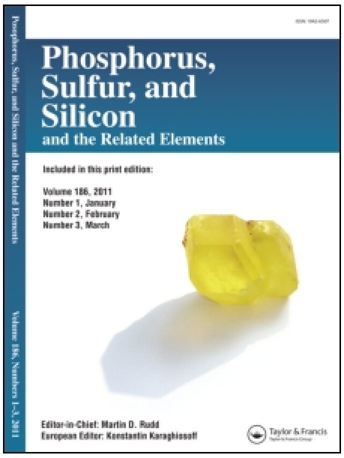

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INFLUENCE OF ELECTRON-WITHDRAWING SUBSTITUENTS IN THE OXAPHOSPHOLE RING ON THE AXIAL CONFORMATIONAL TRANSMISSION IN P^v COMPOUNDS

N. K. De Vries[a]; H. M. Buck[a]
[a] Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

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INFLUENCE OF ELECTRON-WITHDRAWING SUBSTITUENTS IN THE OXAPHOSPHOLE RING ON THE AXIAL CONFORMATIONAL TRANSMISSION IN P^V COMPOUNDS

N. K. DE VRIES* and H. M. BUCK

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

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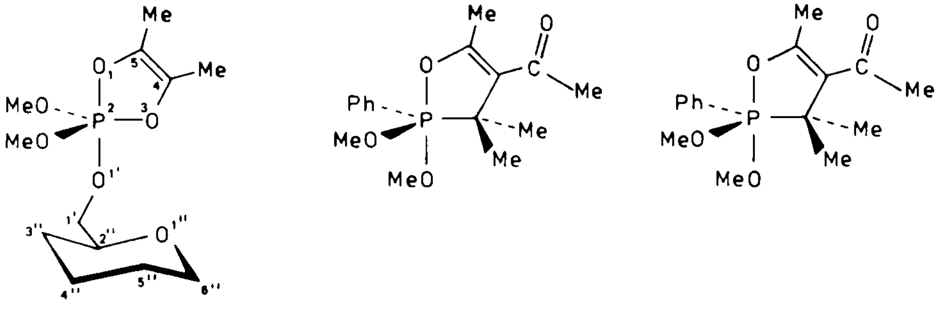
A MNDO and 300-MHz ^{1}H NMR study of some trigonal-bipyramidal (TBP) five-coördinated phosphorus (P^V) compounds is reported. It is shown by the MNDO calculations that, in the oxaphosphole P^V TBP compounds **5a–c**, the electron distribution in the axial bonds of the TBP is affected by the electronegativity of the substituent at C_4 of the oxaphosphole ring. With increasing electronegativity of the substituent at C_4, the electron density on the axial exocyclic oxygen atom $O_{1'}$ decreases whereas the electron density on the axial endocyclic atom O_1 increases. This is supported by a ^{1}H NMR conformational analysis of the $C_{1'}$—$C_{2''}$ bond of the oxaphosphole P^V TBP compounds **6–11**. The gauche(−) rotamer fraction ($O_{1'}$ and $O_{1''}$ trans situated) of these compounds, which is correlated to the electron density on $O_{1'}$, is reduced to 30% as compared to the absolute axial g^- rotamer fraction (59%) of the dioxaphosphole P^V TBP compound **13**, most likely because of the presence of the carbonyl group at C_4 of the oxaphosphole ring. So, both the ^{1}H NMR and MNDO study show that electron withdrawing substituents on the oxaphosphole ring of P^V TBP compounds reverse the electron transfer in the axial P—O bonds of the TBP (as compared to dioxaphosphole compounds), from exocyclic $O_{1'}$ towards endocyclic O_1.

INTRODUCTION

Recently, we have studied the conformation around $C_{1'}$—$C_{2''}$ of the 1′-phosphorylated tetrahydropyran-2″-methyl (THPM) compound **1** (see Scheme I).



1 2 3

Scheme I Compounds **1–3**.

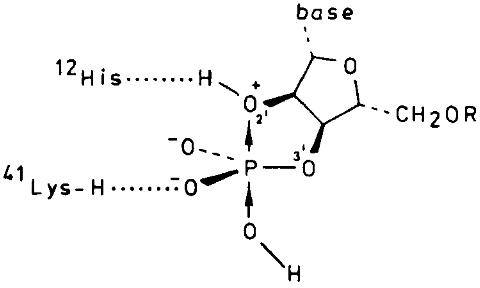


FIGURE 1 Electron transfer in the axial P—O bonds of a P^V dioxaphosphole compound.

It was shown that the fraction of the gauche(−) (g^-) rotamer (maximum distance between $O_{1'}$ and $O_{1''}$) increases to 40% on going from P^{IV} (four-coördinate phosphorus) to P^V (five-coördinated phosphorus) TBP (trigonal bipyramidal) provided that the THPM group is in axial position.[1] This conformational effect can be explained by an increased electron transfer towards the axial exocyclic oxygen atom $O_{1'}$ of the TBP with respect to the corresponding $O_{1'}$ in the P^{IV} compounds, which results in an increased repulsion between the oxygen atoms $O_{1'}$ and $O_{1''}$ (Scheme I). The principle of electron transfer in the axial sites of a P^V TBP appears to be of general importance. For instance, the hydrolysis of a cyclic phosphate, which is an intermediate in the hydrolysis of RNA by Ribonuclease[2] (see Figure 1), proceeds via a transient P^V structure which is formed after axial nucleophilic attack on the cyclic phosphate.

