

# Structure, dynamics and biochemical aspects of phosphoranyl radicals : an ESR study

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STRUCTURE, DYNAMICS AND BIOCHEMICAL ASPECTS OF PHOSPHORANYL RADICALS. AN ESR STUDY

# **STRUCTURE, DYNAMICS AND BIOCHEMICAL ASPECTS OF PHOSPHORANYL RADICALS. AN ESR STUDY**

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE  
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HOOGESCHOOL EINDHOVEN, OP GEZAG VAN DE  
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PROF. DR. TH.J. DE BOER

Voor Judith  
en mijn ouders

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# CHAPTER I

## Introduction

### *I.1 Scope of this thesis*

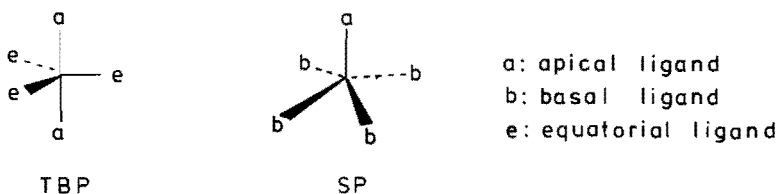
Much recent research concerns the effects of ionizing radiation in living cells. It is found that strand breaks in the DNA chains are induced<sup>1</sup>. The radical products in this process have been studied by Electron Spin Resonance (ESR). On comparison with model ESR studies on irradiated nucleosides and nucleotides a number of mechanisms for strand break in DNA has been proposed. However, the involvement of phosphorus centered radicals in reduction processes upon irradiation has not been recognized, although there is an increasing body of evidence that the conformational properties of DNA are directly related to the presence of phosphorus in the framework<sup>2</sup>. Therefore the study of radicals in which the unpaired electron is centered on phosphorus, i.e.  $P^V$  phosphoranyl radicals is appropriate and is the subject of this thesis.

Moreover the determination of the electronic structure of these radicals and their dynamic behaviour enables to test the different predictions of rivaling theories adequately by experiment. In spite of the large number of investigations concerning phosphoranyl radicals, a satisfactory description of their structure could not be given hitherto, since the majority of these studies concerns isotropic hyperfine splittings which are not a reliable guide to the overall electron spin distribution for these radicals. The aim of this thesis is to establish the possible structures of phosphoranyl radicals in order to understand the behaviour of these intermediates in radiation damage

processes, in particular in DNA.

### *I.2 The structure of penta-coordinated phosphorus compounds*

In  $P^V$  compounds the distribution of the ligands can not be spherically around the central phosphorus atom, i.e. the ligands are not equivalent<sup>3</sup> in contrast to tetra-coordination. Usually two types of structures of very similar energy are considered, the trigonal bipyramidal (TBP) and the square pyramidal (SP)<sup>4</sup>.

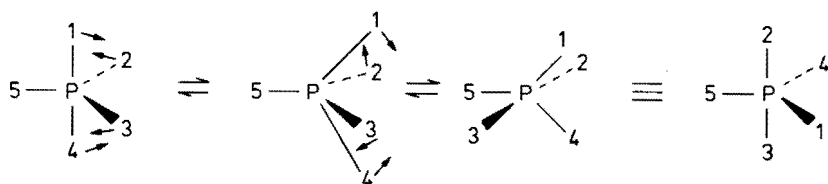


Both of these possible geometries are characterized by non-equivalent bonding: in the TBP there are three equatorial and two apical, and in the SP one apical and four basal substituents. Theoretical considerations based on MO and electrostatic calculations have predicted that the TBP is slightly more stable for acyclic penta-coordinated phosphorus derivatives<sup>3</sup>. In the TBP structure the apical bonds are longer and usually weaker than equatorial bonds, apical sites being preferred by electron withdrawing ligands, whereas electron donating ligands favour the equatorial positions. This "polarity rule" is based on experimental data<sup>5,6</sup> and semi-empirical calculations<sup>7,8</sup>. Furthermore it has been found that small rings spanning equatorial - apical positions are easily accommodated. This "strain rule"<sup>9</sup> is demonstrated by the fact that in most of the stable phosphoranes the phosphorus atom is part of a cyclic system.

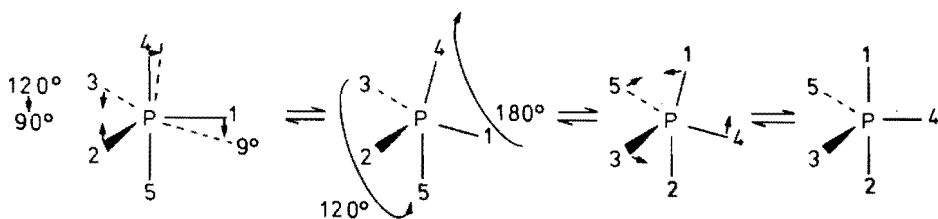
An explanation for the polarity rule is found by inspection of the orbitals involved in bonding in TBP structures. This configuration can be realized by hybridisation of the

$p_z$  and  $d_{z^2}$  orbitals for the apical bonds, combined with three  $sp^2$  orbitals in the equatorial plane, resulting in an  $sp^3d$  hybridisation<sup>10</sup>. The diffuse  $d_{z^2}$  orbital accounts for the elongation of the apical bonds, favouring the accomodation of electron withdrawing ligands, whereas the shorter equatorial orbitals favour donation of electrons from the ligands.

Interestingly,  $P^V$  compounds are stereochemically non-rigid<sup>3</sup>. This was demonstrated first for  $PF_5$  by  $^{19}F$  NMR showing one fluorine resonance<sup>11</sup>, while other methods<sup>12</sup> indicate that the fluorines interconvert their positions fast on the NMR time scale. A mechanism for this process is the Berry pseudorotation<sup>13</sup>.



In this process two equatorial and both apical ligands change place, the remaining ligand being the pivot; the intermediate is the SP structure. An alternative mechanism which accounts for the same permutation is the Turnstile rotation<sup>14,15</sup> which may be favoured in (bi)cyclic phosphoranes.



The energy barrier for Berry pseudorotation may be low for the case that all ligands are identical<sup>3</sup>, whereas on introduction of ligands with different electron withdrawing

character the permutation is hindered. The same applies for the presence of small rings<sup>7</sup>.

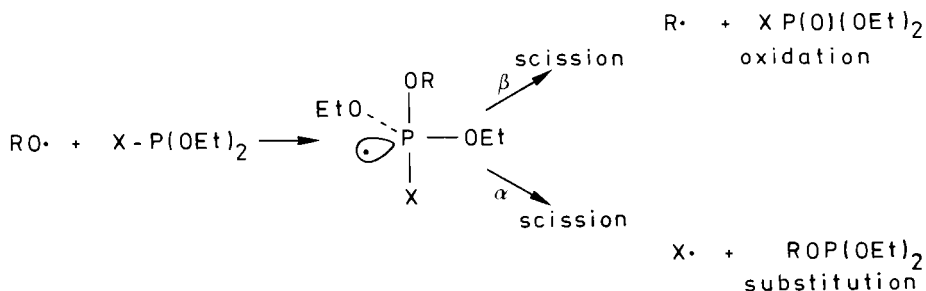
It has been established by X-ray diffraction analysis that in the solid state the structure of P<sup>V</sup> compounds is distorted more or less from an ideal TBP towards an SP geometry<sup>4</sup>. This depends on particular arrangement of ligands differing in electronegativity or inclusion of phosphorus in small four- or five-membered rings leading to stabilization of the SP.

*Note*

Since it will be demonstrated in chapter II.3 that a remarkable degree of s-character in the apical bonds is present, it is noted that the description  $\lambda(sp^2) + \mu(pd)$  is not completely satisfying. However, this s-character is higher for equatorial than for apical bonds, accounting for the observed differences in apical and equatorial sites in the TBP structure.

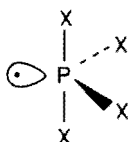
*I.3 Phosphoranyl radicals*

Phosphoranyl P<sup>V</sup> radicals have been suggested to act as intermediates in the reaction of alkoxy and alkyl radicals in the presence of trivalent phosphorus compounds giving products primarily by either  $\alpha$  or  $\beta$  scission processes<sup>16</sup>.

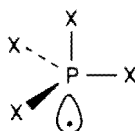


Two important overall processes are observed: oxidation

and substitution. A number of ESR studies has shown that phosphoranyl radicals in fact are formed in these systems<sup>17</sup>. Initially a TBP structure was assigned with the unpaired electron in an equatorial position acting as a fifth (phantom) ligand (TBP-e)<sup>18</sup>. This is based on the isotropic phosphorus h.f.c. obtained from liquid phase ESR work and theoretical predictions.

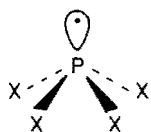


TBP-e

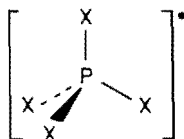


TBP-a

For example, using the unrestricted Hartree-Fock method within a 4-31 G basis set the optimized TBP-a structure of  $\dot{\text{P}}\text{H}_4$  is calculated to be about 15 kcal/mol above the optimized TBP-e form, while the  $C_{4v}$  square pyramidal (SP) structure with axial electron lies 34 kcal/mol above the TBP-e geometry<sup>19</sup>. Moreover, the tetrahedral ( $C_{3v}$ ) form is found 57.5 kcal/mol above the TBP-e form.



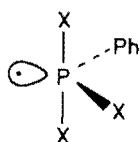
SP



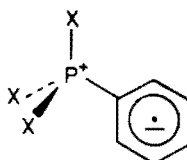
$C_{3v}$

In spite of the observation that phosphoranyl radicals in solution are non-rigid, showing ligand exchange, the analogy with the related phosphoranes has not been considered. It was not taken into account that phosphoranyl radicals with suitably chosen ligands or ring systems might adopt alternative structures. An indication that the ligands are responsible for the ultimate structure of the radical, was found in the ESR-spectra of phenylphosphor-

anyl radicals<sup>18, 20</sup>.



$\sigma$ -radical



$\pi$ -radical

In the case of X = H, MeS, F, Cl, OCH<sub>2</sub>CF<sub>3</sub> a TBP structure is formed ( $\sigma$ -radical), while in the absence of these ligands (X = OMe, NMe<sub>2</sub>) a delocalisation of the electron into the phenyl ligand is detected ( $\pi$ -radical) with the phosphorus adopting a tetrahedral configuration<sup>18</sup>.

