Preparation of Hexacoordinated Tris(bidentate) Phosphorus Compounds with 1,3,2-Dioxaphosphorinane Rings. NMR and X-ray Crystallographic Studies of Their Conformation

Aleksandra Skowrońska,*[,†,§] Jacek Kowara,[†] Rafał Kamiński,*[,†] Grzegorz Bujacz,[‡] and Michał W. Wieczorek*[,‡]

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Department of Heteroorganic Chemistry, Sienkiewicza 112, 90−363 Łódź, Poland, and Technical University of Łódź, Institute of Technical Biochemistry, Stefanowskiego 4/10, 90−924 Łódź, Poland

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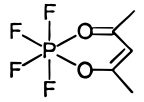
A series of new unstable tris(bidentate) hexacoordinated phosphorus compounds **1** with 1,3,2-dioxaphosphorinane rings was prepared and studied by NMR and X-ray crystallography. The X-ray crystal structures showed that the 1,3,2-dioxaphosphorinane ring adopts different conformations depending on the number and size of substituents at the carbon atom C14. Substituents are deployed around the phosphorus atom in a slightly deformed octahedral structure. Deviations in bond lengths around the phosphorus atom depend on the character of the bonds and the distribution of the negative charge. ^{1}H and ^{13}C NMR measurements showed that in solution the flexibility of 1,3,2-dioxaphosphorinane ring depends on the size of substituents at the carbon C14.

Introduction

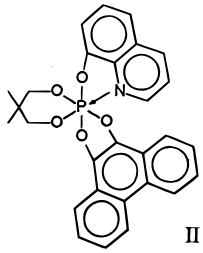
A number of stable hexacoordinated organophosphorus molecules have already been described.[1] These species may play a significant role in phosphorus chemistry.[1,2] They are intermediates in associative nucleophilic substitution at pentacoordinated phosphorus.[2] Most nucleophilic displacement reactions at tetracoordinated phosphorus are discussed in terms of mechanisms involving pentacoordinated intermediates,[3] but hexacoordinated species have been invoked in some mechanistic schemes.[4] The intervention of a hexacoordinated transition state has also been suggested in the hydrolysis of c-AMP catalyzed by c-AMP phosphorodiesterase.[1,4b,5]

Interest in conformation of six-membered ring systems in oxyphosphoranes is growing.[1,6d,j] This interest stems from the role of these pentacoordinated intermediates in enzymatic reactions of nucleoside 3′,5′-monophosphates such as c-AMP.[3,6]

A few neutral hexacoordinated phosphoranes containing a 1,3,2-dioxaphosphorinane ring are known;[1,7−9] they are formed as a result of donor action from more electronegative oxygen (**I**)[8]- and nitrogen (**II**)[9]-containing ligands, for example:



I



II

Recently we studied nucleophilic substitution at pentacoordinated phosphorus in a 1,3,2-dioxaphosphorinane ring of **2** which included isomerization of hexacoordinated intermediates **3** of trans configuration into intermediates **4** of cis configuration.[10] We have found that these intermediates **4** are converted into tris(bidentate) hexacoordinated compounds **1**.

* To whom correspondence should be addressed.
† Polish Academy of Sciences.
‡ Technical University of Łódź.
§ e-mail: askow@bilbo.cbmm.lodz.pl.

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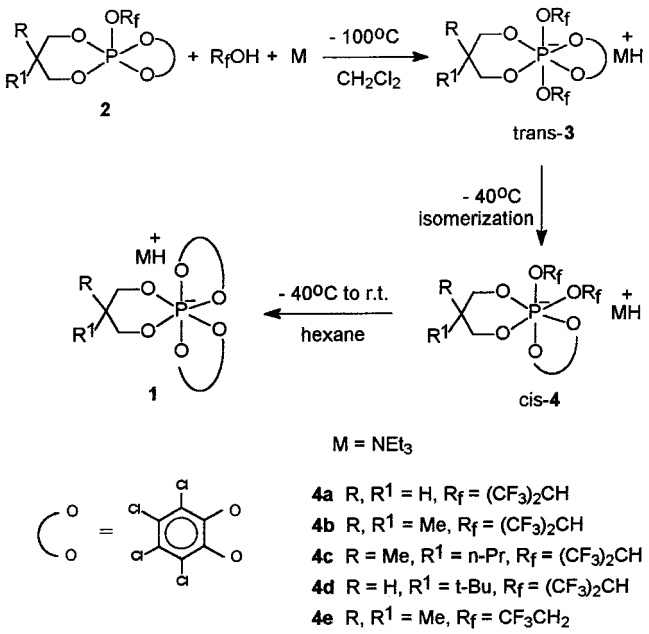
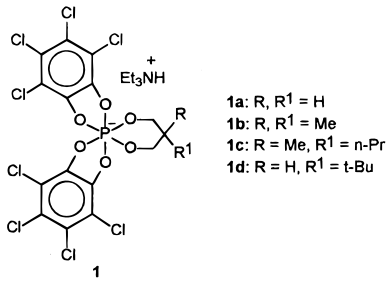
Scheme 1



In the present paper we report preparation and structures of a series of hexacoordinated tris(bidentate) phosphorus compounds **1**, with various R and R^1 substituents in the 1,3,2-dioxaphosphorinane ring determined by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. Compounds **1** represent the first example of structurally characterized nonneutral hexacoordinated phosphorus systems with a six-membered ring.



The interesting thing about compounds **1** is that they, in solid state, take on different six-membered ring conformations depending on the number and size of substituents. In solution the flexibility of the 1,3,2-dioxaphosphorinane ring depends also on the size of substituents.

Results and Discussion

Preparation of 1a−d. The synthesis of the compounds **1** are shown in Scheme 1 and Scheme 2. The phosphoranes **2**, prepared following a procedure reported in the literature,[11] were subjected to reaction with hexafluoropropan-2-ol in the presence of triethylamine at −100 °C. The resulting hexacoordinated compounds **3** of trans configuration rearrange gradually at a higher temperature of −40 °C to compounds **4** of cis configuration. Spectroscopic analysis of the products **3** and **4** was consistent with a hexacoordinated structure. Cis configuration of more stable compounds **4** was assigned on the basis of our previous investigations.[2] For a number of more stable spiro-five-membered hexacoordinated phosphorus compounds (of higher chemical shift values) the cis configuration was determined taking advantage of their chirality. When the triethylammonium counterion was replaced by a (−)-brucynium one, ^{31}P NMR spectra showed two separate signals attributed to two diastereoisomeric salts.[2c] In ^{31}P NMR spectra there is a clearly discernible trend that the chemical shift of the more stable cis isomer is upfield of the shift of the trans configuration.[2] Crystallization of **4** by a solvent diffusion method (see Experimental Section) after several days afforded compounds **1** as solids in about 50% yield and suitable for the X-ray analysis.

A possible mechanism for the transformation of cis hexacoordinated compounds **4** into compounds **1** is presented in Scheme 2. Monitoring the reaction course by variable-temperature ^{31}P NMR spectroscopy, we detected intermediates in the conversion of **4e** ($R_f = CF_3CH_2$, $R,R^1 = CH_3$) to **1b**. At −80 °C the compound **4e** (−124.2 ppm) is present together with spirophosphorane **2e** (−47.9 ppm) and species **5e** (−45.9 ppm). After being slowly warmed to 0 °C, the amounts of compounds **5e** and **2e** decreased as the products **7e** (−66.5 ppm) and **1b** (−100.1 ppm) increased. The compound **7e** is less stable than **1b**. At room temperature the former collapses to a tetracoordinated phosphorus compound. These observations become understandable in the light of equilibrium between cis compound **4e**, the starting spirophosphorane **2e**, and the monocyclic phosphorane **5e**. Compound **5e** undergoes reaction with the $CF_3CH_2O^-$ anion, giving a new monocyclic phosphorane **7e** and the tetrachlorocatechol anion **6**, whereas spirophosphorane **2e** reacts with **6** affording **1b** which precipitates from the reaction mixture.

In our previous investigation of nucleophilic substitution at spiro-five-membered phosphoranes, amounts of tris (bidentate) hexacoordinated phosphorus compounds were observed alongside the main substitution products. Therefore in such reactions equilibria must exist between hexacoordinated phosphorus intermediates, the starting spiro-phosphoranes, and the monocyclic phosphoranes.

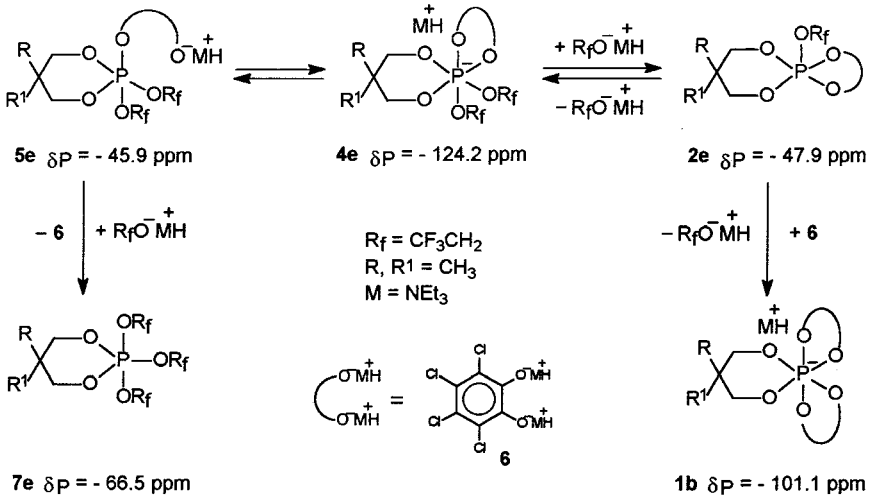
We have also found that reaction of the spirophosphoranes **2** with *o*-tetrachlorocatechol in the presence of triethylamine afforded compounds **1** in good yield (Scheme 3). This result strongly supported the mechanistic scheme proposed for the synthesis of compounds **1** (Scheme 2). However, in this case it was not possible, even after several crystallizations, to obtain crystals suitable for the X-ray analysis.

X-ray Diffraction Studies. Crystal data and experimental details for **1a−d** are compiled in Table 1. The atom labeling schemes for **1a−d** are shown in the ORTEP plots of Figures 1−5, respectively. The bond lengths and selected bond angles around the phosphorus atom, cation−anion interaction distance, torsion angles as well as asymmetry parameters for the dioxaphosphorinane ring, and dihedral angles in the octahedral structure appear in Tables 2−6. The unit cell packing of compounds **1a−d** is illustrated in Figures 6−9, respectively.