The electron density on the axial exocyclic nucleophile is reduced by the opposite axial oxygen atom $O_{2'}$. This oxygen atom is specifically protonated by the His-12 site of the enzym to function as an electron acceptor. Subsequently, the P—$O_{2'}$ bond is broken. Similar electron transfer processes in the axial P—O bonds of the TBP were suggested in the compounds **2–3** (Scheme I).[3,4] In these model compounds, the carbonyl group at C_4 of the oxaphosphole ring acts as an electron acceptor, affecting the electron distribution around this ring. We anticipated that this should result in a decreased electron density on the axial exocyclic oxygen atom $O_{1'}$ (as compared to the electron density on $O_{1'}$ of compound **1**), with an accompanying reversal in the conformational transmission effect (decreased g^- rotamer fraction). This prompted us to study the electron distribution of some P^V structures. In this work we specifically focus on electron transfer in the axial bonds of P^V TBP systems, via MNDO calculations (compounds **4–5**, Scheme II) and a 300-MHz ^{1}H NMR study (compounds **6–11**, Scheme III). Note that the compounds **6–11** are particularly suited for this study since they do not show phosphorus pseudorotation which results in a fixed location of the OR group in the axial position of the TBP. Also, the $O_{1'}$—C—C—$O_{1''}$ fragment in these molecules can be used as a probe for the electron density on the axial oxygen atom $O_{1'}$ (vide infra). The results of the calculations which indeed show a decrease in electron density on the axial exocyclic oxygen atom $O_{1'}$ (see Results and Discussion 1. MNDO calculations), are supported by the ^{1}H NMR study of the compounds **6–11**. The measurements show a decrease in trans orientation between $O_{1'}$ and $O_{1''}$ (g^- rotamer fraction decreases), which is an indication of a reduced repulsion between these two oxygen atoms (see Results and Discussion 2. ^{1}H NMR measurements).

RESULTS AND DISCUSSION

1. *MNDO calculations*

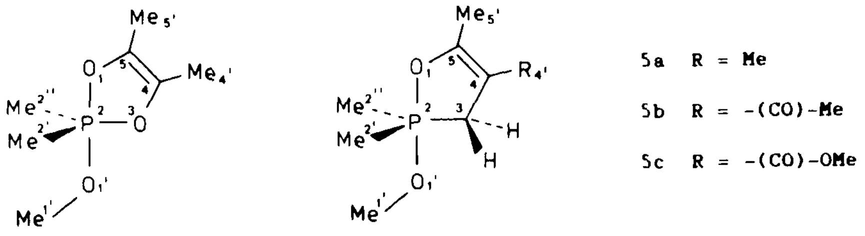
Calculations were carried out with the MNDO program, QCPE version.[5] This program does not include d-orbital functions for phosphorus. However, a number of ab initio studies on P^V compounds revealed that the principal concepts of bonding are adequately described without the introduction of d-functions.[6] Indeed, the results of our MNDO calculations for pentamethoxyphosphorane, listed in Table I, show that the values for the axial P—O bond lengths and the electron density on the axial oxygen atoms are larger than the corresponding values for the equatorial positions. This is in accordance with the TBP structure.[7] The calculated values for the P—O bond lengths are in good agreement with the values obtained from X-ray crystallographic data for pentaphenoxyphosphorane.[8] Therefore, it seems safe to assume that MNDO calculations predict the structure of P^V TBP compounds correctly.

TABLE I

Results of the MNDO calculations for trimethylphosphate and pentamethoxyphosphorane

Compound	P—O bond length (A°)	Electron density on oxygen	O(ax)—P—O(eq)
Trimethylphosphate	1.604	−0.487	—
Pentamethoxyphosphorane	1.63(eq) 1.67(ax)	−0.512(eq) −0.595(ax)	90°

For the calculations we selected the structures of the compounds **4–5** (see Scheme II). The non-pseudorotating P^V TBP compounds **2–3** are represented by the structurally similar compound **5**. To facilitate the calculations without changing the actual structures, the equatorial exocyclic substituents of **2–3** are



4 5

Scheme II Modelcompounds **4–5** for the MNDO calculations.

replaced by methyl groups whereas the methyl groups at C_3 of the oxaphosphole ring are replaced by hydrogen atoms which is presented in **5**. The structure of compound **4** is calculated to see whether the introduction of an equatorial oxygen atom (to form the dioxaphosphole ring) affects the electron density on the axial oxygen atoms, relative to compound **5**. All structures are optimized completely with respect to all variables i.e. bond lengths, bond angles and twist angles. The results of the calculations are listed in Tables II–IV.

TABLE II

Bond lengths in compounds **4**–**5** (A°)

	4	**5a**	**5b**	**5c**
$P—O_1$	1.759	1.824	1.881	1.923
$P—O_{1'}$	1.701	1.715	1.691	1.683
$P—C_3^a$	1.659	1.878	1.884	1.882
$O_1—C_5$	1.343	1.321	1.307	1.299
$C_4—C_5$	1.381	1.382	1.398	1.404

[a] Oxygen in compound **4**.

TABLE III

Bond angles and twist angles in compounds **4**–**5**

	4	**5a**	**5b**	**5c**
$P—O_1—C_5$	114.6	115.7	117.1	116.7
$O_1—P—C_3^a$	86.8	87.4	85.0	84.6
$C_{2'}—P—O_{1'}$	95.2	94.1	96.9	97.5
$C_{1'}—O_{1'}—P—C_{2'}$	63.3	59.5	60.6	61.8
$C_{4'}—C_4—C_5—O_1$	179.7	180.1	179.5	179.8

[a] Oxygen in compound **4**.