Furthermore, the single crystal ESR study of Ph<sub>3</sub>P $\dot{C}$ l showed that its ESR parameters are totally in disagreement with a TBP-e structure, and a  $\sigma^*$ -C<sub>3v</sub> structure has been proposed, with the unpaired electron located in an anti-bonding P-Cl orbital<sup>21</sup>.

Therefore it became necessary to establish the various structures, that phosphoranyl radicals can adopt and the dynamic behaviour of these intermediates. The methods and underlying theories by which this has been achieved, are described in the following chapters.

#### 1.4 ESR of trapped radicals in solids

The spin Hamiltonian for a free radical in which one unpaired electron interacts with one nucleus is given by<sup>22</sup>:

$$\mathcal{H} = \beta \vec{H} \cdot \vec{g} \cdot \vec{S} + \vec{S} \cdot \vec{T} \cdot \vec{I} - g_N \beta_N \vec{H} \cdot \vec{I}$$

The hyperfine term consists of an isotropic part  $a \vec{S} \cdot \vec{I}$  arising from the Fermi contact interaction and an anisotropic part  $\vec{S} \cdot \vec{T} \cdot \vec{I}$  due to the electron-nuclear dipolar interaction. Since phosphorus centered radicals are concerned, which show relatively little g tensor anisotropy the simpler Hamiltonian is adopted:

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + \vec{S}\cdot\vec{T}\cdot\vec{I} - g_N\beta_N\vec{H}\cdot\vec{I}$$

in which  $g$  is a scalar.

The classical expression for the interaction of an electron moment and a nuclear moment is:

$$\mathcal{H}_{\text{dipolar}} = -g\beta g_N\beta_N \left\langle \frac{\vec{S}\cdot\vec{I}}{r^3} - \frac{3(\vec{S}\cdot\vec{r})(\vec{I}\cdot\vec{r})}{r^5} \right\rangle$$

where

$$\begin{aligned}\vec{S} &= S_x + S_y + S_z \\ \vec{I} &= I_x + I_y + I_z \\ \vec{r} &= x + y + z\end{aligned}$$

In matrix notation:

$$\mathcal{H}_{\text{dipolar}} = -g\beta g_N\beta_N \begin{bmatrix} S_x & S_y & S_z \end{bmatrix} \begin{bmatrix} \langle \frac{r^2-3x^2}{r^5} \rangle & \langle \frac{-3xy}{r^5} \rangle & \langle \frac{-3xz}{r^5} \rangle \\ \langle \frac{-3xy}{r^5} \rangle & \langle \frac{r^2-3y^2}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle \\ \langle \frac{-3xz}{r^5} \rangle & \langle \frac{-3yz}{r^5} \rangle & \langle \frac{r^2-3z^2}{r^5} \rangle \end{bmatrix} \begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix}$$

Abbreviated as  $\mathcal{H}_{\text{dip}} = \vec{S}\cdot\vec{T}'\cdot\vec{I}$

The condition for diagonalisation of  $\vec{T}'$  is:  $xy=yz=xz=0$ .

This is obtained by choosing  $\vec{r}$  along one of the coordinate axes. For an electron in a  $p_z$  orbital one obtains, by substituting  $x=r\sin\theta\cos\phi$ ,  $y=r\sin\theta\sin\phi$ ,  $z=r\cos\theta$  ( $\theta$  being the angle between the  $z$ -axis and the magnetic field direction).

$$\begin{aligned}
T'_{xx} &= -\frac{1}{2}g\beta g_N \beta_N \langle (3\cos^2\theta - 1)/r^3 \rangle \\
T'_{yy} &= -\frac{1}{2}g\beta g_N \beta_N \langle (3\cos^2\theta - 1)/r^3 \rangle \\
T'_{zz} &= g\beta g_N \beta_N \langle (3\cos^2\theta - 1)/r^3 \rangle
\end{aligned}$$

Integration over all possible angles for the radius vector to the electron in the  $p_z$  orbital, and then over all radii  $r$  results in:

$$\begin{aligned}
T'_{xx} &= -\frac{2}{5}g\beta g_N \beta_N \langle r^{-3} \rangle = -B_0 \\
T'_{yy} &= -\frac{2}{5}g\beta g_N \beta_N \langle r^{-3} \rangle = -B_0 \\
T'_{zz} &= \frac{4}{5}g\beta g_N \beta_N \langle r^{-3} \rangle = 2B_0
\end{aligned}$$

(The index  $(0)$  indicates that the unpaired spin density is 1 in the  $p$  orbital concerned). Therefore the dipolar contribution is largest and positive along the  $z$ -axis for an electron residing in a  $p_z$  orbital with the magnetic field along the  $z$ -axis. The complete interaction term  $\vec{S} \cdot \bar{\bar{T}} \cdot \vec{I}$  differs only by including the isotropic term  $a \cdot \vec{I} \cdot \vec{S}$ , so  $\bar{\bar{T}}$  is also diagonal in the chosen axis system with

$$\bar{\bar{T}} = \begin{pmatrix} a + T'_{xx} & & \\ & a + T'_{yy} & \\ & & a + T'_{zz} \end{pmatrix}$$

for an axially symmetric system.

It is noted that the dipolar tensor has zero trace so that  $T'_{xx} + T'_{yy} + T'_{zz}$  vanishes and  $a_{iso}$  is just the average of  $T'_{xx}$ ,  $T'_{yy}$ ,  $T'_{zz}$ .

For an electron in a  $3d_{z^2}$  orbital similar expressions can be derived<sup>23</sup>. In this case the trace of the dipolar tensor



$\bar{T}$  consists of:

$$\begin{aligned} T''_{xx} &= -\frac{2}{7}g\beta g_N \beta_N \langle r^{-3} \rangle \\ T''_{yy} &= -\frac{2}{7}g\beta g_N \beta_N \langle r^{-3} \rangle \\ T''_{zz} &= +\frac{4}{7}g\beta g_N \beta_N \langle r^{-3} \rangle \end{aligned}$$

which values are in the same order of magnitude as  $T'_{xx}$ ,  $T'_{yy}$  and  $T'_{zz}$ . Therefore discrimination between  $3p_z$  and  $3d_z^2$  orbital occupation in the phosphoranyl radicals is not possible and in this work the anisotropies observed for phosphorus will be considered to arise from  $3p$  contributions only.

For an unpaired electron residing in an  $s$  orbital on the nucleus the isotropic Fermi-contact contribution is expressed by:

$$a_0 = \frac{8\pi}{3}g\beta g_N \beta_N |\psi(0)|^2$$

where the index  $(0)$  indicates that the unpaired spin density is 1 in the  $s$  orbital concerned. Since the theoretical values of  $|\psi(0)|$  and  $\langle 1/r^3 \rangle$  are known from Hartree-Fock calculations, it is possible to calculate the isotropic coupling constant  $a_0$  and the anisotropic term  $B_0$  associated with respectively the  $ns$  and  $np$  orbital of each atom. (For  $^{31}\text{P}$ ,  $a_0 = 3640$  G,  $B_0 = 103$  G)<sup>24</sup>.

Experimentally, the principal values and directions of the hyperfine coupling are determined, i.e. the parallel h.f.c.  $a_{//}$  which is observed when the magnetic field is parallel with the orbital in which the unpaired electron is located, and the perpendicular h.f.c.  $a_{\perp}$ . From these principal values the isotropic h.f.c.  $a_{\text{iso}}$  and the anisotropic contribution  $B$  of the radical under investigation is calculated

$$\begin{aligned} a_{\text{iso}} &= \frac{1}{3}(a_{//} + 2a_{\perp}) \\ B &= \frac{1}{2}(a_{//} - a_{\text{iso}}) \end{aligned}$$

These values make it possible to give (after comparison with the atomic constants) an estimate of the s character:

$$\rho_s = a_{\text{iso}}/a_0$$

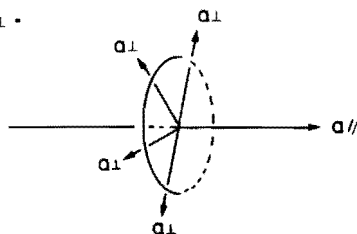
and the p character:

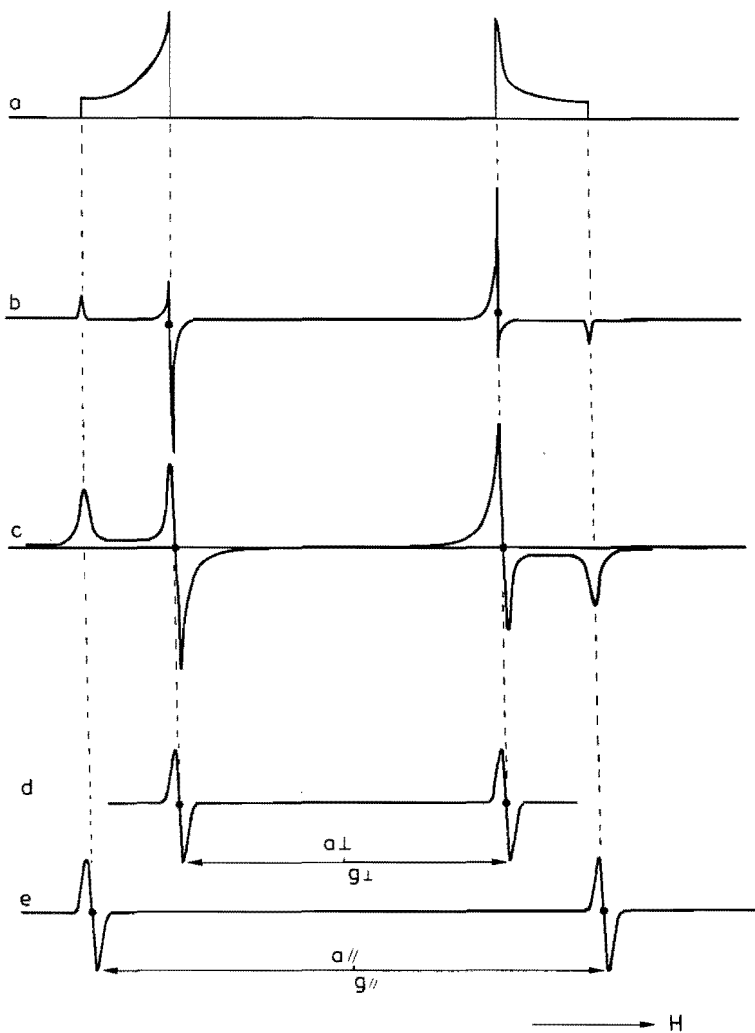
$$\rho_p = B/B_0$$

of the atomic orbital which contains the unpaired electron. Moreover, the direction of this orbital is obtained. From an oriented radical in a solid matrix (i.e. a single crystal) all the ESR parameters,  $a_{//}$ ,  $a_{\perp}$ ,  $g_{//}$  and  $g_{\perp}$  can be derived as well as their directions on rotation around suitably chosen axes. However, extracting the principal directions and values of  $a$  and  $g$  from measurements on a range of arbitrary orientations may be quite laborious. Fortunately, the ESR spectrum of a powdered sample contains also the anisotropic information, because this spectrum does not concern a motionally averaged system, but results from randomly oriented crystallites<sup>23</sup>. Since the  $a$ -value for any orientation is given by:

$$a^2 = a_{//}^2 \cos^2 \theta + a_{\perp}^2 \sin^2 \theta$$

for an axially symmetric system, where  $\theta$  is the angle between the  $a_{//}$  component and the applied field, absorptions will occur at all fields between those associated with  $a_{//}$  and  $a_{\perp}$  respectively. Because there are far more possible orientations of the crystallites that have the  $a_{\perp}$  axes aligned with the applied field than there are orientations that have the  $a_{//}$  axis aligned, the most intense absorption corresponds to  $a_{\perp}$ .