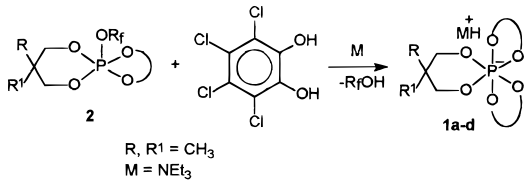
In all four compounds **1a−d**, the central phosphorus atom is surrounded by an octahedral structure. Deformation from an ideal octahedron is observed especially in the inter-ring angle in six-membered rings, which is approximately 7° larger than in five-membered rings. The phosphorus−oxygen bond distances in the five-membered

(11) Bone, S.; Trippett, S.; Whittle, P. J. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2125.

Scheme 2



Scheme 3



rings are generally much longer than the corresponding bond distances in six-membered rings (Table 2).

Two factors influence the bond lengths around the phosphorus atom: the hydrogen bonds of the ammonium cation with oxygen of the phosphorus moiety and the negative charge distribution of the phosphorus anion **1**. Hydrogen connected to nitrogen in the triethylammonium cation interacts with an anion moiety by creating three hydrogen bonds with oxygens O1, O3, and O5 (Table 3). In all structures, the shortest contact is observed between N20 and O5, which is equal to 2.92 Å in compound **1a** and 3.26 Å in compound **1b**. The N20−O1 distance is longer, ranging from 3.27 to 3.40 Å for compounds **1a** and **1b**, respectively. The N20−O3 distance is shorter than N20−O1 in compounds **1c** and **1d**, but these distances are almost the same in compound **1a**. In compound **1b**, the N20−O3 distance is 3.44 Å, the longest seen in these compounds. The cation−anion distances in the methyl derivative compound **1b**—expressed by the distance between the ammonium nitrogen and the closest of the three oxygen atoms are slightly different from those of the three other derivatives; this is probably the result of a different space group and packing. The relative positions of the hexacoordinated phosphorus anion and the ammonium cation are very similar in all of the four crystal structures. The same pattern of interactions observed in all crystal structures indicates that the interaction seen here is preferred. In solution, the interactions probably depend on the polarity of the solvents. Indeed, the ^{1}H NMR spectra of compounds **1** in CD_2Cl_2 and $(CD_3)_2SO$ solution show a different pattern in the part connected with the six-membered ring.

It is interesting to notice that the hydrogen bond formation makes the P−O5 bond in the six-membered ring markedly longer than P−O6. The same occurs with P−O1 and P−O2 in the five-membered ring, but this is not so with the second phospholane ring where P−O4 is slightly longer than P−O3. Large (ca. 0.1 Å) differences in the length of P−O bonds are observed between six- and five-membered rings. Moreover, the average P−O bond length in five-membered rings of compounds **1a**−**d** is much higher than the average P−O distance found for the same substituent in other hexacoordinated phosphorus compounds (1.741 Å in **1b** to 1.755 Å in **1c** toward 1.714 Å or 1.713 Å in triethylammonium tris(tetrachloro-*o*-phenylenedioxy) phosphorane[12a,b]). In addition, the average P−O bond length in triethylammonium tris(*o*-phenylenedioxy)phosphorane[12c] is 1.715 Å, and averaged values of all six P−O bond lengths in compounds **1a**−**d** range from 1.718 to 1.709 Å. We think that the observed differences in the P−O bonds lengths in phospholane and dioxaphosphorinane rings in compounds **1a**−**d** can be interpreted as a result of negative charge distribution. The electron-poor tetrachloro-*o*-phenylenedioxy substituent should increase the negative charge density on the oxygen atoms O1 to O4 and decrease that on O5 and O6. This factor affects the P−O bond length more than the hydrogen bond formation.

Conformational analysis of six-membered rings shows that the conformation depends on the number and size of substituents attached to the carbon C14. Two conformations, chair and boat, seem to be the most preferable. The unsubstituted six-membered ring in compound **1a** has a chair conformation. For the *tert*-butyl- substituted ring in compound **1d**, the twisted chair conformation is observed. Compound **1c** with methyl and propyl substituents on the carbon C14 has a boat conformation, whereas compound **1b**, with two methyl substituents, shows disorder in the six-membered ring region. This disorder can be described by the existence of two different conformations in the crystal lattice. Some of the molecules are in the chair conformation, but the flip of position by atoms C15 and C17 creates another group of molecules with the boat conformation. The ratio of chair to boat conformations is 0.58:0.42.

Tables 4 and 5 show torsion angles and asymmetry parameters for the six- membered heterocyclic rings in

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Table 1. Crystal Data and Experimental Details[a]

	compound **1a**	compound **1b**	compound **1c**	compound **1d**
molecular formula	$C_{15}H_6O_6Cl_8P{\cdot}C_6H_{16}N$	$C_{17}H_{10}O_6Cl_8P{\cdot}C_6H_{16}N$	$C_{19}H_{14}O_6Cl_8P{\cdot}C_6H_{16}N$	$C_{19}H_{14}O_6Cl_8P{\cdot}C_6H_{16}N{\cdot}CH_2Cl_2$
space group	$P2_1/n$	$P1$	$P2_1/n$	$P2_1/n$
a (Å)	9.457(2)	9.334(2)	9.352(1)	11.173(2)
b (Å)	23.007(2)	12.440(1)	24.036(4)	20.883(3)
c (Å)	13.163(2)	13.479(2)	14.422(1)	15.677(2)
α	90(0)	89.76(1)	90(0)	90(0)
β	97.66(2)	95.38(1)	94.86(2)	99.45(1)
γ	90(0)	103.36(1)	90(0)	90(0)
V (Å^3)	2838.4(9)	1515.8(4)	3228.6(5)	3608.2(6)
Z	4	2	4	4
μ (cm^{-1})	83.5	78.2	73.7	80.3
D_c (g/cm^3)	1.414	1.382	1.356	1.369
crystal dimen	0.1, 0.3, 0.8	0.15, 0.25, 0.4	0.1, 0.15, 0.5	0.25, 0.3, 0.6
max 2θ (deg)	150	150	150	150
radiation, λ	Cu Kα	Cu Kα	Cu Kα	Cu Kα
scan mode	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan width	$0.82 + 0.14 \tan\theta$	$0.76 + 0.14 \tan\theta$	$0.90 + 0.14 \tan\theta$	$1.10 + 0.14 \tan\theta$
hkl ranges h	0 11	0 11	−11 0	0 13
k	0 28	−15 15	0 28	−24 0
l	−16 16	−16 16	−16 16	−18 18
no. of reflections:				
total	5627	5258	5445	5967
unique	5303	4934	5114	5663
criterion	$F > 4\sigma$ (F)	$F > 4\sigma$ (F)	$F > 2\sigma$ (F)	$F > 4\sigma$ (F)
observed	3258	3284	3132	3030
decay:				
min correction	0.9997	1.0000	0.9999	1.0000
max correction	1.9231	2.0833	5.2632	2.6316
F(000)	1200	656	1424	1592
no. of parameters	338	375	346	373
R factor	0.0553	0.0585	0.0629	0.0646
R factor, all data	0.1059	0.0916	0.0850	0.0971

[a] Absorption coefficients were not estimated because of crystal decomposition.

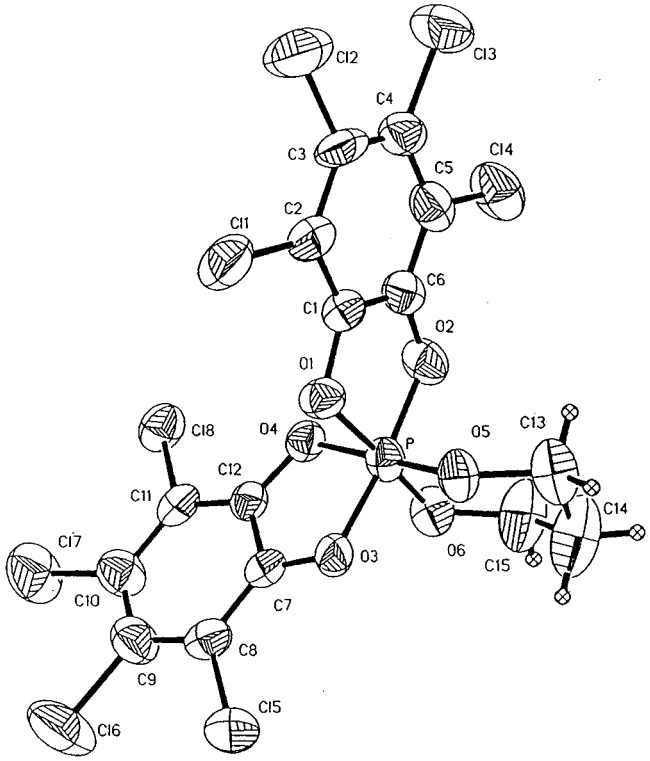


Figure 1. ORTEP plot of compound **1a**. Triethylammonium cation has been omitted.