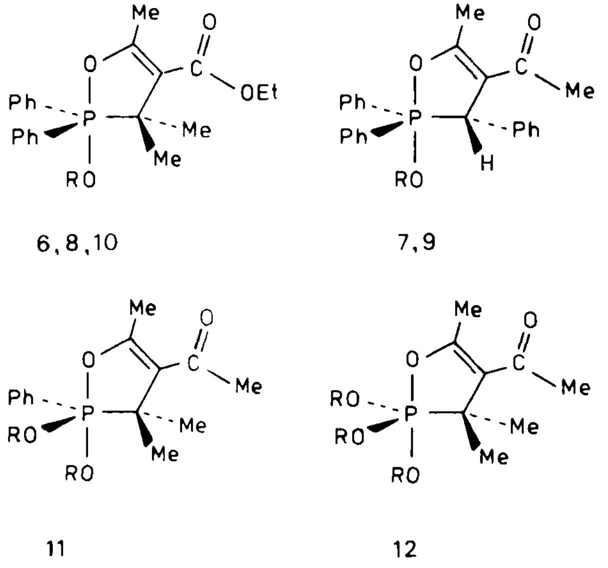
TABLE IV

Electron densities in compounds **4**–**5**

	4	**5a**	**5b**	**5c**
O_1	−0.513	−0.534	−0.546	−0.548
$O_{1'}$	−0.583	−0.617	−0.588	−0.577
C_3	−0.333[a]	0.095	0.138	0.148
P	1.029	0.757	0.718	0.704
C_5	0.018	0.186	0.263	0.297
C_4	−0.096	−0.399	−0.456	−0.454
$C_{4'}$	0.126	0.137	0.302	0.462

[a] Oxygen in compound **4**

As can be seen in Table IV there is a strong polarization of the C=C bond of **5**, induced by the substituent R at C_4 of the oxaphosphole ring, as predicted by Gorenstein and Buono.[3,4] The magnitude of this polarization depends on the nature of this substituent at C_4. A further inspection of the Tables reveals that the effects of the polarization of this π-system are transmitted through the ring, affecting the axial P—O bond lengths and the charge densities on both the axial oxygen atoms. Note that the P—O_1 bond is predicted to be longer than the P—$O_{1'}$ bond. This is related to the pπ–dπ back-bonding.[9] The calculations for compound **4** show that, in the dioxaphophole ring, the C=C bond is hardly polarized. Despite this difference in polarization between **4** and **5** there is not much difference in the calculated electron density on the axial oxygen atom $O_{1'}$ of these compounds. However, within the group of compounds (**5a–c**), which differ only by one substituent R, there is a clear trend towards a decreasing electron density on the axial exocyclic oxygen atom $O_{1'}$ with increasing polarization (increasing electronegativity of the substituent R) of the π-system of the oxaphosphole ring. This could be nicely demonstrated by a 300-MHz ^{1}H NMR study of the conformation around $C_{1'}$—$C_{2''}$ of the non-pseudorotating compounds **6–11** (Scheme III). Three staggered rotamers (g^- and g^+, g^t (Figure 4)) contribute to the conformation around this bond. The maximum distance between $O_{1'}$ and $O_{1''}$ is reached in the g^- rotamer (trans orientation of $O_{1'}$ and $O_{1''}$). Therefore, the g^- rotamer fraction can be used as a probe for the repulsion between these two oxygen atoms. It is shown that the g^- rotamer fraction of the compounds **6–11** is decreased as compared to, for example, compound **1**. This is presumably caused by the decreased electron density on the axial exocyclic oxygen atom $O_{1'}$ (vide infra).



	R
6	THPM[a]
7	THPM
8	CHM[b]
9	CHM
10	THFF[c]
11	THFF
12	THFF

[a] THPM = Tetrahydropyran-2-methyl [b] CHM = Cyclohexylmethyl
[c] THFF = Tetrahydrofurfuryl

Scheme III Modelcompounds **6–12** for the ^{1}H NMR measurements.

2. ^1H *NMR measurements*

We have performed a conformational analysis of the compounds **6–11** (see Scheme III). In these compounds which do not show pseudorotation, the OR group occupies an axial position in the TBP. This is in accordance with the apicophilicity rules.[10]

The axial position of the OR group is confirmed by ^{1}H and ^{13}C NMR. For compound **6**, the two methyl groups at C$_3$ of the oxaphosphole ring are not equivalent and therefore show two doublets, due to an additional phosphorus coupling of 22 Hz[3] (see Figure 2).

It is obvious that this non-equivalency cannot be attributed to an equatorial location of the THPM group since, in that case, the similar compound **8** should also show two doublets. As can be seen in Figure 2, **8** only shows one doublet. Therefore, the non-equivalency has to be attributed to a different shielding of the two methyl groups by the atoms O$_{1'}$ and C$_{3'}$ which are located underneath the methyl groups when the THPM group is located in the axial position of the TBP.[11] Similar arguments for **7** and **9** show that the double doublet of the hydrogen atom at C$_3$ of the oxaphosphole ring reduces to a doublet for compound **9** if the THPM group is in axial position (see Figure 2). Additional evidence comes from the ^{13}C measurements of the non-pseudorotating compounds **10–12**. As can be seen in Figure 3 a doublet at 67 ppm is found for **10** which is assigned to axial C$_{1'}$. For the compounds **11** and **12**, downfield to the axial C$_{1'}$ signal, another ^{13}C signal appears which has equal and double intensity, respectively, with respect to the axial C$_{1'}$ signal. This is assigned to the equatorial C$_{1'}$ atoms since it was shown that equatorial carbon atoms resonate at lower field than axial carbon atoms.[4]

The rotamer populations around C$_{1'}$—C$_{2''}$ are calculated as previously[1] with the aid of an empirically generalized Karplus-relation[12,13] which relates the measured coupling constants $J_{H1'H2''}$ and $J_{H1''H2''}$ to the angle between H$_{1'}$/H$_{1''}$ and H$_{2''}$ (see Figure 4).