- a. Idealized absorption spectrum of powdered sample,  $S = \frac{1}{2}$ ,  $I = \frac{1}{2}$
- b. Idealized first derivative spectrum
- c. Powder ESR spectrum
- d. Single crystal ESR spectrum at  $\theta = 90^\circ$
- e. Single crystal ESR spectrum at  $\theta = 0^\circ$

This results in the following absorption spectrum which is converted into the first derivative spectrum. Therefore the powder ESR spectrum serves as a useful check on the validity of the parameters obtained from the ESR single crystal experiments. It is emphasized that the single crystal experiments are necessary to obtain the directional information. Moreover, rather complex ESR spectra may arise from powdered samples because of overlapping features generated by  $a_{//}$  and  $a_{\perp}$  and because of superimposed h.f.c. due to atoms linked to the central atom. In contrast, in single crystals the parallel and perpendicular features are separated on rotation.

On this basis a method of generating phosphorus centered radicals is chosen which consists in rupture of a labile P-H bond or electron addition at phosphorus initiated by X-irradiation or UV laser irradiation in a single crystal of which the molecular structure is known from X-ray diffraction analysis. Combination of the ESR directional information and the orientation of the molecules in the unit cell then provides a reliable determination of the structure of the radical.

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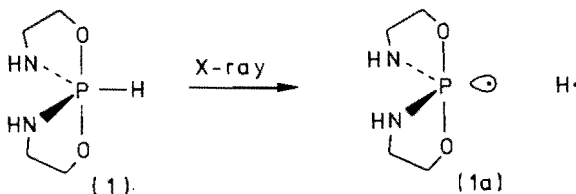
## CHAPTER II

### Phosphoranyl radicals in a trigonal bipyramidal configuration (TBP)

#### II.1 Phosphorus in a TBP structure with the unpaired electron located in an equatorial position (TBP-e)

1. The 1,6-dioxa-4,9-diaza-5-phospha<sup>(V)</sup> spiro[4.4]nonan-5-yl radical

Single crystals of 1,6-dioxa-4,9-diaza-5-phospha<sup>(V)</sup> spiro[4.4]nonane(1) which are grown by slow crystallization from anhydrous benzene, are monoclinic with space group C2/c and have a crystallographic twofold axis along the P-H bond<sup>1</sup>. In (1) the P atom is in a TBP configuration with the adjacent H and nitrogens in the equatorial positions. Four molecules are in a unit cell (fig. I)<sup>2</sup>. By means of the rotating crystal method<sup>3</sup> using CuK<sub>α</sub> radiation, the crystal needle axis was identified to be the crystallographic c-axis. The radical was generated by X-irradiation at room temperature. An X-irradiated crystal glued on a small quartz rod was studied in three planes, i.e. a\*b, bc and a\*c plane. The non-crystallographic a\*-axis is chosen perpendicular to the bc plane.



X-irradiation of (1) gives rise to the ESR spectra (fig.

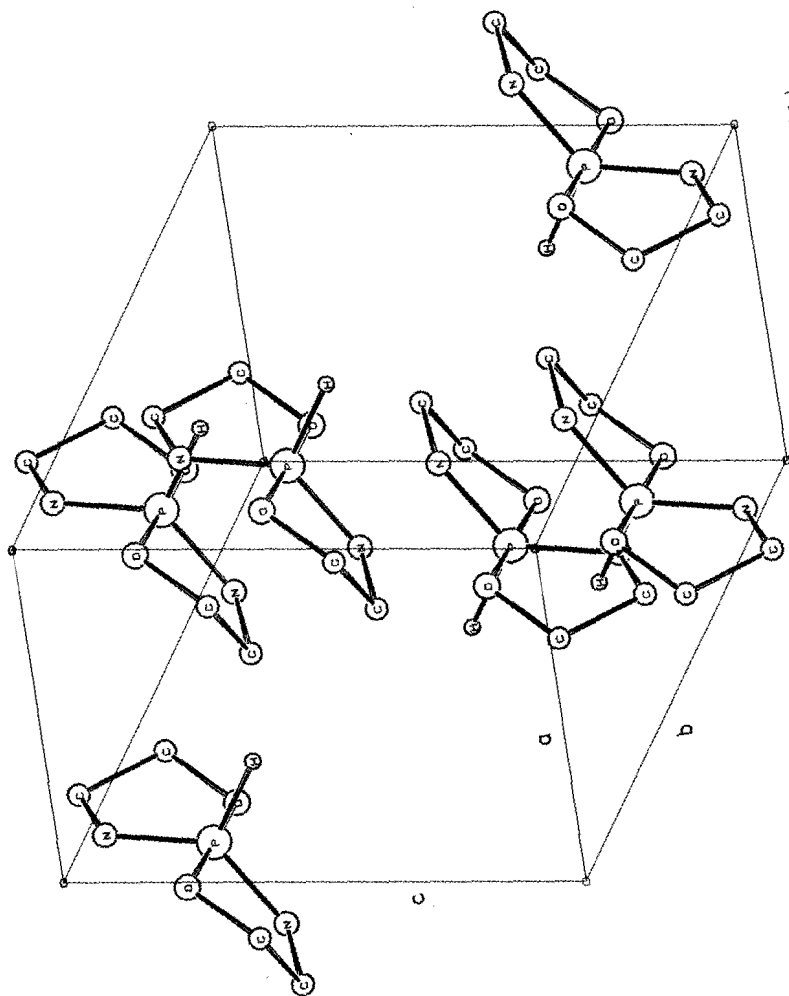


Fig. 1. ORTEP drawing of the unit cell of (1)



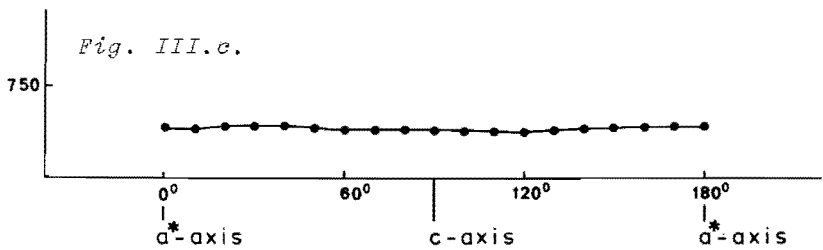
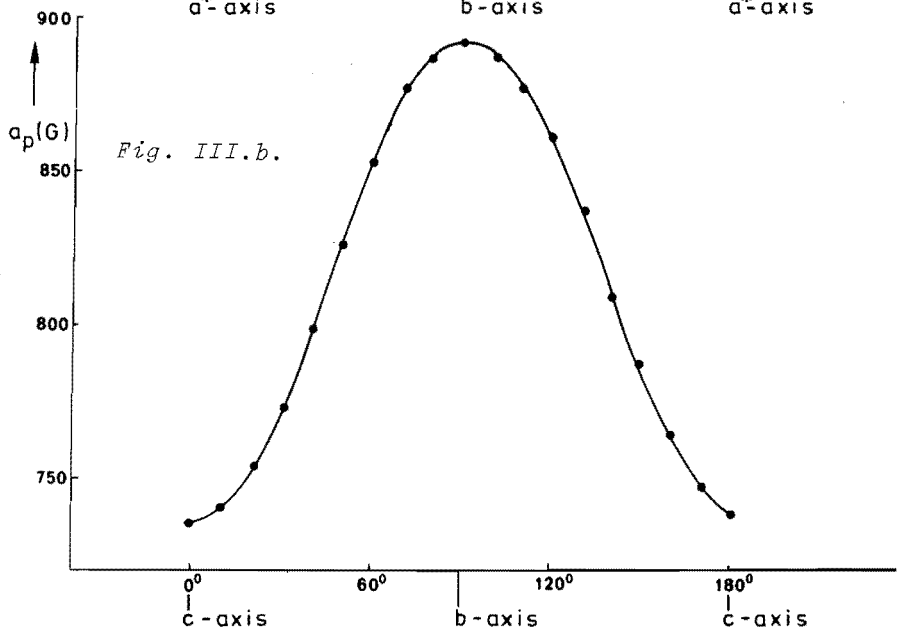
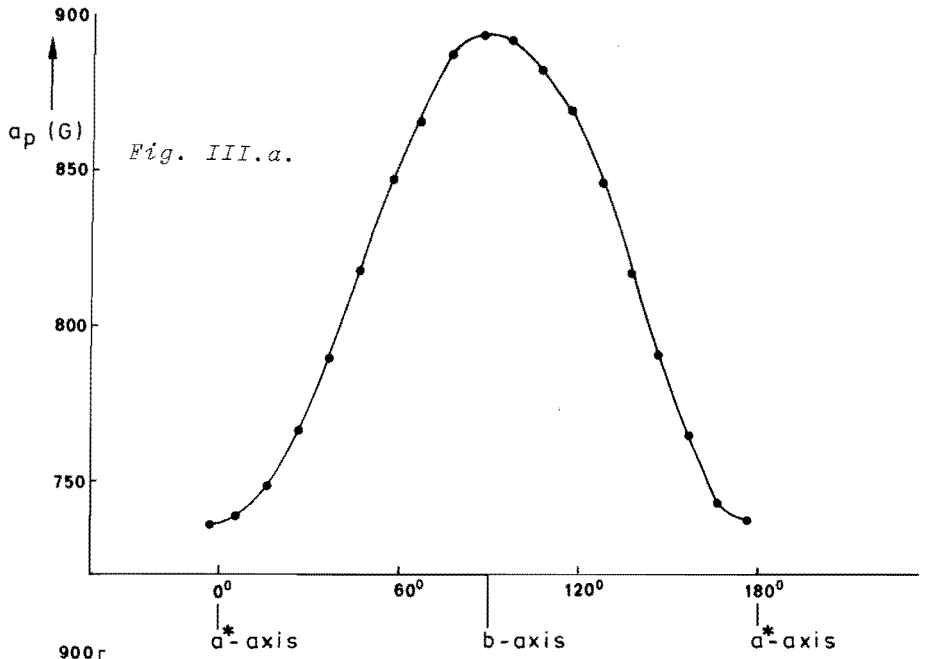


Fig. II. ESR spectra of (1a)

a. powder spectrum

b. spectrum of single crystal  $H_0 // c$ -axis

c. spectrum of single crystal  $H_0 // b$ -axis



II) ascribed to (1a): only one  $^{31}\text{P}$  doublet is observed, no additional couplings have been detected<sup>4</sup>. The angular variations are shown in figure III a,b,c.