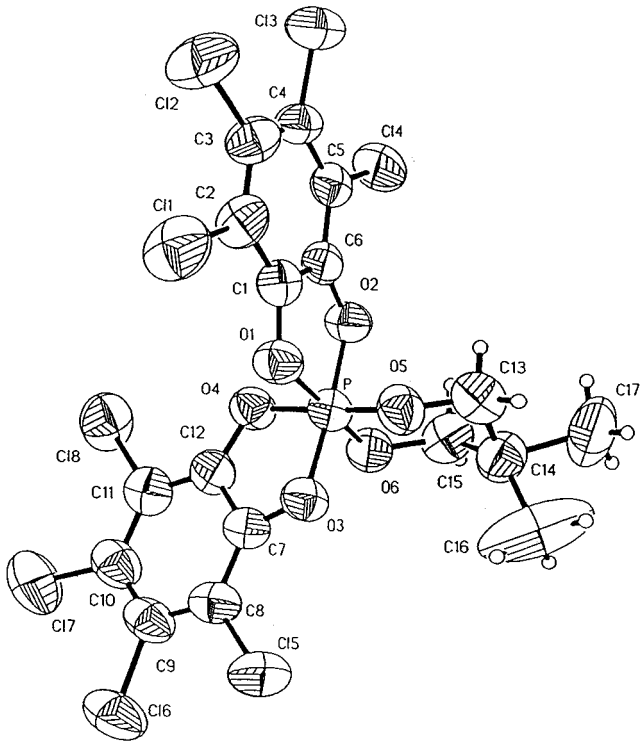


Figure 2. ORTEP plot of compound **1bA**. Triethylammonium cation has been omitted.

compounds **1**. An analysis of these values allows elements of symmetry to be identified. The compound **1a** and molecule **A** in compound **1b** have chair conformations with the best mirror plane going through the phosphorus atom P and central carbon atom C14, described by the lowest values of the ΔC_S(P) parameter. For compound **1d**, a twisted chair conformation is observed, the lowest value of asymmetry parameters noted in the mirror plane going through oxygen atom O6 and carbon atom C13 being ΔC_S(O6) equal to 5.8. Asymmetry parameters for

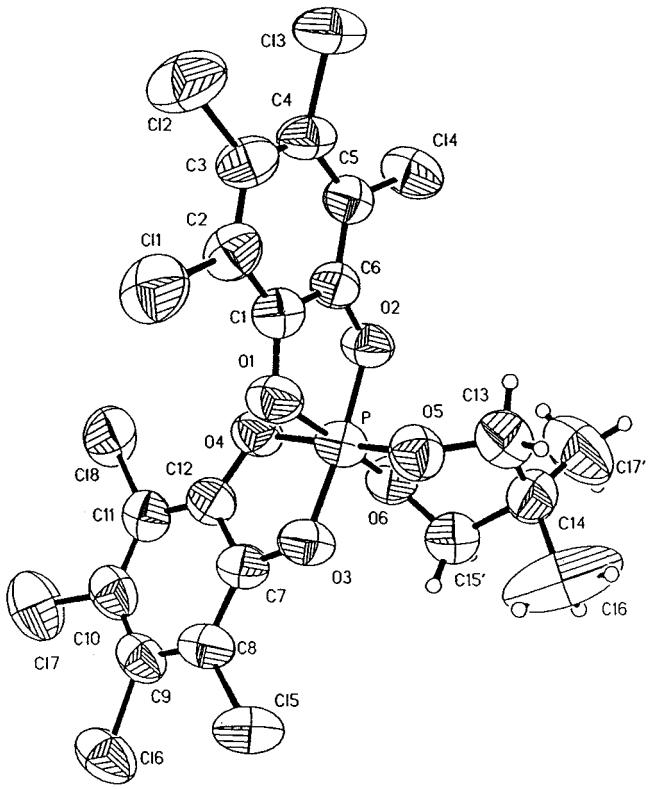


Figure 3. ORTEP plot of compound **1bB**. Triethylammonium cation has been omitted.

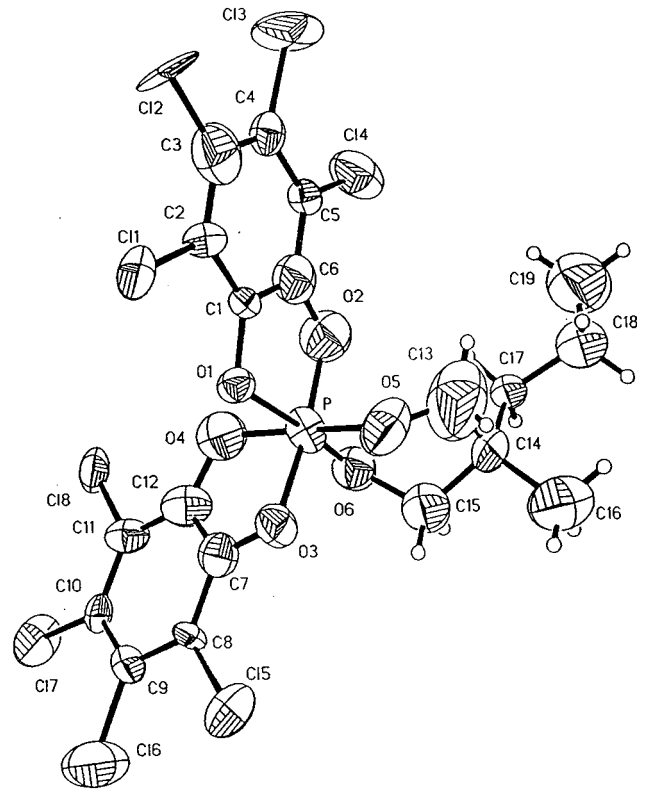


Figure 4. ORTEP plot of compound **1c**. Triethylammonium cation has been omitted.

the two other mirror planes going through the atoms are relatively low in all compounds with the chair conformation. For a chair conformation, three 2-fold axes going through the center of the bonds are characteristic. The

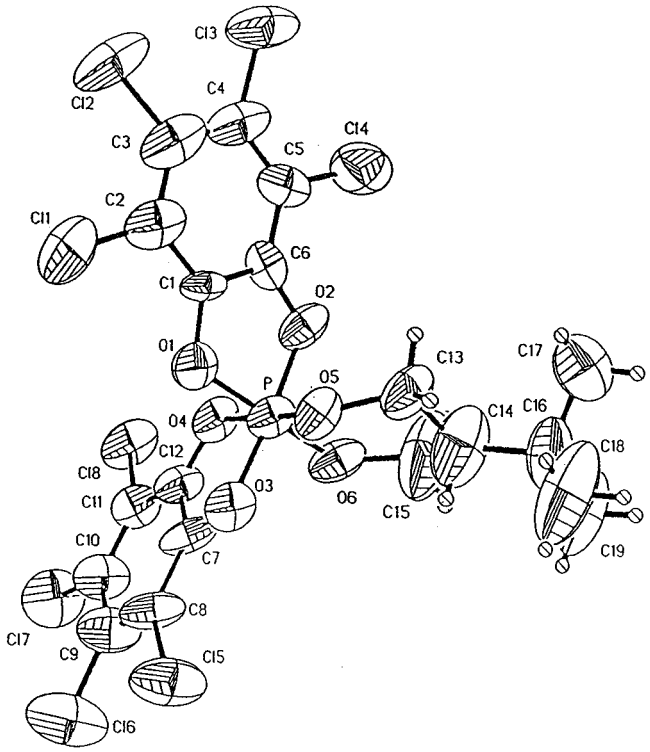


Figure 5. ORTEP plot of compound **1d**. Triethylammonium cation has been omitted.

Table 2. Bond Lengths (Å) and Selected Bond Angles (deg) around the Phosphorus Atom

	1a	1b	1c	1d
P−O1	1.798(4)	1.789(4)	1.772(4)	1.779(6)
P−O2	1.719(4)	1.713(5)	1.742(7)	1.727(7)
P−O3	1.733(4)	1.707(5)	1.748(6)	1.724(7)
P−O4	1.760(4)	1.755(4)	1.756(7)	1.757(5)
P−O5	1.663(4)	1.667(4)	1.655(6)	1.649(5)
P−O6	1.634(4)	1.642(4)	1.637(6)	1.619(6)
O1−P−O2	88.6(2)	89.1(2)	91.9(3)	89.4(3)
O3−P−O4	89.6(2)	89.9(2)	88.0(3)	89.9(3)
O5−P−O6	98.0(2)	97.4(2)	96.0(3)	97.7(3)

Table 3. Cation−Anion Interaction Distance (Å) in 1a−d

	1a	1b	1c	1d
N20−O1	3.398(2)	3.270(2)	3.365(3)	3.394(3)
H201−O1	2.523(6)	2.465(7)	2.667(9)	2.435(8)
N20−O3	3.389(2)	3.445(2)	3.157(3)	3.186(2)
H201−O3	2.498(7)	2.561(7)	2.419(8)	2.239(8)
N20−O5	2.923(2)	3.265(2)	2.996(4)	2.962(3)
H201−O5	1.975(6)	2.489(7)	2.069(9)	1.731(8)

Table 4. Torsion Angles (ω_i) in the Dioxaphosphorinane Ring of 1a−d

	1a	1bA	1bB	1c	1d
P−O5−C13−C14	−56.4(7)	−57.0(8)	−57.0(8)	−62.9(15)	−54.5(9)
O5−C13−C14−C15	58.2(9)	65.4(10)	14.7(10)	10.2(16)	46.7(14)
C13−C14−C15−O6	−53.8(9)	−62.4(12)	41.7(12)	52.4(12)	−36.2(16)
C14−C15−O6−P	45.6(9)	54.5(14)	−68.3(10)	−69.9(10)	32.7(15)
C15−O6−P−O5	−33.4(6)	−32.1(9)	30.4(7)	19.2(6)	−30.8(9)
O6−P−O5−C13	40.0(5)	35.1(5)	35.1(5)	43.4(9)	42.3(6)
$\omega_{average}$	47.9	51.1	42.2	43.0	40.5
$\Sigma\|\omega_i\|$	287.4	306.5	247.2	258.0	243.2

value of the asymmetry parameters ΔC_S and ΔC_2 confirm the presence of these symmetry elements in compounds **1a**, **1b**, and **1d**. Compound **1c** and molecule **B** from compound **1b** have the boat conformation with atoms O5 and carbon C15 in the flap position. Two mirror planes exist for this conformation. The first plane goes through

Table 5. Asymmetry Parameters[a] for the Dioxaphosphorinane Ring in 1a−d. Calculated Errors Are Less Than ±2.3

	1a	1bA	1bB	1c	1d
ΔC_S(P)	7.7	2.8	87.9	92.1	15.5
ΔC_S(*O6*)	10.7	21.0	55.1	69.6	5.8
ΔC_S(*O5*)	17.8	23.5	32.8	22.7	11.7
ΔC_S(P−O6)	98.7	105.6	25.8	20.2	83.2
ΔC_2(C15−O6)	19.3	30.3	16.5	33.2	4.9
ΔC_2(O6−P)	4.4	14.2	101.1	114.3	14.6
ΔC_2(P−O5)	18.5	19.2	85.2	81.1	19.5

[a] Asymmetry parameters measure the degree of departure from ideal symmetry: $\Delta C_S(X) = [(1/n)\Sigma(\omega_i + \omega_i')^2]^{1/2}$ for mirror plane dissecting atom or bond (denoted here as X) and $\Delta C_2(X) = [(1/n)\Sigma(\omega_i - \omega_i')^2]^{1/2}$ for 2-fold axis, where ω_i and ω_i' are related torsion angles.