The results of the 300 MHz ^{1}H NMR measurements and the rotamer fractions around C$_{1'}$—C$_{2''}$ are listed in Table V. From a previous NMR study[1] we have obtained the absolute rotamer fractions for the equatorial and axial THPM groups of compound **13**. The observed rotamer fractions in this pseudorotating compound are an average of the sum of the rotamer populations in the axial and the two equatorial sites. With a variable-temperature ^{1}H NMR study we determined the thermodynamic parameters which govern the rotation around the C$_{1'}$—C$_{2''}$ bond. These parameters allow the calculation of the absolute rotamer fraction for the axial site (59% g$^-$) and for the equatorial site (27% g$^-$) of the TBP (in the corresponding P^{IV} compound 10% is found for g$^-$). Apparently, the absolute g$^-$ rotamer fraction of 59% for the axial site is not reached for the compounds **6–11**, despite the fixed location of the OR group (see Scheme III) in the axial site of the TBP. On addition, the g$^-$ rotamer fraction of **6–11** is below the fraction observed for the pseudorotating compound **14** ($x(g^-) = 0.41$). Note that the only difference in the structures of **14** and **6–7** is the five-membered ring at phosphorus (and especially the substituents on this ring). This reduced g$^-$ rotamer fraction in **6–7** cannot be attributed to an increased sterical hindrance by the substituents at C$_3$ of the oxaphosphople ring (see Scheme III) because this is

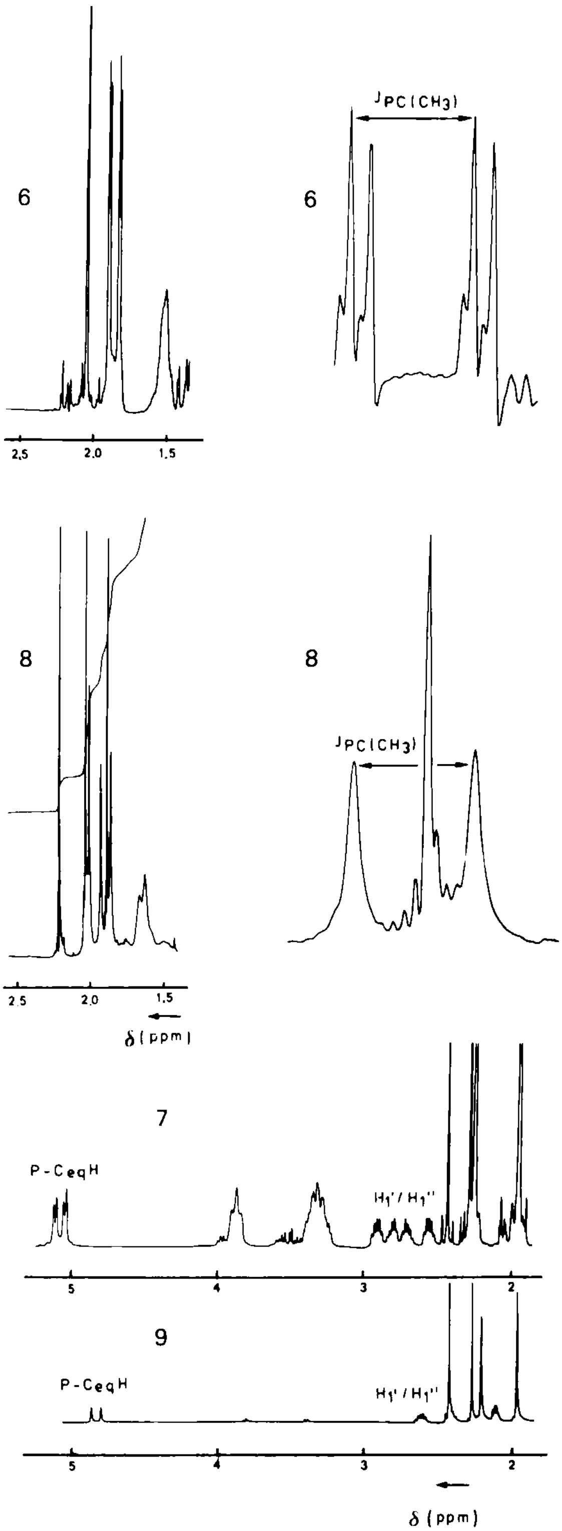


FIGURE 2 300 MHz ¹H NMR spectra of compounds **6–9**.