Rotating the single crystal of (1) around the crystallographic c-axis reveals the maximum anisotropy  $a_{P//}$  to be perpendicular to this axis. Similarly for a rotation about the a\*-axis it was found that  $a_{P//}$  is perpendicular to this a\*-axis. This corresponds with the direction of the P-H linkage in its precursor as determined by X-ray diffraction analysis (fig. I). From figure II it is seen that the h.f.c. is axially symmetric. The same applies to the g-tensor:  $g_{//} = 1.988$  and  $g_{\perp} = 2.005$ . It was found that X-irradiation and UV laser irradiation ( $\lambda = 248$  nm) at 77 K of a powdered sample of (1) gives rise to the same radical. The parameters derived from the powder spectra agreed nicely with those obtained from the single crystal measurements, only the directional information is lacking. The orbital in which the unpaired electron resides, is directed along the initial P-H linkage. Obviously the radical (1a) is generated by P-H bond cleavage. Therefore the structure of (1a) has to be described as a nearly perfect TBP with the unpaired electron and the nitrogen ligands in the equatorial positions and the oxygen ligands in the apical positions. From the anisotropic values of the phosphorus h.f.c.  $a_{P//} = 893$  G,  $a_{P_{\perp}} = 735$  G, the  $a_{P\text{-iso}}$  is calculated<sup>5</sup> to be 788 G. These values indicate a P3s spin density ( $\rho_{3s}^P$ ) of 0.22, and a 3p spin density ( $\rho_{3p}^P$ ) of 0.49, resulting in a total spin density of 0.71 on phosphorus in an  $sp^2$  hybrid orbital. From the line width the  $^{14}\text{N}$  coupling was estimated to be less than 5 G. The remaining spin density is distributed over the apical oxygen ligands.

2. The 1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5-phospha<sup>(V)</sup> spiro [4.4]nona-2,7-dien-5-yl radical

Single crystals of 1,6-dioxa-4,9-diaza-2,3,7,8-dibenzo-5-phospha<sup>(V)</sup> spiro[4.4]nona-2,7-dien (2) were prepared by slow crystallization from anhydrous benzene<sup>1</sup>. Compound (2)

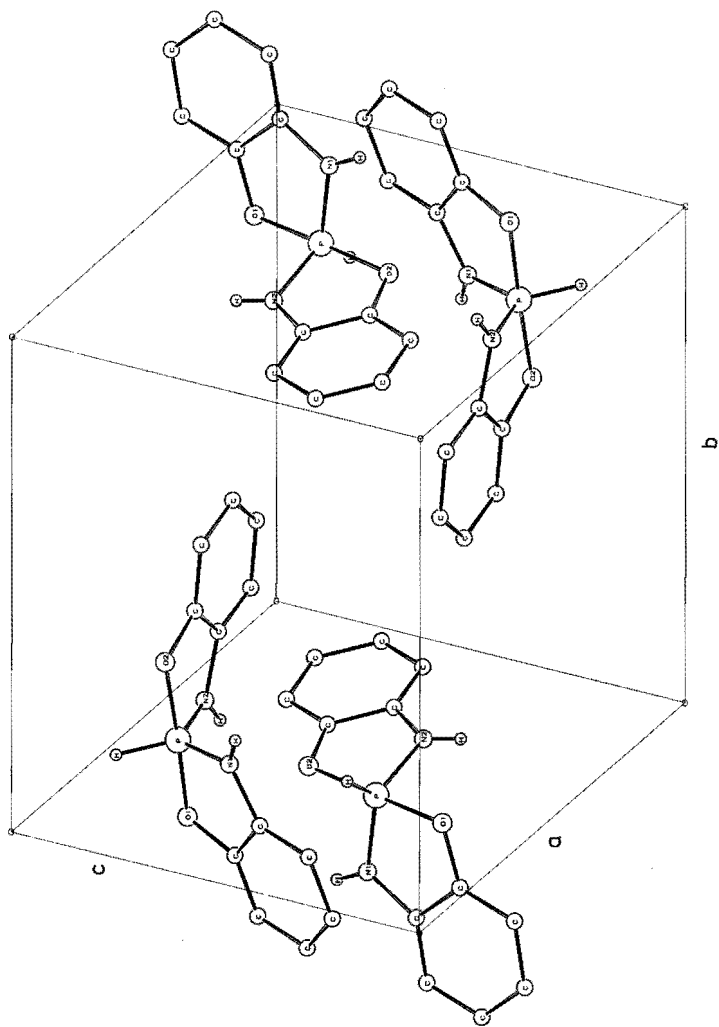
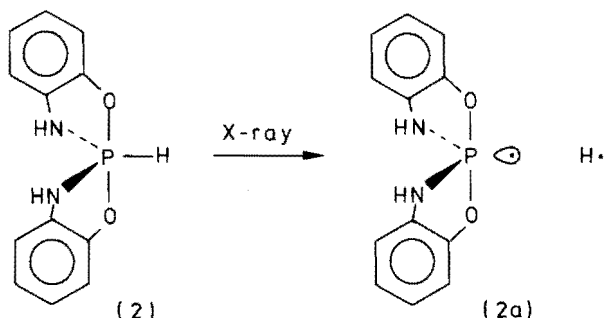


Fig. IV. ORTEP drawing of the unit cell of (2)

crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell (fig. IV)<sup>2</sup> and has an approximate twofold axis along the P-H bond. Using the rotating crystal method<sup>3</sup>, the c-axis was identified in the crystal. The radical was generated by X-irradiation at room temperature. In (2) phosphorus adopts a TBP structure with the adjacent hydrogen and the nitrogen atoms in the equatorial positions.



X-irradiation of (2) generates the phosphoranyl radical assigned to (2a)<sup>4</sup>. At least two sites are expected. The principal  $a_p$  values were easily obtained from an X-irradiated powdered sample. Rotating the crystal around the crystallographic c-axis only one site is observed as is shown in figure V. This is consistent with the crystal symmetry. From the maximum value of  $a_p$  obtained from figure V together with the  $a_{p\parallel}$  value derived from the powder spectrum (fig. VI) it is calculated that the angle between  $a_{p\parallel}$  and the crystallographic c-axis amounts  $35^\circ$ . This is in accordance with the angle of the P-H bond in the precursor with the c-axis, which has been determined to be  $36^\circ$ .

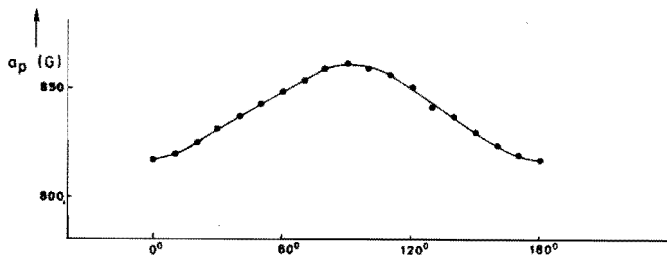


Fig. V. Rotation around the c-axis

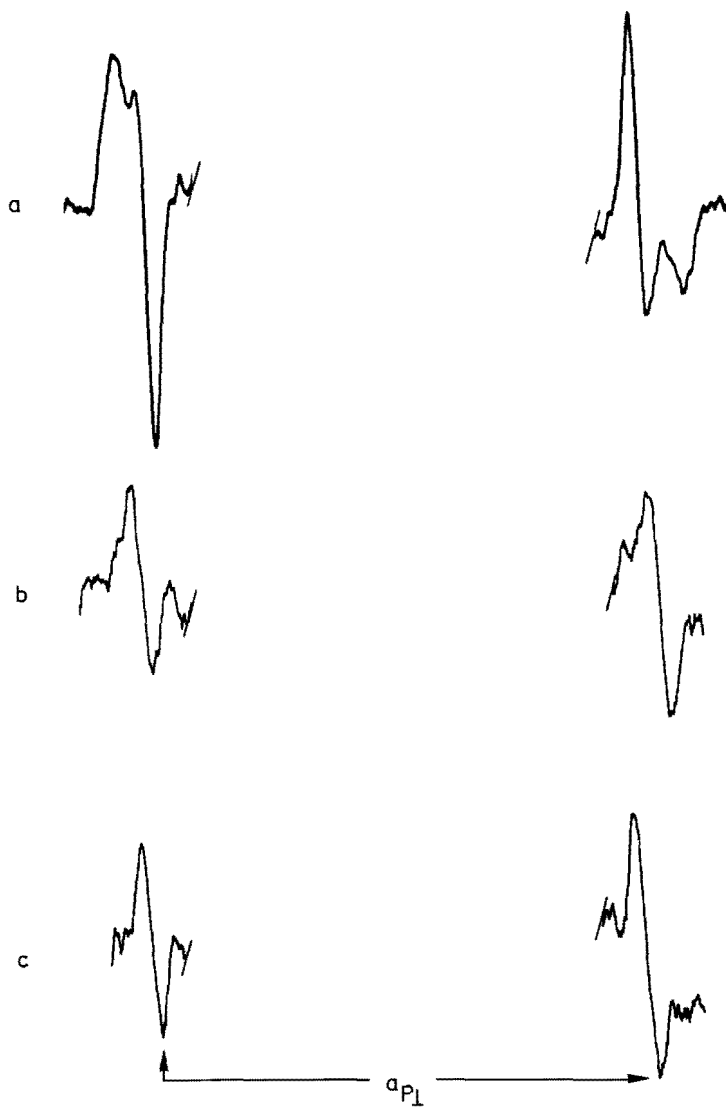


Fig. VI. ESR spectra of (2a)

a. powder spectrum

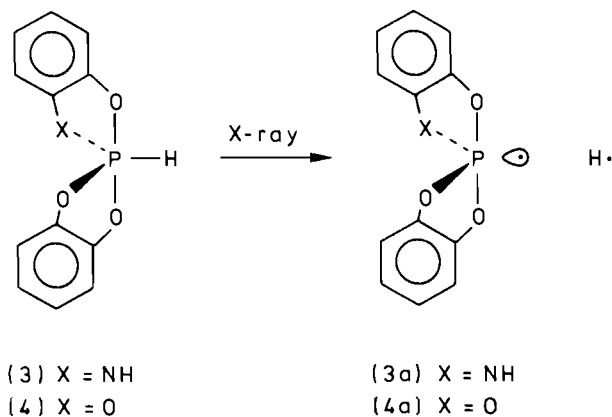
b. maximum  $a_P$  value on rotation around the c-axis

c.  $a_{P_1}$  (rotation around the c-axis)

