhydrous diethyl ether was added dropwise to a stirred and cooled (0 °C) solution of tetrahydrofurfuryl alcohol (900 mmol, 91.5 g) and triethylamine (900 mmol, 90.9 g) in 150 mL of anhydrous diethyl ether. After completion of the addition the mixture was refluxed for 1 h. The precipitated triethylamine hydrochloride was removed by filtration and washed with two 20-mL portions of anhydrous diethyl ether. After removal of the solvent the oily residue was distilled under reduced pressure to afford the desired product as a colorless liquid (265 mmol, 88%), bp 163–165 °C (0.05 mm), ^{31}P NMR δ 138.4.

Tri(tetrahydrofurfuryl) Phosphate (5). This compound was prepared from tri(tetrahydrofurfuryl) phosphite according to the procedure that was described for the preparation of **3a**. The product could not be purified by distillation in vacuo. ^1H NMR δ 1.7–2.1 (12 H, m, $H_{2'}/H_{3'}$), 3.8–4.0 (6 H, m, $H_{1'}$), 4.0–4.1 (6 H, m, $H_{5'}$), 4.1–4.2 (3 H, m, $H_{4'}$); ^{31}P NMR δ 1.2; ^{13}C NMR δ 27.1 ($C_{2'}$), 29.2 ($C_{3'}$), 69.5 ($C_{1'}$), 70.6 ($C_{5'}$, J_{POC} = 6 Hz), 78.7 ($C_{4'}$, J_{POCC} = 7 Hz).

2,2,2-Tri(tetrahydrofurfuryl)-2,2-dihydro-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (6). This compound was prepared from tri(tetrahydrofurfuryl) phosphite and butanedione according to the procedure that was described for the preparation of **3c**. The product was obtained as a yellowish viscous oil. ^1H NMR δ 1.7–2.1 (12 H, m, $H_{2'}/H_{3'}$), 1.9 (6 H, s, CH_3), 3.7–3.9 (6 H, m, $H_{1'}$), 3.8–3.9 (6 H, m, $H_{5'}$), 4.1–4.2 (3 H, m, $H_{4'}$); ^{31}P NMR δ −50.3; ^{13}C NMR δ 10.9 (CH_3), 26.8 ($C_{2'}$), 28.9 ($C_{3'}$), 69.0 ($C_{1'}$), 69.9 ($C_{5'}$, J_{POC} = 10 Hz), 78.4 ($C_{4'}$, J_{POCC} = 9 Hz), 130.0 (olefinic C, J_{POC} = 2 Hz).

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Appendix

Part A. Assuming that λ is the mole fraction that corresponds to axial location of the tetrahydrofurfuryl group in **1c** it follows that

$$\frac{\mathrm{d}\ \ln\ (x(\mathrm{j})/x(\mathrm{g}^-))}{\mathrm{d}\ (1/T)} = [\lambda\Delta H^\circ_{ax}(\mathrm{g}^-,\mathrm{j}) + (1-\lambda)\Delta H^\circ_{eq}(\mathrm{g}^-,\mathrm{j})]R^{-1}$$

where $\mathrm{j} = \mathrm{g}^+,\mathrm{g}^t$. Since i (Figure 5) is the only stereoisomer that does not represent violations of the polarity and/or strain rules, it can be concluded that $\lambda \rightarrow 1$ with decreasing temperature. The first derivatives of the curves in Figure 4 then approach $\Delta H^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^+)R^{-1}$ and $\Delta H^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^t)R^{-1}$.

Part B. Since the three tetrahydrofurfuryl groups in **6** are divided over one axial and two equatorial sites in the TBP it holds that $x^{exp}(\mathrm{i}) = {}^1/_3x_{ax}(\mathrm{i}) + {}^2/_3x_{eq}(\mathrm{i})$ where $\mathrm{i} = \mathrm{g}^+,\mathrm{g}^t,\mathrm{g}^-$. The time-averaged $C_{4'}$–$C_{5'}$ conformation which is obtained under pseudorotation conditions is determined by eight thermodynamic parameters. Four of them refer to axial tetrahydrofurfuryl ($\Delta H^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^+)$, $\Delta H^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^t)$, $\Delta S^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^+)$, and $\Delta S^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^t)$) and four to equatorial tetrahydrofurfuryl ($\Delta H^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^+)$, $\Delta H^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^t)$, $\Delta S^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^+)$, and $\Delta S^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^t)$). These parameters can be substituted in the aforementioned equation (with $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$) as

$$x_{ax}(\mathrm{j}) = \frac{\exp[-\Delta G^\circ_{ax}(\mathrm{g}^-,\mathrm{j})(RT)^{-1}]}{1 + \exp[-\Delta G^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^+)(RT)^{-1}] + \exp[-\Delta G^\circ_{ax}(\mathrm{g}^-,\mathrm{g}^t)(RT)^{-1}]}$$

$$x_{eq}(\mathrm{j}) = \frac{\exp[-\Delta G^\circ_{eq}(\mathrm{g}^-,\mathrm{j})(RT)^{-1}]}{1 + \exp[-\Delta G^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^+)(RT)^{-1}] + \exp[-\Delta G^\circ_{eq}(\mathrm{g}^-,\mathrm{g}^t)(RT)^{-1}]}$$

where $\mathrm{j} = \mathrm{g}^+,\mathrm{g}^t$. In this way, two independent equations in the eight unknown thermodynamic parameters are obtained for each temperature. An iterative computer program, based on the FORTRAN subroutine by Powell,[22] was used to solve the set of eight equations that resulted from the NMR measurements on **6** at 318, 276, 249, and 217 K.

Registry No. 1a, 91237-85-3; **1b**, 91237-86-4; **1c**, 91237-87-5; **1d**, 91237-88-6; **2a**, 91237-89-7; **2b**, 91237-90-0; **2c**, 91237-91-1; **3a**, 71774-92-0; **3b**, 3513-92-6; **3c**, 91237-92-2; **3d**, 91237-93-3; **4a**, 91237-94-4; **4b**, 91237-95-5; **4c**, 91237-96-6; **4d**, 91237-97-7; **5**, 10427-00-6; **6**, 91237-98-8; Ph_2PCl, 1079-66-9; $CH_3C(O)C(O)CH_3$, 431-03-8; PhC(O)C(O)Ph, 134-81-6; $(EtO)_2PCl$, 589-57-1; PCl_3, 7719-12-2; (tetrahydrofurfuryloxy)diphenylphosphine, 91237-99-9; tetrahydrofurfuryl alcohol, 97-99-4; (cyclopentylmethoxy)diphenylphosphine, 91238-00-5; cyclopentylmethanol, 3637-61-4; tetrahydrofurfuryl diethyl phosphite, 91238-01-6; 2-(tetrahydrofurfuryloxy)-1,3,2-dioxaphospholane, 91238-02-7; 2-chloro-1,3,2-dioxaphospholane, 822-39-9; tris(tetrahydrofurfuryl) phosphite, 5971-30-2.

(22) Powell, M. J. D. "A FORTRAN Subroutine for Solving Systems of Non-linear Algebraic Equations", Harvell Report, AERE-R5947, H.M.S.O., 1968.

(23) **Note Added in Proof**: We recently obtained independent evidence for the impact of O_5–$O_{1'}$ charge repulsion on the C_4–$C_{5'}$ conformation in 5′-P^{IV} tetrahydrofurfuryls (e.g., **1a**) by conformational analyses in various solvents. It was found that lowering the solvent polarity *indeed* results in an increased g^- population (**1a** in D_2O $x(g^-) = 0.00$, CCl_4 $x(g^-) = 0.23$). Full details will be published.