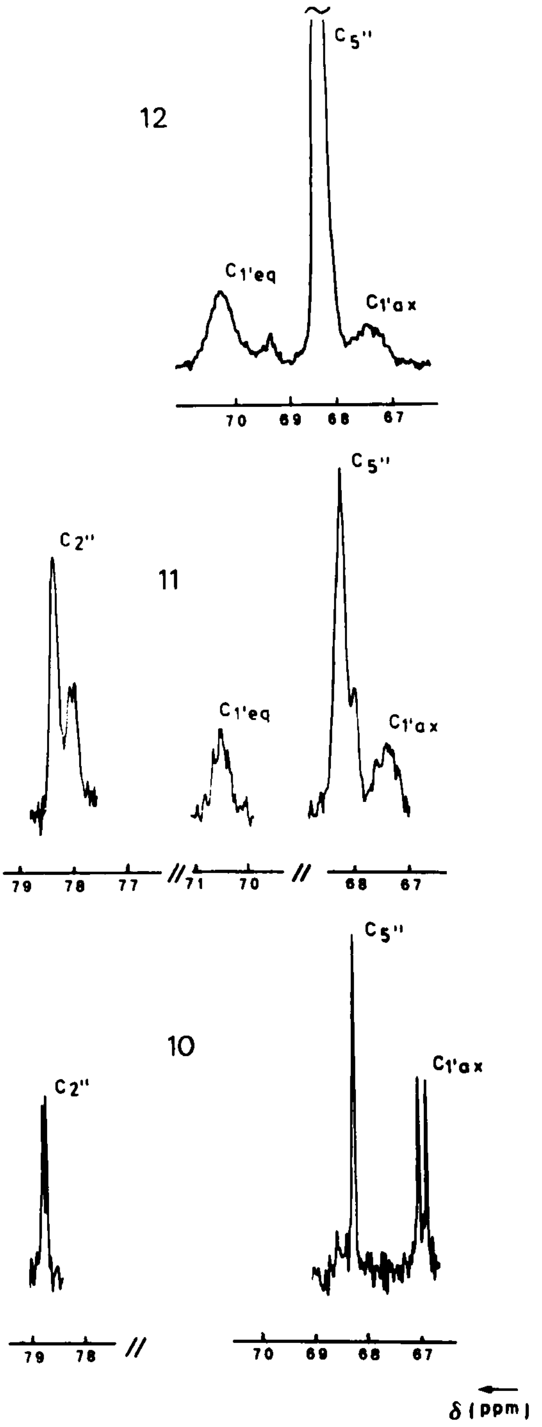


FIGURE 3 ^{13}C NMR spectra of compounds **10–12**.

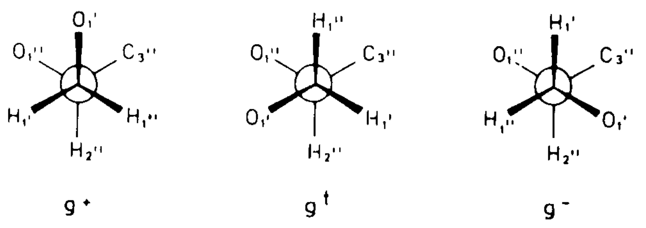


FIGURE 4 Rotamers around the $C_{1'}$—$C_{2''}$ bond.

TABLE V

^{1}H NMR parameters and the corresponding $C_{1'}$—$C_{2''}$ rotamer populations for compounds **6–11**

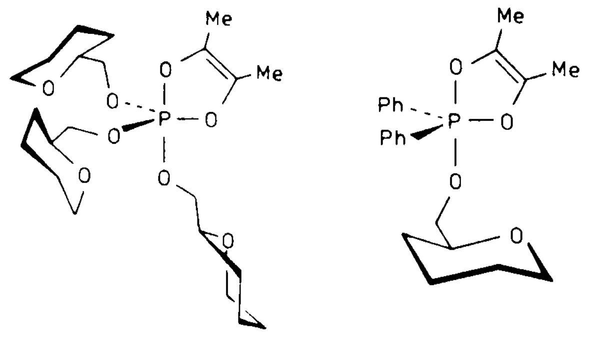
Compound	Solvent	$J_{H1'H2}$	$J_{H1''H2}$	$x(g^+)$	$x(g^t)$	$x(g^-)$
6	$(CD_3)_2CO$	5.22	3.91	0.520	0.185	0.295
6	CCl_4	5.37	4.55	0.455	0.240	0.315
7[a]	$(CD_3)_2CO$	5.20	5.15	0.400	0.310	0.290
		5.00	5.15	0.410	0.325	0.265
8	$(CD_3)_2CO$	—[b]	—[b]		—	
9	$CDCl_3$	6.03	6.13	0.235	0.370	0.395[c]
10	$(CD_3)_2CO$	—[b]	—[b]		—	
11	$CDCl_3$	5.33	5.53	0.350	0.345	0.305

[a] The compounds **7** and **11** exist as a mixture of stereoisomers. For **11**, the parameters of only one of the stereoisomers are shown.

[b] The coupling constants of these compounds could not be obtained due to a negligible chemical shift difference.

[c] See Note 14.

in contradiction with the observed random distribution about the three rotamers (see Table V). More likely, in view of the electronic nature of the conformational transmission effect,[1] the low g^- rotamer fractions of **6–11** must be attributed to electronic effects. These results are in good agreement with the MNDO calculations which show a clear trend towards a decreasing charge on $O_{1'}$ with increasing electronegativity of the substituent R at C_4 of the oxaphosphole ring.



13 14

FIGURE 5 Modelcompounds **13–14**.