In this radical the unpaired electron is directed along the initial P-H bond. Therefore (2a) possesses a TBP structure with the unpaired electron and the nitrogen atoms in equatorial positions, and the oxygens in apical positions. The axially symmetric  $^{31}\text{P}$  h.f.c.,  $a_{P_{\parallel}} = 960$  G,  $a_{P_{\perp}} = 808$  G, give  $a_{P\text{-iso}} = 859$  G and the anisotropy is 50 G. This indicates a  $\rho_{3s}^P = 0.24$  and  $\rho_{3p}^P = 0.47$ , resulting in 0.71 spin density on phosphorus in an  $sp^2$  orbital<sup>5</sup>. From the line width it was estimated that  $a_N < 5$  G (not resolved). The remaining spin density is distributed over the apical ligands. The  $g$  values are  $g_{\parallel} = 1.983$  and  $g_{\perp} = 2.008$ .

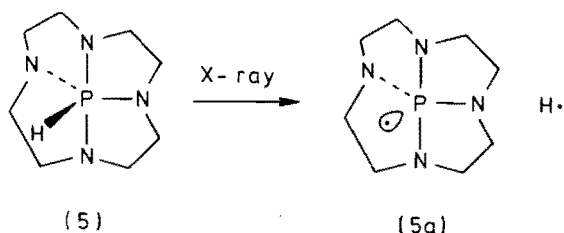
### 3. Analogous TBP-e structures

Analogous TBP-e structures were obtained for the following X-irradiated compounds, (3), (4), (5).



From X-ray diffraction analysis it is known that (3), (4) and (5) possess a nearly perfect TBP structure with the P-H bond located equatorially<sup>6,7</sup>. The  $a_P$  values of the TBP-e radical structures are compiled in the table. The structure of (5a) which will be described in detail in chapter IV because of its interesting dynamic behaviour, is also TBP-e and was studied both in powder and single crystal. Its  $^{31}\text{P}$  h.f.c. values are  $a_{P_{\parallel}} = 715$  G,  $a_{P_{\perp}} = 606$  G and h.f.c. of  $a_{N_{\parallel}} = 26.3$  G,  $a_{N_{\perp}} = 24.0$  G due to the two nitrogen atoms in the apical positions, while the equator-

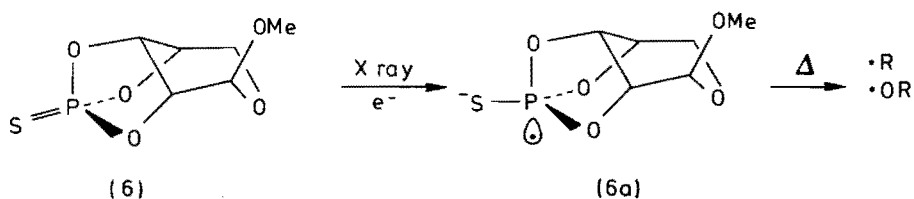
ial nitrogens did not have resolved h.f.c. (< 5 G from linewidth).



*II.2 Phosphorus in a TBP structure with the unpaired electron located in an apical position (TBP-a)*

The thiophosphate 0,0,0-triester of methyl- $\beta$ -D-ribose radical anion

Single crystals of the thiophosphate 0,0,0-triester of methyl- $\beta$ -D-ribose(6)<sup>8</sup> which are grown by slow crystallization from (diethyl) ether, are orthorhombic with space group  $P_{2_1}2_12_1$  with four molecules in a unit cell (fig. VII)<sup>2,9</sup>. Crystal alignment was performed by use of a polarization microscope. From the extinction curve<sup>10</sup> the directions of the crystallographic axes were obtained. These axes were easily identified by means of the rotating-crystal method<sup>3</sup>, using  $\text{CuK}_\alpha$  radiation. The radical was generated by X-irradiation at 77 K. Irradiated crystals, glued on a small quartz rod, were studied at 203 K on a Varian E-4 ESR spectrometer equipped with a single axis goniometer.



X-irradiation at 77 K of a single crystal of (6) gives rise to the ESR spectrum assigned to (6a)<sup>11</sup>. The other (central)



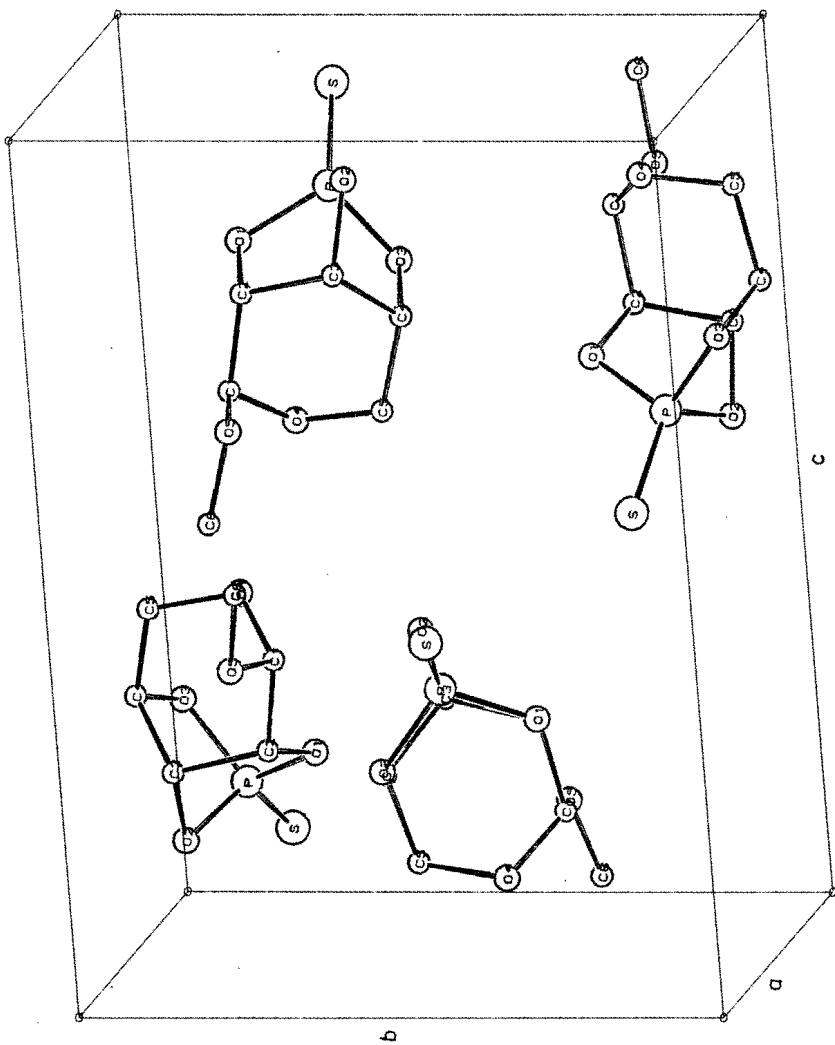


Fig. VII. ORTEP drawing of the unit cell of (6)

features, which are analogous to those reported for comparable sugar radicals<sup>12</sup>, are not analyzed here. The concentration of (6a) is increased by raising the temperature reaching an optimum at 203 K, while its ESR signal disappeared at about 243 K. The ESR spectrum of (6a) consists of two sets of  $^{31}\text{P}$  doublets (fig. VIII), each set possessing an additional  $^1\text{H}$  coupling.

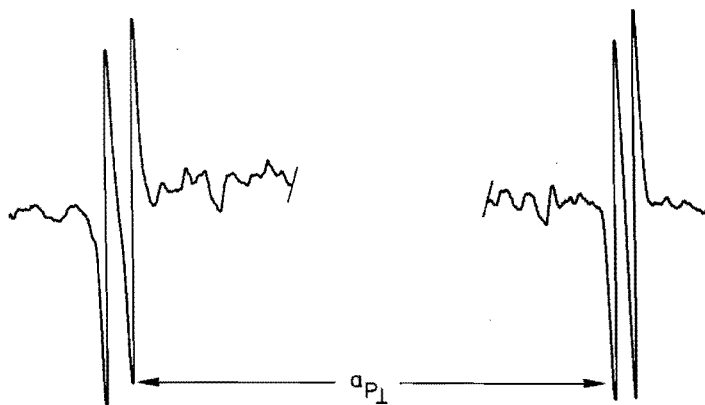


Fig. VIII. Single crystal ESR spectrum of (6a)  
 $\varphi = 30^\circ$  in the  $ab$  plane

The angular variations are shown in figure IXa and IXb. On rotation around the crystallographic  $c$ -axis two identical radicals with an angle between their  $a_{P_{\parallel}}$  components of  $60^\circ \pm 2$  are present (fig. IXa). Upon rotation around the crystallographic  $b$ -axis only one site was detected (fig. IXb). Furthermore, the  $a_p$  value obtained from fig. IXa along the crystallographic  $a$ -axis equals that found from fig. IXb along the same axis. From this it is concluded that the  $a_{P_{\parallel}}$  components of both sites are located in the  $ab$  plane.