Table 6. Dihedral Angles between the Least Squares Planes in 1a−d

Planes Definition			
	1a and **1bA**	**1bB** and **1c**	**1d**
plane 1	O5,O6,C13,C15	P,O6,C13,C14	P,O5,C14,C15
plane 2	O5,P,O6	P,O5,C13	P,O6,C15
plane 3	C13,C14,C15	C14,C15,O6	C13,C14,O5
for all compounds			
plane 4	P,O1,O2,C1,C6		
plane 5	P,O3,O4,C7,C12		
plane 6	P,O5,O6		

Dihedral Angles						
	1a	**1bA**	**1b**	**1bB**	**1c**	**1d**
plane 1/plane 2	30.1(2)	28.8(3)		37.0(4)	44.5(7)	31.4(5)
plane 1/plane 3	50.8(6)	56.1(5)		51.7(6)	53.7(8)	43.5(5)
plane 4/plane 5	88.8(1)		89.5(2)		86.8(2)	89.5(2)
plane 4/plane 6	87.0(1)		87.3(2)		89.9(2)	87.3(2)
plane 5/plane 6	87.6(2)		88.2(2)		88.3(2)	88.2(5)

flap atoms O5 and C15, and the second through the center of bonds P−O6 and C13−C14.

Different bond lengths within the phosphorinane ring cause deformation from the ideal conformation. In general, however, molecules in the chair conformation are less deformed from the ideal than molecules in the boat conformation. The extent of deformation of a six-membered ring can be described by the average and the sum of the torsion angles. This parameter shows that the dioxaphosphorinane ring in compounds **1c**, **1d**, and **1bB** is flatter than that in compounds **1a** and **1bA** (Table 4).

The general conformation of the phosphorinane ring depends mostly on the number of substituents and on their sizes. No substitution or monosubstitution by a large substituent allows the chair conformation. Two small methyl substituents in compound **1b** have the effect that two conformations, boat and chair, are almost equally preferred. For one small methyl and a large propyl substituent, a crystal shows the preferable boat conformation. Crystal packing is not very tight, and there seems to be enough space for conformational flexibility.

It is possible to get interesting information about the geometry of these molecules by analyzing dihedral angles between selected least-squares planes (Table 6). In a six-membered ring, the "seat" and "deck" planes (plane 1) for chair and boat conformations were selected by calculating the plane through all six atoms and selecting the four atoms which least deviated from planarity. The base plane calculated here also confirms the observation from asymmetry parameters mentioned earlier. The two atoms which deviate most, with their two neighboring atoms, create two additional planes (called planes 2 and 3). The dihedral angles between plane 1 and planes 2 and 3 show the type of conformation and degree of bending of the six-membered ring. The dioxaphosphorinane ring is more flattened around the phosphorus and oxygen atoms than around the carbon atoms. The dihedral angle between base plane 1 and the plane containing the phosphorus atom (plane 2) is lower than the corresponding angle with plane 3. This is especially evident for chair conformations in compounds **1a** and **1bA**, where differences between these two angles are around 20°. For boat conformations in compounds **1bB** and **1c**, and for the twisted chair conformation in compound **1d**, this difference is not so large. For these conformations the central atom in plane 2 is oxygen O5 for **1bB** and **1c**, and O6 for **1d**.

The planes of the two five-membered rings (planes 4 and 5), and plane O5−P−O6 (plane 6) located around the phosphorus atom, are approximately perpendicular. The lowest value of the dihedral angle is between planes 4 and 5 in compound **1c**, equal to 86.8°. The fact that the dihedral angles are close to perpendicular confirms the octahedral structure around the central phosphorus atom.

In all four compounds, the methylene groups of the ammonium cation are disordered. In compounds **1a** and **1b**, we were able to model this disorder directly by refinement of the secondary carbon atoms in two different positions for the same atom. For compounds **1c** and **1d**, high-temperature factors for those atoms indicate the high flexibility in this moiety but the lower quality of the data does not allow the introduction of a more precise model. Disorder in a triethylammonium cation is not unusual, and is even observed in the very well refined simple structure of triethylammonium chloride.[12d,e]

NMR Studies. Conformational Analysis of Compounds 1 in Solution. Selected ^{1}H and ^{13}C NMR data for the 1,3,2-dioxaphosphorinane ring in compounds **1a−d** are tabulated in Tables 7 and 8. Some features should be noted: The NMR spectra of **1** are much less complex in the region referring to the dioxaphosphorinane ring when both substituents at C14 are identical. For example, the ^{1}H NMR spectrum of **1a** (H,H) shows the pair of triplets whereas in the spectrum of **1d** (H,t-Bu) shows the multiplet of 19 lines. Moreover, in the ^{13}C NMR spectrum of **1a** and **1b** (symmetrically substituted at ring atom C14) only one resonance for both *O*-methylene carbons is observed, whereas in the case of **1c** (Me,Pr) or **1d** (H,t-Bu) the separate resonances for each methylene carbon atoms occur. These observations can be explained in terms of loss of symmetry of the molecule. Due to the propeller-like arrangement of aromatic rings in the molecule **1** the equishielding surfaces (coming from ring current effects) have the C_2 axis that dissects atoms P and C14, if the ideal planar confomation of dioxaphosphorinane ring is assumed. Clearly, existing conformers or their equilibria make the time-averaged locations of *O*-methylene carbon atoms more or less symmetrical toward C_2, and the difference in ^{13}C chemical shift of C13 and C15 occurs as observed in **1c** ($\Delta\delta_C = 0.05$ ppm) and **1d** ($\Delta\delta_C = 0.16$ ppm). The latter value shows that the geometry of dioxaphosphorinane ring is significantly perturbed by the t-Bu substituent, as expected. The nonequivalence of methylene groups in **1d** is also visible in the ^{1}H NMR spectrum. Chemical shifts of the protons H_A and H_B (at C13) are almost the same, whereas chemical shifts of H_C and H_D

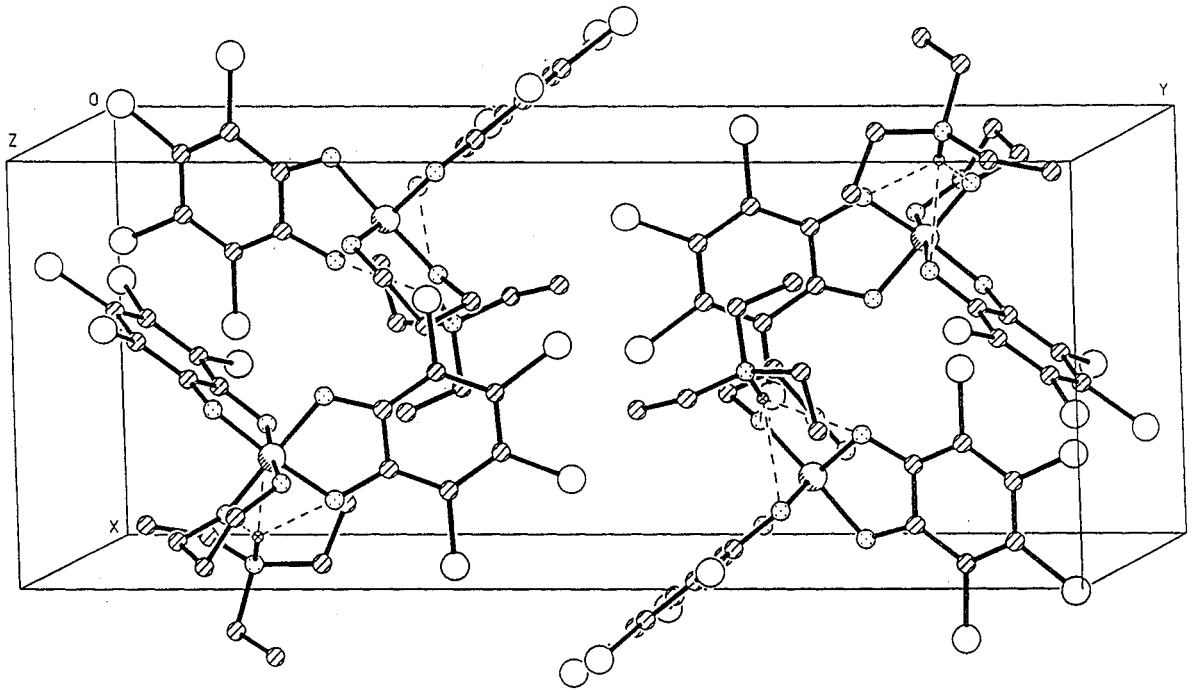


Figure 6. View of the packing arrangement of **1a**. For clarity only hydrogen atoms creating hydrogen bonds are represented.