Since the electron density on $O_{1'}$ is related to the g^- rotamer fraction, the carbonyl group at C_4 may indeed have caused the decreased $x(g^-)$ value of 30% for **6–11** as compared to the absolute $x(g^-)$ value of 59% for dioxaphosphole compounds, demonstrating that the electron transfer in the axial bonds of the TBP is controlled by the electronic effects of the substituents. So, as was shown in a previous ^{1}H NMR study,[1] electron donation increases the electron density on axial exocyclic $O_{1'}$. This triggers the conformational transmission process towards an increased g^- rotamer fraction. Now, we have shown that electron accepting substituents reverse the electron transfer process by decreasing the electron density on the axial exocyclic oxygen atom, which results in a reduced conformational transmission effect (reduced g^- rotamer fraction).

CONCLUSION

It is shown by MNDO calculations that electronegative substituents at C_4 of the oxaphosphole ring change the electron density on the oxygen atoms in the axial position of the TBP. The electron density on the axial endocyclic oxygen atom is increased whereas the electron density on the axial exocyclic oxygen atom is decreased. This is supported by the conformational analysis of the oxaphosphole P^V TBP compounds **6–11**. The g^- rotamer fraction of these compounds, which is correlated to the electron density on the axial exocyclic oxygen atom, is strongly decreased as compared to the absolute g^- rotamer fraction measured for dioxaphosphole P^V TBP compounds. This is probably caused by the presence of the carbonyl group at C_4 of the oxaphosphole ring.

EXPERIMENTAL

Solvents and reagents were reagent grade. All reactions were carried out under an atmosphere of dry nitrogen. Phosphines and phosphites were purified by distillation, prior to their conversion to P^V compounds. ^{1}H NMR spectra were recorded in the FT mode on a Bruker CXP-300 spectrometer at 300.1 MHz, using a 32 K point data set. Chemical shifts are given relative to the CHD_2COD_3 quintet at δ 2.17, or relative to TMS ($CDCl_3$, CCl_4), with an accuracy of 0.05 Hz. Coupling constants were measured from expansions of the patterns and were analyzed using an iterative program.[16] The accuracy of the calculated rotamer populations is about 3% (absolute). ^{31}P NMR spectra were recorded in the FT mode at 36.4 MHz on a Bruker HX-90R. Chemical shifts are related to 85% H_3PO_4 as external standard. ^{13}C NMR spectra were recorded in the FT mode on a Bruker CXP-300 spectrometer at 75.3 MHz. Chemical shifts are related to the acetone-septet at 30.7 ppm or to TMS ($CDCl_3$).

The compounds **1** and **13** were prepared according to procedures described in Reference 1.

Tetrahydropyran-2-methyloxy diphenylphosphine. To a stirred and cooled (0°C) solution of tetrahydropyran-2-methanol (2.6 gr, 25 mmol) and triethylamine (2.53 gr, 25 mmol) in 30 ml of sodium-dried ether was added dropwise a solution of chlorodiphenylphosphine (5.53 gr, 25 mmol) in 15 ml ether. After completion of the addition (0.5 h), the suspension was refluxed for 2 h. The mixture was cooled, triethylamine hydrochloride was filtered off and the solvent was evaporated. This yielded a colorless oil which, according to ^{31}P and ^{1}H NMR spectroscopy, was pure. ^{1}H NMR (acetone): δ 1.25–2.0 (m, 6H, H(3)–H(5)), 3.15–4.20 (m, 5H, H(1′), H(2) and H(6)), 7.25–7.90 (m, 10H, ArH). ^{31}P NMR (acetone): δ 119.74.

Cyclohexylmethyloxy diphenylphosphine. This compound was prepared from cyclohexylmethanol and chlorodiphenylphosphine by the method described for tetrahydropyran-2-methyloxydiphenylphosphine. Distillation (b.p. 162–166°C, 0.3 mm) yielded a colorless oil. ^{1}H NMR (acetone): δ 1.1–2.3

(m, 11H, H(1)-H(6)), 3.45–4.20 (m, 2H, H(1′)), 7.3–7.9 (m, 10H, ArH). ^{31}P NMR (acetone): δ 116.99.

Tetrahydrofurfuryloxy diphenylphosphine.[15] ^{1}H NMR (acetone): δ 1.70–2.05 (m, 4H, H(3)-H(4)), 3.55–4.30 (m, 6H, H(1′), H(2), H(5)), 7.20–7.70 (m, 10H, ArH). ^{31}P NMR (acetone): 119.52.

Phenyl bis(tetrahydrofurfuryloxy) phosphine.[17] ^{1}H NMR (CDCl$_3$): δ 1.4–2.3 (m, 8H, H(3), H(4)), 3.50–4.40 (m, 10H, H(1′), H(2) and H(5)), 7.20–7.90 (m, 5H, ArH). ^{31}P NMR (CDCl$_3$): δ 158.82, 158.77, 156.70 (ratio 2:1:1).

Tris(tetrahydrofurfuryl) phosphite.[15] ^{1}H NMR (CDCl$_3$): δ 1.60–2.20 (m, 12H, H(3), H(4)), 3.45–4.25 (m, 15H, H(1′), H(2) and H(5)). ^{31}P NMR (CDCl$_3$): δ 139.0.