The directions of the  $a_p$  components show a perfect fit with the stereo-projection of the unit cell along the  $c$ -axis upon the  $ab$  plane (fig. X). The projections of the  $\text{P-O}_2$  linkages in this plane make angles of  $56^\circ$ . Therefore

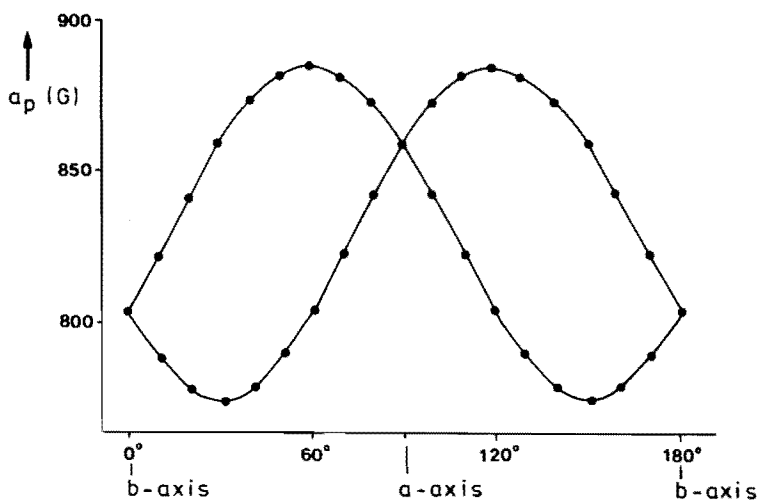


Fig. IX.a. Angular variation of  $a_p$  in the  $ab$  plane

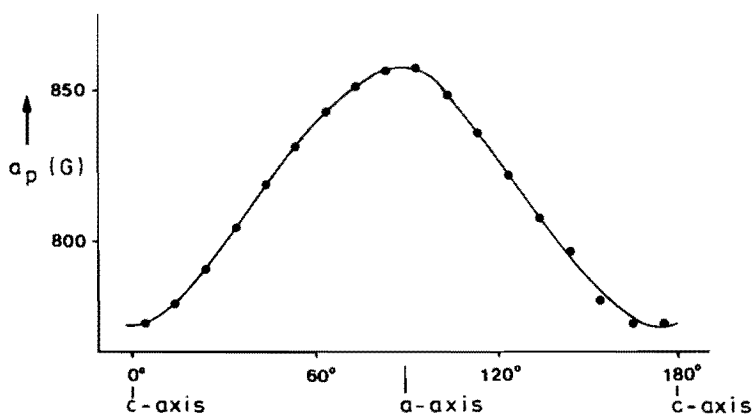
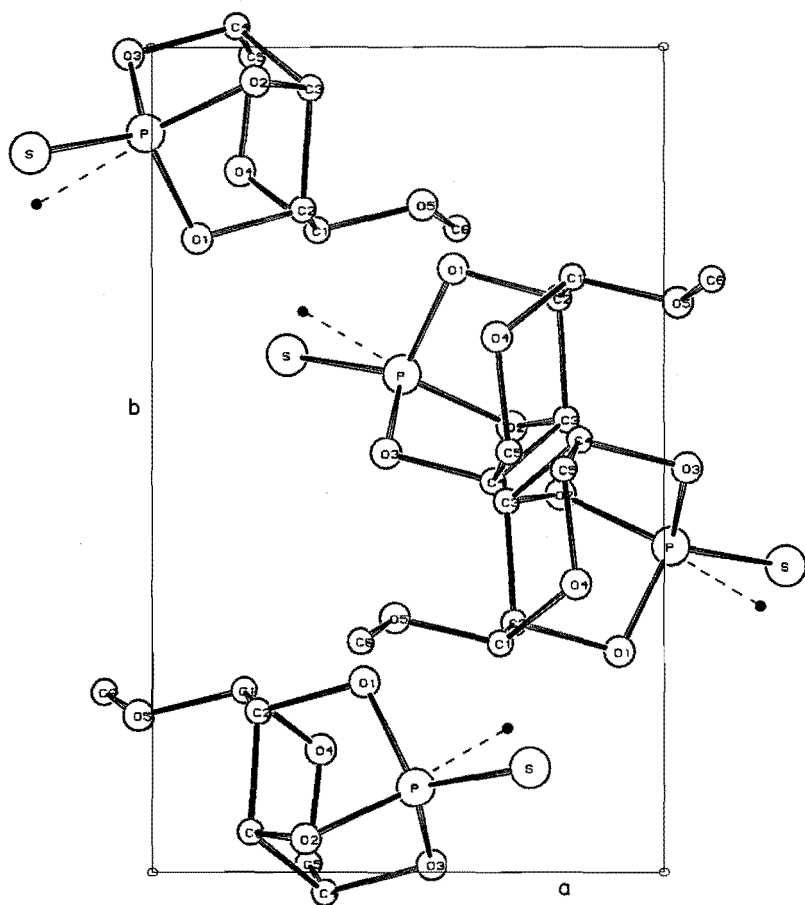


Fig. IX.b. Angular variation of  $a_p$  in the  $ac$  plane



*Fig. X. Projection of the unit cell of (6) along the c-axis, the location of the unpaired electron is indicated*

we indicate the direction of the  $a_{P//}$  components as shown in fig. X. Furthermore, the P-O<sub>2</sub> linkages make an angle of 108° (or supplementary) with the crystallographic c-axis. Thus the structure of (6a) has to be described as trigonal bipyramidal (TBP) with the O<sub>2</sub> oxygen ligand and the unpaired electron in the apical positions, the O<sub>2</sub>-P-· angle being 162°, while the O<sub>2</sub>-P-S angle probably will decrease from 121° to 90°. From the anisotropic values of the phosphorus hyperfine coupling constants,  $a_{P//} = 886$  G and  $a_{P\perp} = 776$  G, the  $a_{P-iso}$  is calculated<sup>5</sup> to be 813 G. These values indicate a  $\rho_{3S}^P$  of 0.22 and a  $\rho_{3P}^P$  of 0.35, resulting in a total spin density of 0.57 located on phosphorus in apical position. An additional hyperfine coupling of 5 G is due to the hydrogen in quasi-apical position C<sub>3</sub>-H. The remaining spin density is distributed over the equatorial ligands, O<sub>1</sub>, O<sub>3</sub> and S.

The ESR spectra described above are not attributed to a radical which is the result of rupture of the P-O<sub>2</sub> bond, i.e. a phosphonyl radical, on the basis of the  $a_P$  values of (6a); in the case of e.g. (MeO)<sub>2</sub> $\dot{P}O$  an  $a_{P-iso} = 700$  G has been observed<sup>13</sup>. Furthermore the h.f.c. due to one proton is difficult to match with such phosphonyl P<sup>IV</sup> radical. Two equivalent H splittings are expected in that case. Obviously, radical (6a) has been generated by electron capture at phosphorus. Its TBP structure will be stabilized by the two five-membered rings which span apical-equatorial positions, placing the six-membered ring diequatorially<sup>14</sup>. Electronically it is conceivable that the negative sulfur ligand favours the equatorial position in this rigid framework.

On warming, the ESR signal disappeared at -30°C indicating  $\alpha$  or  $\beta$  scission which processes are known to occur readily in P<sup>V</sup> radicals, giving rise to relatively stable alkyl and alkoxy radicals.

### II.3 TBP-e and TBP-a isomers

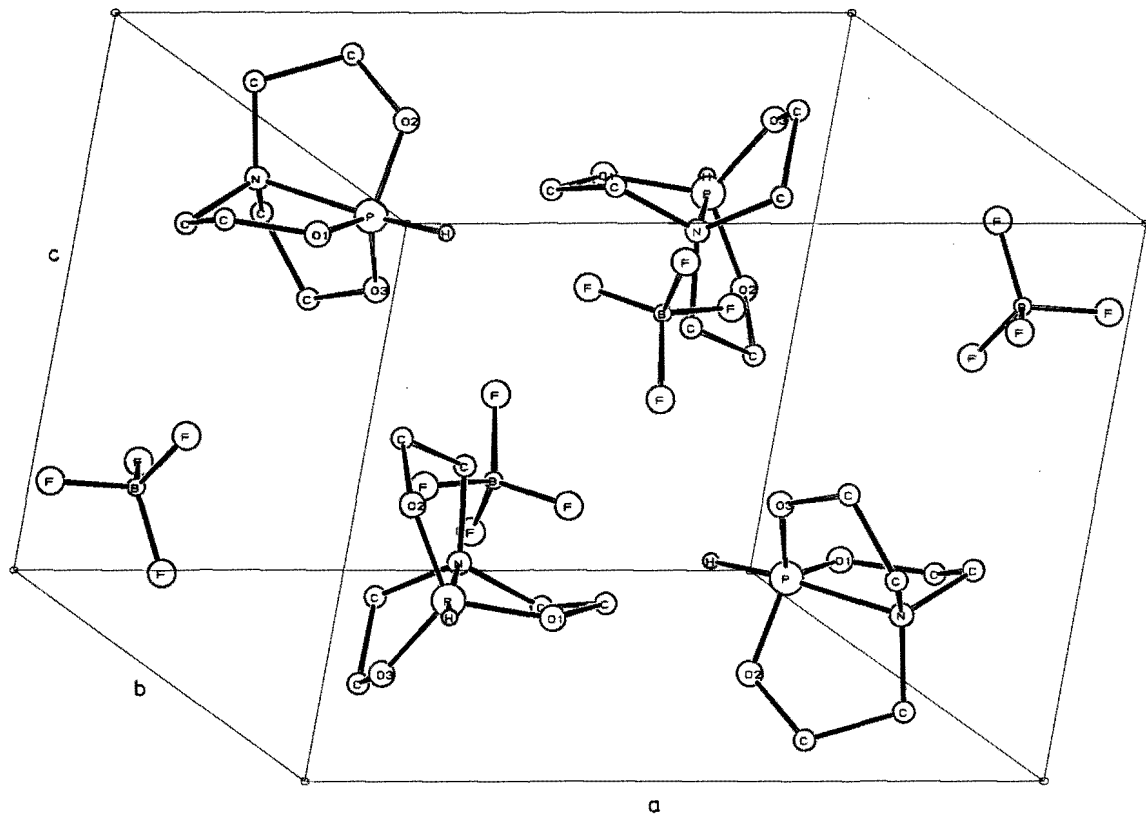
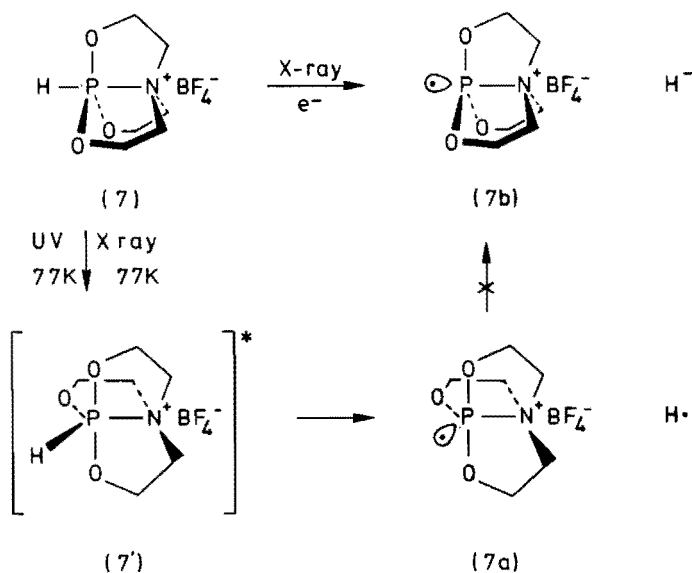