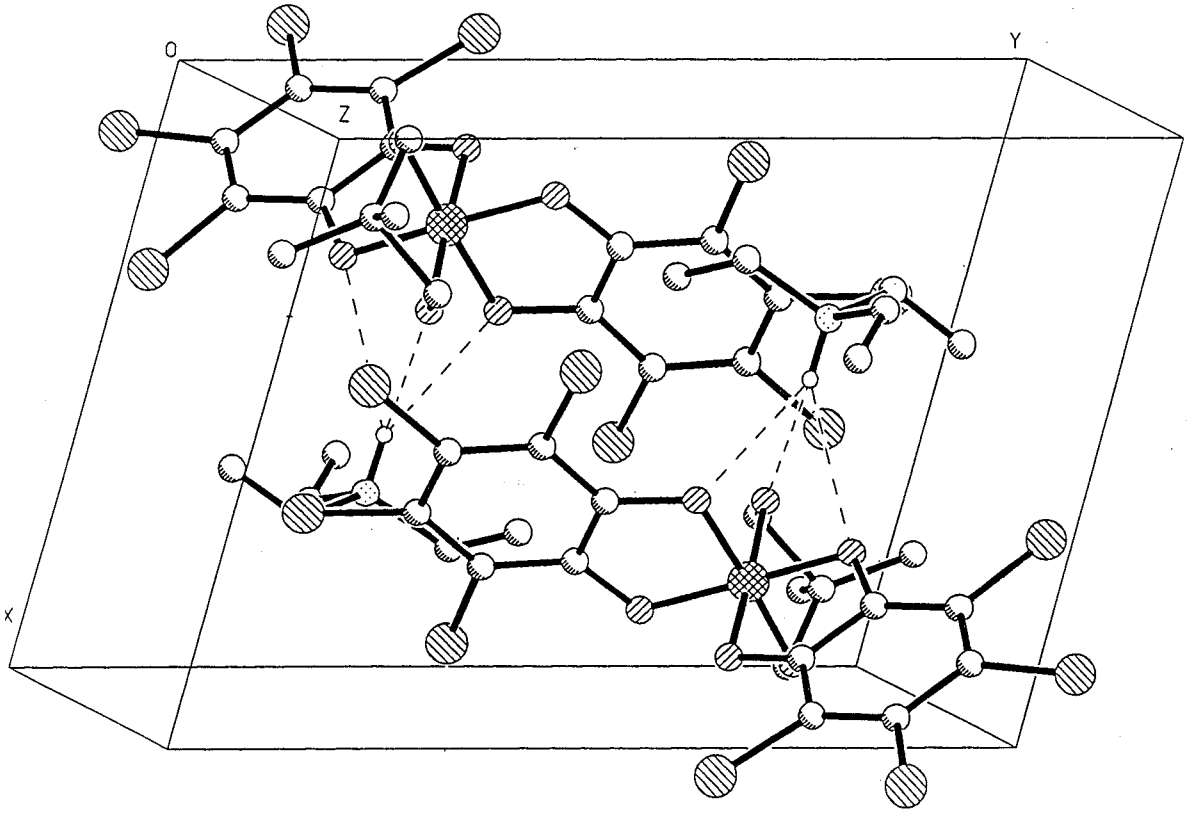


Figure 7. View of the packing arrangement of **1b**. For clarity only hydrogen atoms creating hydrogen bonds are represented.

protons at C15 differ significantly ($\Delta\delta_H = 0.3$ ppm, see Table 7), showing that the methylene group bearing H_C and H_D might be slooped against the aromatic system (the methylene proton in neighbarhood of the aromatic ring plane is always denoted as H_C). The Dreiding model offers two possible locations for this methylene group (CH_CH_D); the first puts the proton H_C in the direction between the two phospholane rings, and the other brings it into the proximity of the phospholane. The $^1H-^{13}C$ HMQC experiment shows that the protons H_C and H_D are attached to the upfield methylene carbon atom; hence, the CH_CH_D methylene group is the one in the proximity of the phospholane, due to the interactions with the aromatic rings (ring current effect). In contrast to H_C and H_D the ^1H NMR resonance of H_A and H_B protons are very close together ($\Delta\delta$ in ppb only); moreover, the

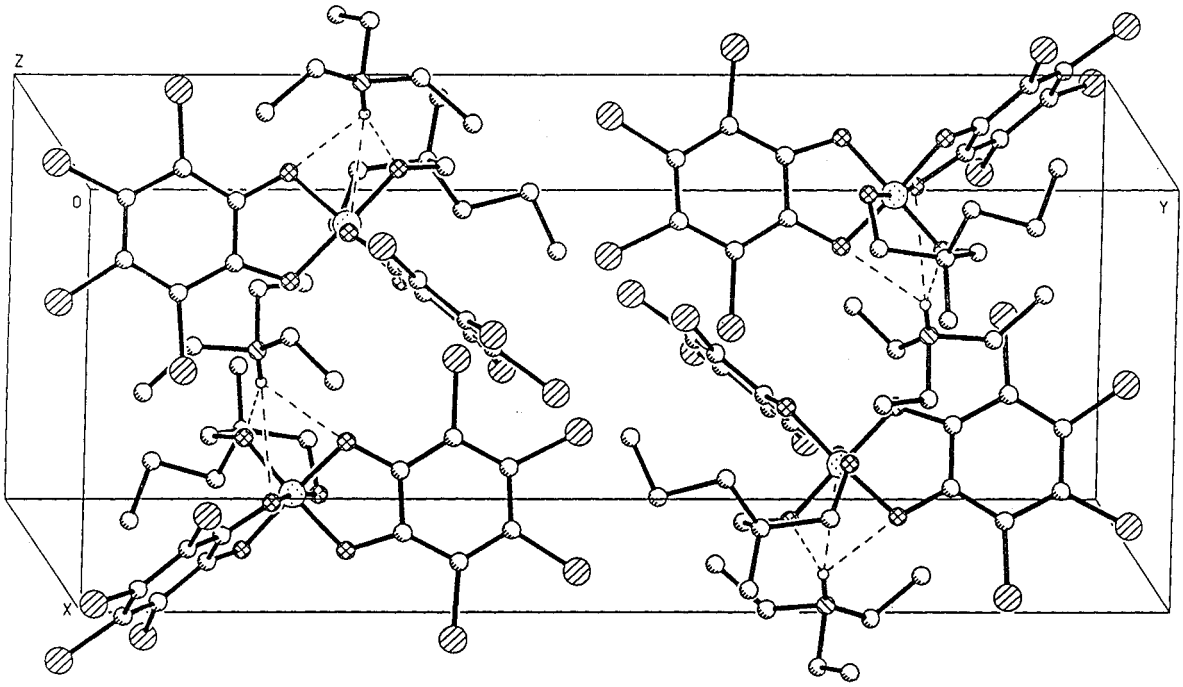


Figure 8. View of the packing arrangement of **1c**. For clarity only hydrogen atoms creating hydrogen bonds are represented.

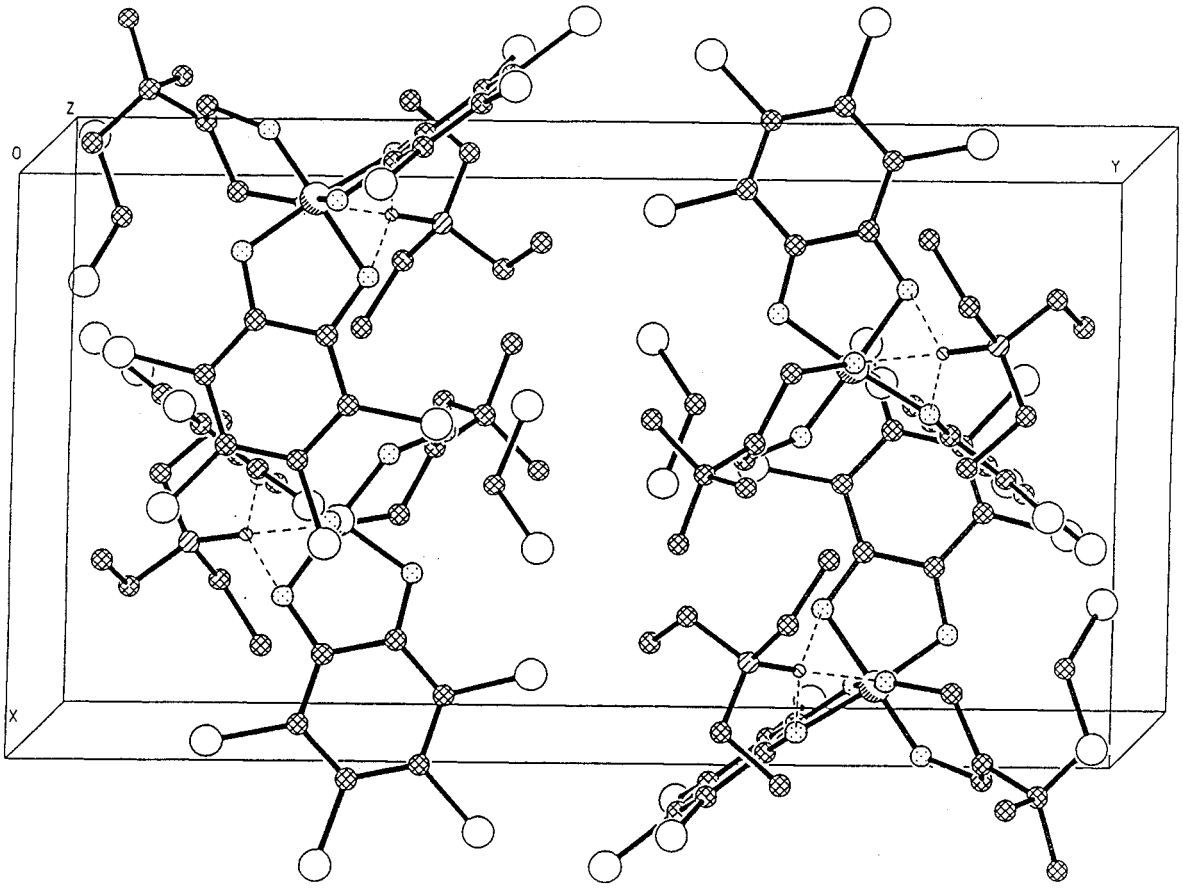


Figure 9. View of the packing arrangement of **1d**. For clarity only hydrogen atoms creating hydrogen bonds are represented.

geminal coupling of H_A and H_B is not visible in the NMR spectrum, and the vicinal couplings of these protons with H_E (at C14) are identical ($^3J_{HH}$= 6.8 Hz). Clearly, this part of the dioxaphosphorinane ring moves rapidly whereas the remaining part (C14−C15−O5−P) is almost rigid.

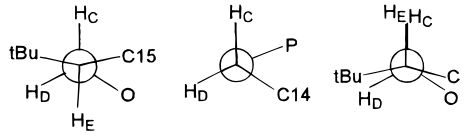
The knowledge of the coupling constants $^3J_{HCHE}$ and $^3J_{HDHE}$ provides the opportunity to establish the conformation of six-membered ring in **1d** as well as to compare the ring conformations in the solution and in solid state. Although the hydrogen atoms of methylene groups in X-ray analysis were set geometrically, the torsion angles

Table 7. ^{1}H and ^{13}C Chemical Shifts (in ppm) of the 1,3,2-Dioxaphosphorinane Ring in the Compounds 1 at Room Temperature

compound	H_A	H_B	H_C	H_D	C15; C13	C14
			CD_2Cl_2			
1a	4.14	4.14	4.14	4.14	65.66	27.01
1b	3.86	3.80	3.86	3.80	77.02	32.05
1c	3.96	3.78	3.93	3.75	(76.22; 76.17)[a]	35.34
1d	4.05	4.05	4.11	3.81	66.16; 66.00	45.79
			$(CD_3)_2SO$			
1b	3.79	3.52	3.79	3.52	75.44	30.99
1c	3.85	3.59	3.75	3.51	(74.38; 74.21)[a]	33.96

[a] Correlation H on C was not performed.