2,2-Diphenyl-2-(tetrahydropyran-2-methyloxy)-2,2,2,3-tetrahydro-4-ethoxycarbonyl-3,3,5-trimethyl-1,2-oxaphosphole (**6**). An equimolar quantity of ethyl α-isopropylidene acetoacetate[18] was added to a cooled solution (0°C) of tetrahydropyran-2-methyloxy diphenylphosphine in dry acetone. After five days, ^{31}P NMR spectroscopy indicated the reaction to be complete. After several weeks, white crystals separated which were filtered and washed with a small amount of ether. ^{1}H NMR (acetone): δ 1.17 (t, 3H, OEt), 1.3–1.95 (m, 6H, H(3″)-H(5″)), 1.95 (dd, 6H, CH$_3$-C(3), $J_{PCCH} = 21$ Hz), 2.03 (s, 3H, CH$_3$-C(5)), 2.88 (m, 2H, H(1′), H(1″)), 3.35 (m, 2H, H(2″), H(6″)ax), 3.90 (m, 1H, H(6″)eq), 4.07 (q, 2H, OEt), 7.4–8.0 (m, 10H, ArH). ^{13}C NMR (acetone): δ 14.7–29.9 (C(3″)-C(5″), 3 CH$_3$, CH$_3$—C=O), 47.64 (d, C(3), $J_{CP} = 121.7$ Hz), 59.35 (s, O—CH$_2$—C), 68.53 (d, C(1′), $J_{COP} = 11.4$ Hz), 69.03 (s, C(6″)), 78.26 (d, C(2″), $J_{CCOP} = 5.1$ Hz), 107.3 and 167.43 (C=C), 129.1–137.3 (Ar). ^{31}P NMR (acetone): δ −28.14. Anal. Calc. for C$_{27}$H$_{35}$O$_5$P: C 68.95, H 7.50. Found: C 66.69, H 7.63.

2,2,3-Triphenyl-2-(tetrahydropyran-2-methyloxy)-2,2,2,3-tetrahydro-4-acetyl-5-methyl-1,2-oxaphosphole (**7**). An equimolar quantity of 2,4-pentadione-3-(phenylmethylene) was added to a cooled solution (0°C) of tetrahydropyran-2-methyloxy diphenylphosphine in dry acetone. After 1 day, white crystals separated which were filtered and washed with cold acetone. ^{1}H NMR (acetone): δ 1.1–1.9 (m, 6H, H(3″)-H(5″)), 1.96 (3H, CH$_3$-C(5)), 2.16 (3H, CH$_3$—C=O), 2.55–2.95 (m, 2H, H(1′), H(1″)), 3.35 (m, 2H, H(2″), H(6″)ax), 3.90 (m, 1H, H(6″)eq), 5.10 (dd, 1H, H(3), $J_{PCH} = 20.1$ Hz), 7.2–8.0 (m, 10H, ArH). ^{13}C NMR (acetone): δ 18.65 (CH$_3$—C(5)), 23.56–29.24 (C(3″)—C(5″)), 29.64 (CH$_3$—C=O), 50.56 (dd, C(3), $J_{PC} = 114$ Hz), 67.51 (t, C(1′), $J_{COP} = 9.87$ Hz), 68.27 (C(6″)), 77.28 (t, C(2″), $J_{CCOP} = 4.88$ Hz), 112.0 and 137.96 (C=C), 127–135 (Ar). ^{31}P NMR (acetone): δ −26.80, −27.30. Anal. Calc. for C$_{30}$H$_{33}$O$_4$P: C 73.75: H 6.81. Found: C 74.32: H 6.94.

2,2-Diphenyl-2-(cyclohexylmethyloxy)-2,2,2,3-tetrahydro-4-ethoxycarbonyl-3,3,5-trimethyl-1,2-oxaphosphole (**8**). This compound was prepared from diphenylcyclohexylmethyloxy phosphine and ethyl α-isopropylidene-acetoacetate by the procedure described for **6**. ^{1}H NMR (acetone): δ 0.95–1.67 (m, 11H, H(1″)-H(6″)), 1.19 (t, 3H, OEt), 1.89 (d, 6H, CH$_3$—C(3), $J_{PCCH} = 20.7$ Hz), 2.01 (s, 3H, CH$_3$—C(5)), 2.66 (m, 2H, H(1′)), 4.05 (kw, 2H, OEt). ^{31}P NMR (acetone): δ −27.23.

2,2,3-Triphenyl-2-(cyclohexylmethyloxy)-2,2,2,3-tetrahydro-4-acetyl-5-methyl-1,2-oxaphosphole (**9**). This compound was prepared from diphenylcyclohexylmethyloxy phosphine and 2,4-pentadione-3-(phenylmethylene) by the procedure described for **7**. The white solid which separated immediately was filtered and washed with cold acetone. Recrystallization from chloroform/hexane yielded white crystals. M.p.: 183.0–184.5°C. ^{1}H NMR (CDCl$_3$): δ 0.7–1.73 (m, 11H, H(1″)—H(6″)), 1.97 (3H, CH$_3$—C(5)), 2.19 (3H, CH$_3$—C=O), 2.60 (m, 2H, H(1′)), 4.83 (d, 1H, H(3), $J_{PCH} = 20.6$ Hz), 7.03–7.46 (m, 10H, ArH). ^{13}C NMR (CDCl$_3$): δ 19.42 (CH$_3$—C(5)), 25.93–30.07 (C(1″)—C(6″), CH$_3$—C=O), 50.21 (d, C(3), $J_{CP} = 111.80$ Hz), 69.21 (d, C(1′), $J_{COP} = 10.40$ Hz), 111.7 and 137.1 (C=C), 127.0–134.0 (Ar). ^{31}P NMR (CDCl$_3$): δ −20.22.