Fig. XI. ORTEP drawing of the unit cell of (7)

The  $\overline{\text{P}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\text{BF}_4^-}$  radical

A single crystal of  $\overline{\text{HP}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\text{BF}_4^-}$  (7) was grown by slow crystallization from anhydrous acetonitrile<sup>15,16</sup>. It crystallizes in the orthorhombic space group Pnam with four molecules in the unit cell (fig. XI)<sup>2</sup>. In (7) the P atom possesses a TBP configuration with nitrogen and the adjacent hydrogen in the apical positions as revealed by X-ray crystallography. Crystal alignment was performed by the Laue Back Reflection method using  $\text{CuK}\alpha$  radiation<sup>17</sup>. The irradiations were performed at 77 K on a crystal of  $\overline{\text{HP}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\text{BF}_4^-}$  either with X-ray or UV laser ( $\lambda = 193$  nm or 248 nm).



X-irradiation of a single crystal of (7) at 77 K yields the spectrum of (7a), with  $a_{P//} = 1120$  G,  $a_{P\perp} = 930$  G, while <sup>14</sup>N splitting is not resolved<sup>18</sup>. On rotation about the crystallographic c-axis two orientations are present with an angle between their  $a_{P//}$  components of  $70^\circ \pm 2$  (fig. XII). The angular variations of <sup>31</sup>P h.f.c. are shown in figure XIII. Raising the temperature, these signals start to disappear irreversibly at 193 K and those ascribed to (7b) become apparent. Again on rotation about the c-axis, two

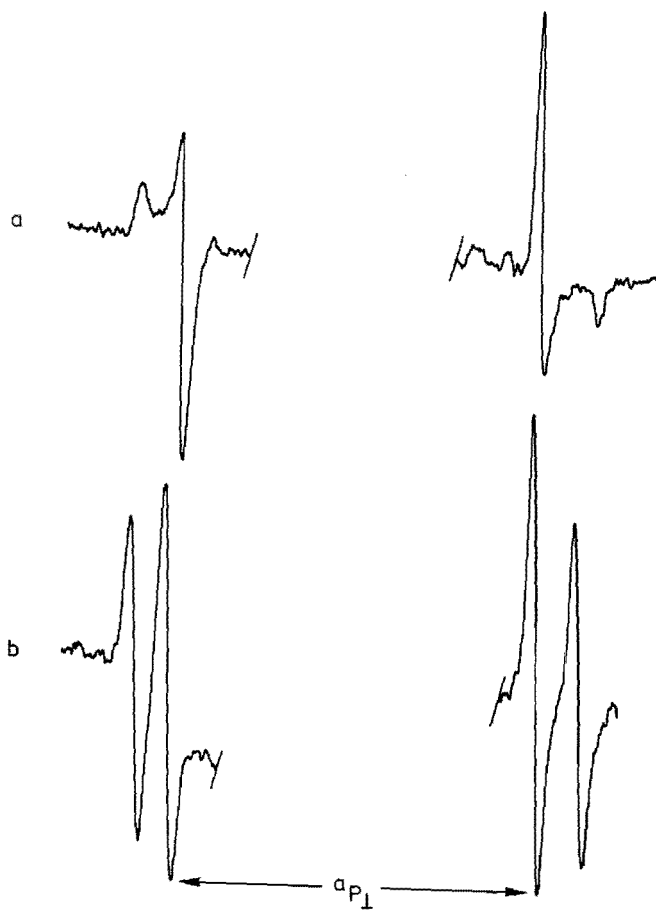


Fig. XII. ESR spectra of (7a)

a. powder spectrum

b. single crystal spectrum,  $\varphi = 30^\circ$  in the ab plane



identical radicals with an angle between their  $a_{P//}$  components of  $90^\circ \pm 2$  are present<sup>19</sup>. The occurrence of differently oriented radicals is consistent with the X-ray diffraction analysis results of precursor (7) which also show two orientations in the unit cell. By means of the Laue Back Reflection method it is shown that the  $a_{P//}$  of (7b) is oriented approximately along the initial P-H linkage, the N-P- angle being  $168^\circ$ . Furthermore one  $^{14}\text{N}$  h.f.c. is present. Because of severe overlap of the two sites the ESR spectra of the irradiated single crystal could only be analysed in the regions of maximum separation (fig. XIV). Nevertheless, on rotation about the c-axis the principal values of (7b) are obtained, as was checked by comparison with the powder ESR spectrum of (7b) (fig. XV).

In the plane perpendicular to the crystal mounting axis (c-axis), the directions of  $a_{P//}$  of (7b) and (7a) differ by  $35^\circ$  or the complementary angle of  $55^\circ$ , which cannot be assigned uniquely due to the presence of two orientations in the unit cell. Surprisingly, UV laser irradiation at 77 K of a crystal of (7) generates only radical (7a) without any trace of (7b) on warming. The direction of  $a_{P//}$  of (7b) is approximately along the P-N axis, the -P-N angle being  $168^\circ$ . Therefore it is concluded that radical (7b) possesses a TBP structure with the unpaired electron and nitrogen in the apical positions. The anisotropic  $^{31}\text{P}$  h.f.c.,  $a_{P//} = 888$  G,  $a_{P\perp} = 753$  G result in a spin density of 0.21 in the phosphorus 3s orbital and 0.43 in its 3p orbital, indicating that the unpaired electron resides in an  $sp^2$  orbital on phosphorus. The  $^{14}\text{N}$  h.f.c.,  $a_{N//} = 21.2$  G,  $a_{N\perp} = 22.7$  G with  $a_{N\text{-iso}} = 22.2$  G indicates<sup>5</sup> a spin density of 0.05 in the 2s orbital of nitrogen. The anisotropic contribution (0.5 G) can be attributed to dipole-dipole interaction. Apparently, the remaining spin density is distributed over the equatorial oxygen ligands. It is found that the directions of the  $a_{P//}$  components of (7b) and (7a) differ by  $35^\circ$  or  $55^\circ$ , both angles inferring a TBP-e geometry for (7a). Furthermore the  $a_p$  values of (7a) are consistent with those found for the closely re-

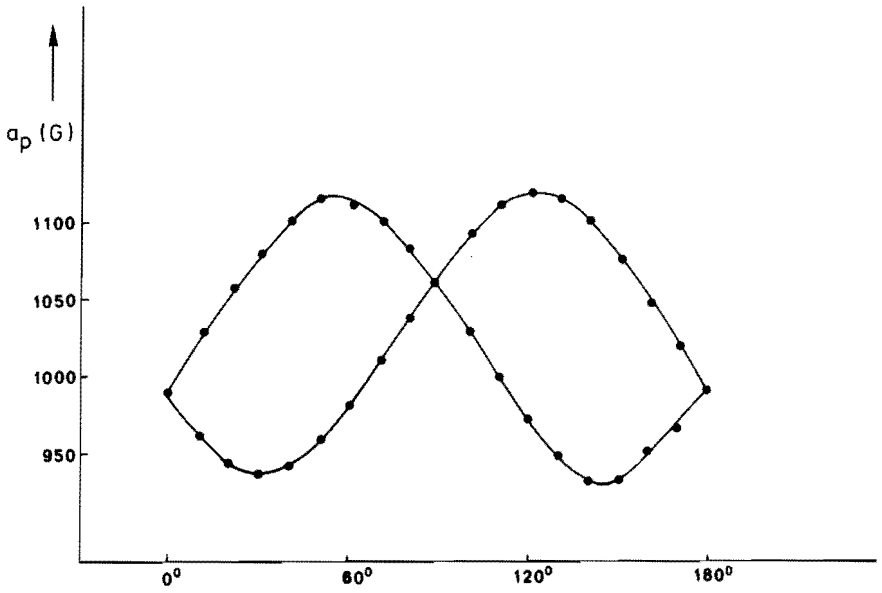


Fig. XIII. Rotation around the  $c$ -axis (7a)

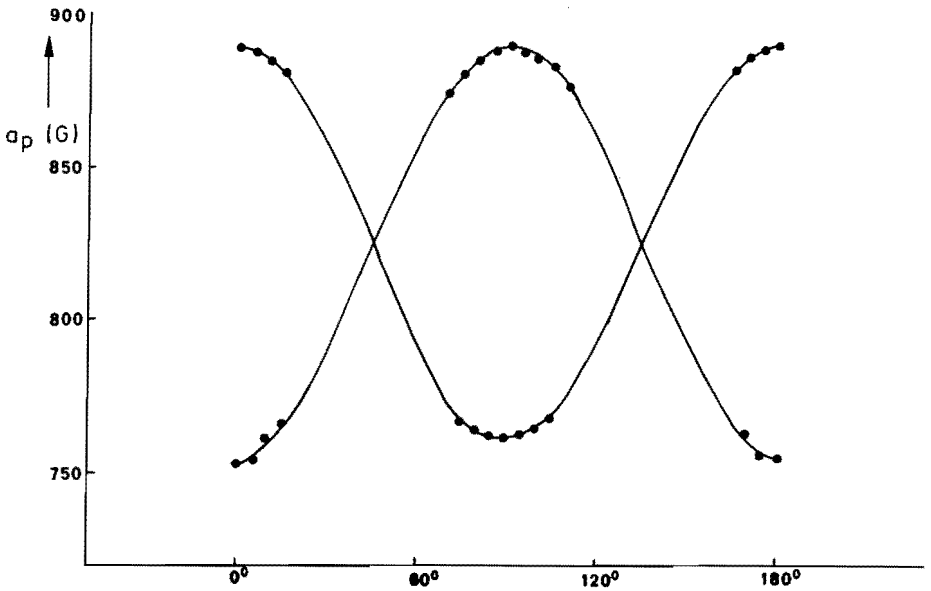


Fig. XIV. Rotation around the  $c$ -axis (7b)