HCCH derived from crystallographic data are not away from the correct ones in solid **1d**. The Newman projection along the C13−C14 bond in solid **1d** is depicted in structure **8** showing the antiperiplanar location of H_C and H_E. If this arrangement is retained in the solution, our rather high value of coupling constant of H_C and H_E ($^3J_{HCHE} = 11.1$ Hz) could be rationally explained. Several H−H coupling constant data for dioxaphosphorinanes involving pentacoordinated phosphorus are available now. Generally, in nonchair conformers the $^3J_{HCHE}$ values were found[6d] to be as large as 9.1−10.6 Hz and $^3J_{HDHE}$ 6.9−7.9 Hz, while for the ring in the predominantly chair conformation (e−e attachment forced) the coupling constants are respectively:[13a,b] 11.6 Hz vs 4.4−4.5 and 11.8 Hz vs 4.4 Hz; or 11.3 Hz vs 4.3 Hz for the boat conformation with O and C at the bowsprit positions.[13c] Our data for **1d** (11.1 Hz vs 6.3 Hz) are placed between those for chair and twist conformers. If H−H coupling relationships in dioxaphosphorinanes are not influenced by negative charge in hexacoordinated phosphorus compounds, only small twisting along C13−C14 bond is possible in the solution that leads to decrease of torsion angle H_E−C−C−H_C and probably t-Bu −C−C−H_C.



8 **9** **10**

The Karplus-like relationship for hexacoordinated phosphorus has not yet been recognized; however, it undoubtedly exists as shown by the P−H coupling constants collected in the Table 8. Also the structure **9** shows the Newman projection along the C13−O5 bond in the solid **1d**. The phosphorus atom is antiperiplanar to the proton H_D, and this agrees fairly well with the large value of coupling constant J_{HDP} =29.9 Hz (Table 8), assuming that the dependence of J_{HP} on torsional angle H−C−O−P in hexacoordinated phosphorus compounds is similar to that observed in phosphates.[14] The J_{HCP} =7.8 Hz (only 21% of the sum J_{HCP} and J_{HDP}) is also in accordance with the gauche position of H_C. Therefore, we can assert that the conformation of this part of the dioxaphosphorinane ring remains unchanged in CD_2Cl_2 solution. Our NMR observations show that the dioxaphosphorinane ring of compound **1d** in CD_2Cl_2 solution resembles the "half-chair", slightly twisted at the H_CH_D methylene group. The other methylene group moves rapidly, and this tendency is retained in the crystal and is probably responsible for the 50% displacement probability elipsoid of C15, which is much larger than that of the C13 atom (see Figure 5).

Although the "pseudomirror" conformation, in which the functions of the methylene groups are exchanged, might be considered (structure **10**), for the large $^3J_{HCHE}$, a strictly eclipsed arrangement of protons H_C and H_E as well as of H_D and t-Bu is required. This makes this conformation strongly unfavorable, accounting for the pendant the other methylene group.

Although in compound **1a** the vicinal couplings are present ($^3J_{HH} = 5.8$ Hz), the conformations of the dioxaphosphorinane ring in this molecule cannot be established. All *O*-methylene protons are isochronous; moreover, the geminal coupling for these protons as well as for C14-protons is not observed. The conclusion is that in **1a** at room temperature (in CD_2Cl_2) fast exchange occurs between numerous available conformers of the six-membered ring and measured δ and J are time-averaged values.

The case of **1b** is slightly different. In the ^{1}H NMR spectrum the multiplet of methylene protons may be analyzed as an ABX system, showing that only two types of protons coupled to each other are present in the solution. The ^{13}C NMR spectrum reveals also one type of the methylene group with $^2J_{CP} = 8.6$ Hz. It might be assumed that the six-membered ring adopts a well defined conformation with magnetically equivalent methylene groups (for example the twist conformer might be considered). But this is not the case, as the observed values of $^3J_{HP} = 18.6$ and 15.8 Hz in CD_2Cl_2 or $^3J_{HP} =$ 18.0 and 17.5 Hz in $(CD_3)_2SO$ do not agree with a single twist conformation since large differences in the P−H coupling constants are expected in such a conformation.[6d] Similar behavior of the 5,5-dimethyl-1,3,2-dioxaphosphorinane ring was found in the pentacoordinated phosphorus compounds,[13d] where the differences in H−P coupling constants 20.2 Hz vs 16.3 or 19.0 Hz vs 17.3 Hz were observed only when the geminal coupling occurred. A reasonable explanation for the pentacoordinated phosphorus compounds are dynamic intramolecular ligand exchange processes based on pseudorotation in TBP structures.[13d,15f] Although in the octahedral structures of **1a** and **1b** both P−O5 and P−O6 bonds have almost the same length and the O5−P−O6 angles are only slightly larger than 90° (see Table 2) and the pseudorotation processes known for TBP do not operate in the hexacoordinated phosphorus compounds, the fast equilibrium

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Table 8. Coupling Constants J_{HP}, J_{CP}, and J_{HH} of the 1,3,2-Dioxaphosphorinane Ring in the Compounds 1 at Room Temperature

	J_{HP} [Hz]				J_{CP} [a] [Hz]		J_{HH} [a] [Hz]					
compound	H_A	H_B	H_C	H_D	C15; C13	C14	H_AH_B	H_CH_D	H_AH_E	H_BH_E	H_CH_E	H_DH_E
					CD_2Cl_2							
1a	18.0	18.0	18.0	18.0	9.0	5.9	–[b]	–[b]	5.8	5.8	5.8	5.8
1b	18.6	15.8	18.6	15.8	8.6	5.1	11.1	11.1	–	–	–	–
1c	17.7	17.0	14.0	21.9	(7.3; 7.3)[c]	4.5	10.9	10.9	–	–	–	–
1d	19.2	20.8	7.8	29.9	8.6; 7.0	2.5	–[b]	11.1	6.8	6.8	11.1	6.3
					$(CD_3)_2SO$							
1b	18.0	17.5	18.0	17.5	9.5	5.2	10.5	10.5	–	–	–	–
1c	17.3	18.9	17.1	18.5	(8.3; 8.7)[c]	4.9	10.7	10.7	–	–	–	–

[a] Absolute values are given. [b] Not observed. [c] Correlation H on C was not performed.

between conformers occurs at room temperature. Interestingly, because of 2-fold symmetry of molecule **1b** (substituents at C14 are identical) the methylene groups are indistinguishable in NMR even if quite different conformers would be involved in the equilibrium process. Thus the conformers **1bA** and **1bB** (Figure 2 and Figure 3) that are present in the solid are not excluded in the solution. Due to lack of the vicinal H−H coupling constants, we cannot determine conformations of the dioxaphosphorinane ring in the solution. The triethylammonium cation also may perturb the population of conformers. In $(CD_3)_2SO$ the differences in $^3J_{HP}$ values are much lower ($\Delta J = 0.5$ Hz) and this is probably due to solvation effects on the cation as well as to the decay of hydrogen bonds in this solvent.

The conformation of the dioxaphosphorinane ring in compound **1c** could not be determined precisely because of lack of the proton at C14. In the solid state the shape of the six-membered ring is intermediary between **1b** and **1d,** and the same is probably valid in CD_2Cl_2 solution as shown by the J_{CP} values as well as J_{HP} of protons H_C and H_D in this solvent. Again, as in the case of **1b**, time-averaged J_{HP} values are observed. Thus for the compound **1c** in solution, the fast equilibrium between two "pseudo-mirror" twist conformers looks most probable. However, the dioxaphosphorinane ring in the twist conformation is bent because of the *n*-propyl substituent at C14.

Comparison of the coupling constants in CD_2Cl_2 and in $(CD_3)_2SO$ reveals the influence of both counterion and substituent at C14 on the conformations of six-membered ring.

Summary

From the above NMR data it can be concluded that the flexibility of the 1,3,2-dioxaphosphorinane rings in compounds **1a**−**d** is strongly controlled by the size of substituents at the C14 atom. Unsubstituted six-membered ring in **1a** is highly mobile at room temperature in CD_2Cl_2 solution. Methyl group in **1a** and methyl and *n*-propyl groups in **1c** do not prevent conformations equilibrium. The six-membered ring with *tert*-butyl group in **1d** has a slightly distorted chair conformation. However, in this case the ring is only partially rigid with the flickering methylene group.

X-ray crystallography shows that two conformations, chair and boat, are the most preferable in the solid state. The six-membered ring in **1a** has a chair conformation and in **1d** a twisted chair conformation. The ring in **1c** has a boat conformation, whereas in **1b** two conformations, boat and chair, are almost equally preferred. Ellipsoids of 50% displacement in the 1,3,2-dioxaphosphorinane rings in the compounds **1a**−**d** are relatively large. This shows some tendency to flexibility of the six-membered rings in the solid state.

It has been reported[13b,15,16] that in pentacoordinated phosphorus compounds the 1,3,2-dioxaphosphorinane ring in apical-equatorial positions in solution and in the solid-state adopts rather nonchair (twist or boat conformations). However, it was found, recently, that in neutral hexacoordinated phosphorane such a ring has distorted chair conformation (85% chair).[9]

Experimental Section

X-ray Single-Crystal Structure Determination. Hexacoordinated tris(bidentate) phosphorus compounds **1a**−**d** were obtained directly in the form of suitable crystals. Selected crystals were mounted in Lindemann glass capillaries with a diameter from 0.3 to 0.5 mm and sealed. All manipulations of crystals were made in a glovebag under a dry argon atmosphere. Selected crystals were set up on an automatic CAD4 diffractometer, and X-ray data were collected using Cu Kα radiation. Unit cell dimensions with estimated standard deviations were obtained from a least-squares refinement of the setting angles of 25 centered reflections. The decline in intensities of three control reflections was 48% for **1a**, 52% for **1b**, 81% for **1e**, 62% for **1d**, during 74, 71, 68, and 86 h of exposure, respectively. For this reason, the collected data were corrected for radiation decay using the DECAY program. For compounds **1a** and **1b**, which showed an almost ideal linear decrease of intensity, a single run of this program was enough. For compounds **1c** and **1d**, the data sets were divided into four and two parts, respectively, according to the rate of loss of intensity. Each part was corrected separately, scaled individually, and then scaled together according to the initial intensity of control reflections. The structures were solved by direct methods using the SHELXS program.