2,2-Diphenyl-2-(tetrahydrofurfuryloxy)-2,2,2,3-tetrahydro-4-ethoxycarbonyl-3,3,5-trimethyl-1,2-oxaphosphole (**10**). This compound was prepared from diphenyl tetrahydrofurfuryloxy phosphine and ethyl α-isopropylidene-acetoacetate by the procedure described for **6**. ^{1}H NMR (acetone): δ 1.16 (t, 3H, OEt), 1.4–1.9 (m, 4H, H(3″)—H(4″)), 1.88 (d, 6H, CH$_3$—C(3), $J_{PCCH} = 20.76$ Hz), 2.02 (s, 3H, CH$_3$—C(5)), 2.83 (m, 2H, H(1′)), 3.70 (m, 2H, H(2″), H(5″)), 3.93 (m, 1H, H(5″)), 4.01 (q, 2H, OEt), 7.20–8.05 (m, 10H, ArH). ^{13}C NMR (acetone): δ 14.46–25.99 (C(3″)—C(5″), 3 CH$_3$, CH$_3$—C—O), 46.47 (d, C(3), $J_{CP} = 121.47$ Hz), 58.99 (s, C—CH$_2$—O), 67.05 (d, C(1′),

J_{COP} = 11.66 Hz), 68.35 (s, C(5″)), 78.95 (d, C(2″), J_{CCOP} = 4.77 Hz), 95.80 (d, C=C), 128.0–135.0 (Ar). ^{31}P NMR (acetone): δ −28.26.

2-Phenyl-2,2-bis(tetrahydrofurfuryloxy)-2,2,2,3-tetrahydro-4-acetyl-3,3,5-trimethyl-1,2-oxaphosphole (**11**). 2,4-Pentadione-3-(1-methylethylidene) (1 eq) was added to a solution of phenyl bis(tetrahydrofurfuryloxy) phosphine (1 eq) in dry $CDCl_3$ under an argon atmosphere. After 10 days at room temperature, ^{31}P NMR indicated the reaction to be nearly complete (90%). ^{1}H NMR ($CDCl_3$): δ 1.76 (dd, 6H, CH_3—C(3), J_{PCCH} = 20.5 Hz), 1.6–2.0 (m, 8H, H(3″)—H(4″)), 2.12 (s, 3H, CH_3—C(5)), 2.21 (s, 3H, CH_3—C=O), 3.02–3.58 (2H, m, H(1′)ax), 3.72–4.32 (m, 8H, H(1′)eq, H(2″), H(5″)), 7.40–7.90 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$): δ 18.5–31.3 (C(3″)—C(4″), 4CH_3), 45.50 (d, C(3), J_{CP} = 121 Hz), 67.4 (m, C(1′)ax), 68.2 (C(5″)), 70.5 (m, C(1′)eq), 78.3 (m, C(2″), 86.0 (C=C), 126.0–133.0 (Ar). ^{31}P NMR ($CDCl_3$): δ −18.45, −18.52, −18.70 (ratio 1:1:2).

2,2,2-Tris(tetrahydrofurfuryloxy)-2,2,2,3-tetrahydro-3,3,5-trimethyl-4-acetyl-1,2-oxaphosphole (**12**). This compound was prepared from 2,4-pentadione-3-(1-methylethylidene) and tris(tetrahydrofurfuryl) phosphite by a literature procedure for a similar compound[3] (trimethylphosphite). ^{1}H NMR (CD_2Cl_2): δ 1.5–2.05 (m, 12H, H(3″)—H(4″), 1.90 (6H, CH_3—C(3)), 2.23 (s, 3H, CH_3—C(5)), 2.28 (s, 3H, CH_3—C=O), 3.60–4.23 (m, 15H, H(1′), H(2″), H(5″)). ^{13}C NMR ($CDCl_3$): δ 18.5–31.2 (C(3″)—C(4″), 4CH_3), 43.8 (d, C(3), J_{CP} = 125 Hz), 67.4 (m, C(1′)ax), 68.3 (C(5″)), 70.3 (m, C(1″)eq), 77.5 (m, C(2″)).

2,2-Diphenyl-2-(tetrahydropyran-2-methyloxy)-2,2-dihydro-4,5-dimethyl-1,3,2-dioxaphosphole (**14**). An equimolar quantity of 2,3-butadione was added to a cooled solution (0°C) of tetrahydropyran-2-methyloxy diphenylphosphine in dry acetone-d_6. After 2 hours, ^{31}P NMR indicated the reaction to be complete. ^{1}H NMR (acetone): δ 1.38–1.69 (m, 6H, H(3″)—H(5″)), 2.01 (s, 6H, OCH_3), 3.50–3.78 (m, 2H, H(2″), H(6″)ax), 4.04 (m, 1H, H(6″)eq), 4.13 (m, 2H, H(1′)), 7.40–8.05 (m, 10H, ArH). ^{31}P NMR (acetone): δ −23.89.

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    $x(g^t) = -0.054J_{H(1')H(2'')} + 0.104J_{H(1'')H(2'')} + 0.061$

    $x(g^-) = 0.129J_{H(1')H(2'')} - 0.003J_{H(1'')H(2'')} - 0.364$

14. The $x(g^-)$ value of **9** deviates from the values of the other compounds because **9** doesn't possess the ring oxygen atom $O_{1''}$. Comparable values for the rotamer populations were found for 2,2-diphenyl-2-cyclopentylmethoxy-2,2-dihydro-4,5-dimethyl-1,3,2-oxaphosphole.[15]
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