Most of the non-hydrogen atoms were found directly, with some atoms (especially the atoms with lower occupancy factor) in disordered regions found after the first run of refinement on a difference Fourier map. The structures were refined by full matrix least-squares calculations using structure factors and the program SHELXTL. A high σ cutoff was used because the intensities decayed rapidly during the data collection, producing significantly different data quality at the beginning and end of the experiment. The benzene rings were restrained to be ideal. The occupancy factors of atoms in the disordered region (in the triethylammonium cation of compounds **1a** and **1b**, and in the 1,3,2-dioxaphosphorinane ring of compound **1b**) were restrained to give a sum equal to one. For compounds **1a**−**d**, all hydrogen atoms connected to carbon atoms were set geometrically and were refined as "riding". The hydrogen atom from the ammonia cation was found on a difference Fourier map.

Atomic coordinates and complete lists of bond angles, bond lengths, and thermal parameters have been deposited at the

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Cambridge Crystallographic Data Centre. For detailed instructions on the deposition of crystallographic data to the CCDC, see "Instructions to Authors" in *J. Chem. Soc., Perkin Trans. 2* **1996**, *1*.

NMR Experiments. The NMR tubes were sealed under vacuum. Coupling constants *J* were found generally in the first-order analysis (with the exception of **1b**) supported by full phosphorus decoupling experiments {^{31}P}. Only absolute values of coupling constants are given.

Materials. Solvents and commercial reagents were purified and dried by conventional methods. 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane,[17] 2-chloro-1,3,2-dioxaphosphorinane,[18] 2-chloro-5-*tert*-butyl-1,3,2-dioxaphosphorinane,[19] 2-chloro-5-methyl-5-propyl-1,3,2-dioxaphosphorinane,[20] 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane,[19] 2-(2,2,2-trifluorethoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane,[19] 2-(1,1,1,3,3,3- hexafluoro-2-propoxy)-1,3,2-dioxaphosphorinane,[18] 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5-*tert*-butyl-1,3,2-dioxaphosphorinane,[6d] and 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5-methyl-5-propyl-1,3,2-dioxaphosphorinane[19] were prepared by conventional methods.

Preparation for Phosphoranes 2a−e. General Procedure. To a solution of the corresponding phosphorinane (0.01 mol) in benzene (50 mL) was added dropwise a solution of *o*-tetrachloroquinone (0.01 mol) in benzene (50 mL) at room temperature. Stirring was continued until no red color persisted (approximately 20 h). The solvent was removed under reduced pressure. The crude product was crystallized from methylene chloride−hexane (2:1) and dried under reduced pressure.

(1,1,1,3,3,3-Hexafluoro-2-propoxy)(propanediyl-1,3-dioxy)(tetrachloro-*o*-phenylenedioxy) phosphorane, [(CF$_3$)$_2$CHO](C$_3$H$_6$O$_2$)(Cl$_4$C$_6$O$_2$)P (2a). From 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-1,3,2-dioxaphosphorinane was prepared 4.77 g (92%) of **2a** as white powder: ^{31}P NMR ($CDCl_3$, 81.0 MHz) δ_P −48.28, J_{HP} = 14.8 Hz, J_{HcyclP} = 17.3 Hz; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 2.06−2.19 (2H, m, CH_2), 4.23−4.52 (4H, m, OCH_2), 5.43−5.62 (1H, m, $OCHCF_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ_C 24.54 (d, J_{CP} = 7.97 Hz, CH_2), 66.31 (d, J_{CP} = 8.66 Hz, OCH_2), 71.50−74.50 (m, J_{CP} = 11.2 Hz, J_{FCC} = 34.7 Hz, OCH), 114.62 (d,J_{CP} = 8.80 Hz, Ar), 120.27 (q, J_{FC} = 274.2 Hz, CF_3), 125.14 (s, Ar), 139.44 (d, J_{CP} = 8.57 Hz, Ar).

(1,1,1,3,3,3-Hexafluoro-2-propoxy)(2,2-dimethylpropanediyl-1,3-dioxy)(tetrachloro-*o*-phenylenedioxy) phosphorane, [(CF$_3$)$_2$CHO](Me$_2$C$_3$H$_4$O$_2$)(Cl$_4$C$_6$O$_2$)P, (2b). From 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane was prepared 4.75 g (87%) of **2b** as white powder: ^{31}P NMR ($CDCl_3$, 81.0 MHz) δ_P −48.86, J_{HP} = 14.6 Hz, J_{HcyclP} = 21.1 Hz; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 1.01 (3H, s, CH_3), 1.14 (3H, s, CH_3) 3.85−4.17 (4H, m. OCH_2), 5.39−5.63 (1H, m, $OCHCF_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ_C 23.68 (s, CH_3), 24.17 (s, CH_3), 32.39 (d, J_{CP} = 4.77 Hz, >C<), 71.70−74.40 (m, J_{FCC} = 34.7 Hz, J_{CP} = 11.1 Hz, OCH), 77.37 (d, J_{CP} = 8.29 Hz, OCH_2 and solvent), 114.65 (d, J_{CP} = 18.9 Hz, Ar), 120.42 (q, J_{FC} = 279.4 Hz, CF_3), 125.21 (s, Ar), 139.39 (d, J_{CP} = 8.68 Hz, Ar).

(1,1,1,3,3,3-Hexafluoro-2-propoxy)(2-methyl-2-propylpropanediyl-1,3-dioxy) (tetrachloro-*o*-phenylendioxy) phosphorane, [(CF$_3$)$_2$CHO](MePrC$_3$H$_4$O$_2$)(Cl$_4$C$_6$O$_2$)P, (2c). From 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5-methyl-5-propyl-1,3,2-dioxaphosphorinane was prepared 5.51 g (96%) of **2c** as white powder: ^{31}P NMR ($CDCl_3$ + CH_2Cl_2, 81.0 MHz) δ_P −47.97, −48.10 (diastereoisomers 3:4); ^{1}H NMR ($CDCl_3$ + CH_2Cl_2, 200 MHz) δ_H 0.82−1.05 (6H, m, C**H**$_3$CH$_2$, CH_3), 1.08−1.34 (4H, m, CH_2CH_2), 3.86−4.18 (4H, m, OCH_2), 5.31−5.55 (1H, m, OCH); ^{13}C NMR ($CDCl_3$ + CH_2Cl_2, 50.3 MHz) δ_C 14.30 (s, **C**H_3CH$_2$), 16.52 (d, J_{CP} = 7.51 Hz, CH_2CH_2), 21.06 (d, J_{CP} = 25.3 Hz, C**C**H_3), 35.15 (s, >C<), 39.15 (d, J_{CP} = 36.4 Hz, CH_3**C**H_2), 74.40−71.70 (m, J_{FCC} = 34.7 Hz, J_{CP} = 11.1 Hz, OCH), 75.92 (m, OCH_2, solvent), 114.39 (d, Ar), 120.26 (q, J_{FC} = 285.61 Hz, CF_3), 124.82 (s, Ar), 139.31 (d, J_{CP} = 8.90 Hz, Ar).

(1,1,1,3,3,3-Hexafluoro-2-propoxy)(2-*tert*-butylpropanediyl-1,3-dioxy)(tetrachloro-*o*-phenylenedioxy) phosphorane, [(CF$_3$)$_2$CHO](tBuHC$_3$H$_4$O$_2$)(Cl$_4$C$_6$O$_2$)P, (2d). From 2-(1,1,1,3,3,3-hexafluoro-2-propoxy)-5-*tert*-butyl-1,3,2-dioxaphosphorinane was prepared 5.11 g (89%) of **2d** as white powder: ^{31}P NMR ($CDCl_3$, 81.0 MHz) δ_P −47.31, −47.86 (diastereoisomers, 7:8), J_{HP} = 14.5 Hz, J_{HcyclP} = 17.9 Hz and J_{HP} = 19.1 Hz, J_{HcyclP} = 16.4 Hz; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 0.81−1.06 (9H, m, $(CH_3)_3$C), 2.05−2.28 (1H, m, CH), 4.05−4.42 (4H, m, OCH_2), 5.40−5.61 (1H, m, OCH); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ_C 26.86 (s, CH_3), 31.37 (s, >C<), 44.99−45.06 (m, >CH), 68.08 (m, OCH_2), 74.16−72.07 (m, J_{FCC} = 34.9 Hz, J_{CP} = 10.3 Hz, OCH), 114.43, 114.80 (Ar), 120.36 (q, J_{FC} = 281.3 Hz, CF_3), 125.03, 125.31 (Ar), 139.22 (d, Ar), 139.50 (d, Ar).

(2,2,2-Trifluoroethoxy)(2,2-dimethylpropanediyl-1,3-dioxy)(tetrachloro-*o*-phenylenedioxyl)phoshorane, (CF$_3$CH$_2$O)(Me$_2$C$_3$H$_4$O$_2$)(Cl$_4$C$_6$O$_2$)P, (2e). From 2-(2,2,2-trifluoroethoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane was prepared 4.35 g (91%) of **2e** as light pink powder: ^{31}P NMR ($CDCl_3$, 81.0 MHz) δ_P −47.04; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 1.04 (3H, s, CH_3), 1.09 (3H, s, CH_3), 3.85−4.17 (4H, m, OCH_2), 4.40−4.62 (2H, m, OCH_2CF_3); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ_C 23.95 (s, CH_3), 24.54 (s, CH_3), 32.44 (d, J_{CP} = 4.1 Hz, >C<), 64.6−67.0 (m, J_{FCC} = 36.94 Hz, J_{CP} = 9.98 Hz, **C**H_2CF_3), 76.92 (d, J_{CP} = 8.1 Hz, O**C**H_2 (cycl), solvent), 122.61 (q, J_{FC} = 277.8 Hz, J_{CP} = 12.8 Hz, CF_3), 113.75 (d, J_{CP} = 19.4 Hz, Ar), 124.68 (s, Ar), 139.65 (d, J_{CP} = 7.04 Hz, Ar).

Preparation of Hexacoordinated Phosphorus Compounds 1a−d. General Procedures. Method A (Scheme 1). To the solution of the corresponding phosphorane **2** (0.001 mol) in methylene chloride (5 mL) was added dropwise a solution of 1,1,1,3,3,3-hexafluoro-2-propanol (0.001 mol) and triethylamine (0.001 mol) in methylene chloride (5 mL) at −100 °C. The reaction mixture was slowly warmed to −20 °C. After the mixture was cooled to −100 °C, hexane (10 mL) was added to reaction vessel to create the separate solvent layer. Then the reaction mixture was warmed slowly to room temperature and remained under dry argon atmosphere for 5−7 days. Precipitated crystals were filtered, washed with dry hexane, and dried under reduced pressure.

Method B (Scheme 2). In the reaction vessel (10 mL) equipped with a Teflon stopcock was placed dry tetrachlorocatechol (0.001 mol) followed by the solution of phosphorane **2** in methylene chloride (ca. 3 mL). The mixture was degassed on the vacuum line (p < 0.001 Torr), and into the cooled (liq N_2) reaction vessel was condensed dry triethylamine (0.001 or 0.002 mol) followed by 1 mL of methylene chloride. On warming to room temperature the catechol crystals dissolved. The reaction vessel was cooled again and the hexane (5 mL) was distilled into the reaction mixture. After 24−48 h at r.t. the precipitated **1** was filtered and (optionally) recrystallized (methylene chloride/hexane, 2:1).

Triethylammonium Bis(tetrachloro-*o*-phenylenedioxy)(propanediyl-1,3-dioxy)phosphorane, Et$_3$NH$^+$(C$_3$H$_6$O$_2$)(Cl$_4$C$_6$O$_2$)$_2$P$^-$, (1a). Method A. From **2a** was obtained 0.321 g (46%) of **1a** as colorless crystals. **Method B.** From 0.85 × 10^{-3} mol of **2a** was obtained 0.242 g (0.345 × 10^{-3} mol) (41%) of **1a**. ^{31}P NMR (solid,[21] 121.5 MHz;) δ_{Piso} −100.1 (Ω 55); ^{31}P NMR (CD_2Cl_2, 81.0 MHz) δ_P −97.83, J_{HP} = 17.9 Hz; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ_H 1.24−1.36 (9H, m, C**H**$_3$CH$_2$N), 1.84−1.95 (2H, m, CH_2), 3.17−3.33 (6H, m, CH_2N), 4.07−4.27 (4H, m, OCH_2), 8.13 (br s, NH); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ_C 8.77 (br s, **C**H_3CH$_2$), 27.01 (d, J_{CP} = 5.9 Hz, CH_2), 47.75 (br s, NCH_2), 65.66 (d, J_{CP} = 8.99 Hz, OCH_2), 113.70 (d, J_{CP} = 19.5 Hz, Ar), 114.17 (d, J_{CP} = 18.1 Hz, Ar),121.42 (s, Ar), 122.95 (s, Ar), 142.79 (d, J_{CP} = 7.4 Hz, Ar), 143.73 (d, J_{CP} = 5.5 Hz, Ar).

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Triethylammonium Bis(tetrachloro-*o*-phenylenedioxy)-(2,2-dimethylpropanediyl-1,3-dioxy) phosphorane, $Et_3NH^+(Me_2C_3H_4O_2)(Cl_4C_6O_2)_2P^-$, (1b). Method A. From **2b** was obtained 0.3267 g (45%) of **1b** as colorless crystals. **Method B.** From 0.28×10^{-3} mol of **2b** was obtained 0.156 g (0.215×10^{-3} mol) (77%) of **1b**. ^{31}P NMR (solid, 121.5 MHz) δ_{Piso} −97.8 (Ω 51); ^{31}P NMR (CD_2Cl_2, 81.0 MHz) δ_P −99.98, J_{HP} = 17.3 Hz; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ_H 0.95−1.08 (6H, br s, CH_3), 1.21−1.34 (9H, m, C**H**$_3CH_2$), 3.20−3.67 (6H, m, NCH_2), 3.74−4.00 (4H, m, OCH_2); ^{1}H NMR ($(CD_3)_2SO$, 200 MHz) δ_H 0.94 (6H, s, CH_3-), 1.13−1.20 (9H, m, C**H**$_3CH_2$), 3.03−3.14 (6H, m, NCH_2), 3.45−3.86 (4H, m, OCH_2); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ_C 8.78 (s, **C**H_3CH_2), 22.65 (s, **C**H_3), 32.05 (d, J_{CP} = 5.07 Hz, >C<), 47.61 (s, NCH_2), 77.02 (d, J_{CP} = 8.60 Hz, OCH_2), 113.26 (d, J_{CP} = 25.0 Hz, Ar), 113.63 (d, J_{CP} = 26.0 Hz, Ar),120.97 (s, Ar), 122.48 (s, Ar), 142.16 (d, J_{CP} = 4.77 Hz, Ar), 143.15 (d, J_{CP} = 6.89 Hz Ar); ^{13}C NMR ($(CD_3)_2SO$, 50.3 MHz) δ_C 8.31 (s, **C**H_3CH_2), 21.92 (s, CH_3), 30.99 (d, J_{CP} = 5.21 Hz,>C<), 45.46 (s, NCH_2), 75.44 (d, J_{CP} = 9.49 Hz, OCH_2), 111.25 (d, J_{CP} = 19.3 Hz, Ar), 118.23 (s, Ar), 119.86 (s, Ar), 142.25 (d, J_{CP} = 6.99 Hz, Ar), 143.23 (d, J_{CP} = 5.16 Hz, Ar).

Triethylammonium Bis(tetrachloro-*o*-phenylenedioxy)-(2-methyl-2-propylpropanediyl-1,3-dioxo)phosphorane, $Et_3NH^+(MePrC_3H_4O_2)(Cl_4C_6O_2)_2P^-$, (1c). Method A. From **2c** was obtained 0.361 g (48%) of **1c** as colorless crystals. **Method B.** From 1.0×10^{-3} mol of **2c** was obtained 0.291 g (0.385×10^{-3} mol) (39%) of **1c**. ^{31}P NMR (solid, 121.5 MHz) δ_{Piso} −93.7 (Ω 58); ^{31}P NMR (CD_2Cl_2, 81.0 MHz) δ_P −99.85 J_{HP} = 17.5 Hz; ^{1}H NMR (CD_2Cl_2, 200 MHz) δ_H 0.79−0.94 (3H, m, CH_2CH_3), 1.00 (3H, s, CCH_3), 1.16−1.63 (13H, m, C**H**$_3CH_2N$, CH_2CH_2), 3.21−3.32 (6H, m, NCH_2), 3.61−4.02 (4H, m, OCH_2); ^{1}H NMR ($(CD_3)_2SO$, 200 MHz) δ_H 0.79−0.88 (6H, m, CH_3), 1.07−1.49 (13H, m, CH_3, CH_2CH_2), 3.03−3.14 (6H, m, CH_2N), 3.43−3.92 (4H, m, CH_2O); ^{13}C NMR (CD_2Cl_2, 125.8 MHz) δ_C 9.28 (s, CH_3CH_2N), 15.51 (s, **C**H_3CH_2), 17.40 (s, CH_3**C**H_2), 20.66 (s, C**C**H_3), 35.34 (d, J_{CP} = 4.45 Hz, >C<), 38.97 (s, C**C**H_2), 48.24 (s, NCH_2), 76.20 (s, OCH_2), 113.62−114.33 (m, Ar), 121.47 (d, J_{CP} = 10.3 Hz, Ar), 122.97 (d, J_{CP} = 2.2 Hz, Ar), 142.71 (d, J_{CP} = 6.60 Hz, Ar), 143.63 (br s, Ar); ^{13}C NMR ($(CD_3)_2SO$, 50.3 MHz) δ_C 8.56 (s, **C**H_3CH_2N), 14.89 (s, CH_3), 16.05 (s, CH_2CH_3), 19.64 (s, **C**H_3CH_2), 33.96 (d, J_{CP} = 4.86 Hz, >C<), 37.60 (s, C**C**H_2), 45.71 (s, NCH_2), 74.29 (dd, J_{CP} = 8.26 Hz, J_{CP} = 8.69 Hz, OCH_2), 111.11 (d, J_{CP} = 22.8 Hz, Ar), 111.99 (d, J_{CP} = 20.8 Hz, Ar), 118.54 (s, Ar), 120.11 (s, Ar), 142.56 (d, J_{CP} = 6.62 Hz, Ar), 143.34 (d, J_{CP} = 10.9 Hz, Ar).

Triethylammonium Bis(tetrachloro-*o*-phenylenedioxy)-(2-*tert*-butylpropanediyl-1,3-dioxy) phosphorane, $Et_3NH^+(tBuHC_3H_4O_2)(Cl_4C_6O_2)_2P^-$, (1d). Crystalization of **1d** from the mixture of methylene chloride and hexane provided crystals of **1d** containing methylene chloride (1:1) as shown by X-ray analysis (see Figure 9). **Method A.** From **2d** was obtained 0.328 g (38%) of **1d**·CH_2Cl_2 as colorless crystals. **Method B.** From 0.445×10^{-3} mol of **2d** was obtained 0.284 g (0.338×10^{-3} mol) (76%) of **1d**·CH_2Cl_2. ^{31}P NMR (CD_2Cl_2, 81.0 MHz) δ_P −95.24 (5%, H,P coupling not resolved), −95.56 (95%, J_{HP} = 19−20 Hz,); ^{1}H NMR (CD_2Cl_2, 200 MHz) δ_H 0.90 (9H, br s, $(CH_3)_3C$), 1.27−1.34 (9H, m, C**H**$_3CH_2N$), 2.00−2.11 (1H, m, CH), 3.22−3.33 (6H, m, NCH_2), 3.71−4.21 (4H, m, OCH_2), 8.02 (1H, br s, NH); ^{13}C NMR (CD_2Cl_2, 50.3 MHz) δ_C 8.82 (s, **C**H_3CH_2N), 27.19 (s,(**C**$H_3)_3C$), 31.62 (s,CH<), 45.79 (s, >C<), 47.82 (s, NCH_2), 66.07 (m, OCH_2), 112.95−114.09 (m, Ar), 121.05 (d, J_{CP} = 15.5 Hz, Ar), 122,40 (d, J_{CP} = 8.93 Hz, Ar), 142.40 (m, J_{CP} = 4 Hz, Ar), 143.16 (m, J_{CP} = 4 Hz, Ar).

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