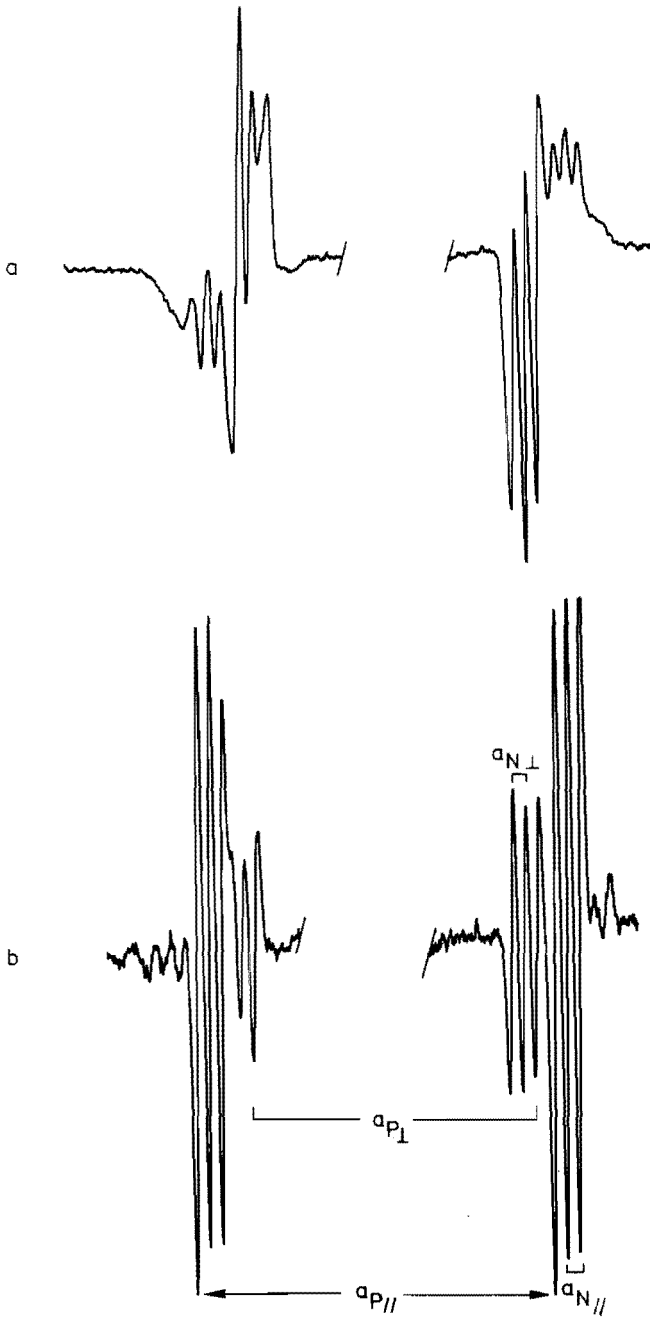


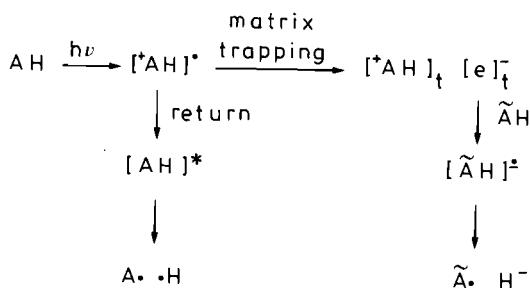
Fig. XV. ESR spectra of (7b)

a. powder spectrum

b. single crystal spectrum,  $\phi = 90^\circ$  in the ab plane

lated phosphoranyl radical (3a) generated by X-irradiation of (3) which is known to possess a nearby perfect TBP structure as revealed by X-ray diffraction analysis<sup>7</sup>. From the anisotropic <sup>31</sup>P h.f.c. values obtained for (7a) an  $a_{P-iso} = 993$  G is calculated<sup>5</sup>, indicating the  $\rho_{3s}^P$  is 0.27, while the anisotropic contribution places 0.61 of the spin density in the P3p orbital, which gives a total spin density of 0.88 on phosphorus.

It is generally accepted that the primary process resulting from the interaction of high energy quanta and a molecule, is the ejection of an inner electron. This electron can be trapped in the matrix, or may return to the parent cation<sup>5</sup>. The resulting molecule which is in a high vibrational groundstate will frequently have sufficient energy to undergo homolytic bond rupture. Furthermore, it is observed that the trapped electrons are mobilized on warming or by UV irradiation, giving rise to reaction with the medium or the substrate. Schematically:



The formation of (7a) and (7b) from irradiated (7) can be understood on the basis of this scheme. Primarily, compound (7) is ionized. Return of an electron generates a molecule which is in a high vibrational groundstate (7')\*. Subsequently (7')\* undergoes P-H bond cleavage with retention of configuration, producing (7a). Electronically, structure (7') with the hydrogen atom in equatorial position is favoured over (7) with the hydrogen atom in

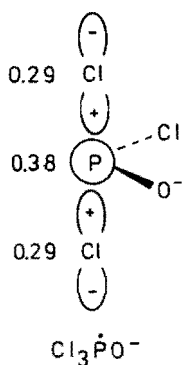
apical position. In contrast, the strain energy in structure (7') is enhanced with respect to that of (7). However, the latter factor may be less important in (7')\* since in this high vibrational groundstate the bond lengths are increased. Therefore, in (7')\* the electronic factor has become dominant. It appears that the concentration of (7a) increases on warming. Therefore, the return of an electron to the parent cation is a thermodynamically controlled process.

It is conceivable that trapped electrons attack (7) at higher temperature, generating a radical anion which produces (7b) by subsequent loss of  $H^-$  from the apical axis of the TBP. It has been confirmed that trapped electrons are involved in the formation of (7b) by an experiment in which compound (7) is X-irradiated at 77 K, showing (7a). Subsequently this sample is UV irradiated at 77 K which leads to loss of (7a). On warming the concentration of (7a) is increased, whereas radical (7b) does not show up at all. Obviously, UV irradiation delocalizes the trapped electrons which attack both (7a) leading to a diamagnetic product, and (7), resulting in (7b). However, in this experiment (7b) is not detected, simply because this radical is lost upon UV irradiation as was proven independently.

It is concluded that homolytic P-H bond rupture is favoured in an equatorial position of the TBP, whereas this process is inhibited in an apical position. In contrast, loss of  $H^-$  takes place in an apical position preferentially.

## II.4 Discussion

The single crystal ESR study of (1a) and (2a) in combination with the X-ray diffraction results of the precursor establishes unequivocally that the orbital the unpaired electron resides in, is directed along the initial P-H linkage. As a consequence the unpaired electron is characterized as a real ligand in the TBP-e structure. The TBP-e structure obtained here is in sharp contrast with the structure assumed for  $\text{Cl}_3\dot{\text{P}}\text{O}^-$  which was obtained by  $\gamma$ -irradiation of a single crystal of  $\text{Cl}_3\text{PO}$  <sup>21</sup>. Surprisingly, an isotropic  $^{31}\text{P}$  h.f.c. was observed and two anisotropic large equivalent chlorine h.f.c. together with one small chlorine h.f.c. A TBP structure was proposed with the unpaired electron residing in the Cl-P-Cl apical axis because of the relatively large spin density in the two equivalent chlorines and the isotropic  $^{31}\text{P}$  h.f.c.



This model has been accepted as representative for phosphoranyl radicals in general. However, in view of the results obtained here for (1a) and (2a) the interpretation of the  $\text{Cl}_3\dot{\text{P}}\text{O}^-$  radical has to be revised basically (chapter IV). The TBP-e structure of (1a) and (2a) is in agreement with that assigned to  $\dot{\text{P}}\text{F}_4$  in a  $\gamma$ -irradiated single crystal of  $\text{PF}_3$  <sup>22</sup>. Its anisotropic ESR spectrum showed h.f.c. due to one  $^{31}\text{P}$  nucleus, two large equivalent fluorine h.f.c. with principal directions perpendicular to  $^{31}\text{P}$  principal

values, and two small fluorine h.f.c. From this a TBP-e structure is deduced tentatively with the unpaired electron and the two fluorines with small h.f.c. located equatorially, and the other two fluorines in the apical positions. In this case the assignment has been based totally on the directions and magnitudes of the h.f.c. However, since the radical was produced by addition of  $\dot{\text{F}}$  to  $\text{PF}_3$  no correlation could be made between the ESR parameters and X-ray analysis. From the single crystal ESR studies of (6a) and (7b) it is evident that the TBP-a and TBP-e structures exhibit very similar ESR parameters. In fact, the structures could only be assigned unambiguously because of the availability of the X-ray diffraction results. Consequently reliable structural information regarding phosphoranyl radicals can only be obtained by the methods outlined here, unless phosphorus bears only ligands which have a magnetic moment. Therefore, much of the earlier work on phosphoranyl radicals needs reinvestigation, because invariably in these cases a TBP-e structure is assigned in which the unpaired electron occupies an equatorial position<sup>23</sup>. This structure seems to be supported by the p/s ratio of approximately 2 which is frequently observed. However, in spite of similar spectral data for (6a) and (7b) these compounds show a quite different (TBP-a) geometry, probably as a result of the molecular and crystal constraints.

The  $\text{C}_{3v}$  structure observed for (6a, 7b) has also been found for  $\text{Ph}_3\dot{\text{P}}\text{Cl}$ <sup>24</sup>. In contrast, in this case the electron spin density is assumed to reside in the P-Cl anti-bonding ( $\sigma^*$ ) orbital as inferred from the fact that the principal directions of  $a_p$  and  $a_{\text{Cl}}$  are nearly parallel and from the high spin density on chlorine. However, similar spin densities on the apical ligands adjacent to phosphorus have been observed for TBP-e structures (e.g.  $\dot{\text{P}}\text{F}_4$ ) also, and as a consequence this argument does not support the  $\sigma^*$  structure at all. It is pointed out that this  $\sigma^*$  model which concerns the excited state of the radical, should be less stable than the TBP-a structure which deals with a

non-excited state of the phosphoranyl radical. Moreover, since we demonstrated the ligand character of the unpaired electron in these radicals, the TBP-a structure applies very well to the  $\text{Ph}_3\dot{\text{P}}\text{Cl}$  radical reconciling the directional data excellently. As a matter of fact both isomers TBP-a and TBP-e are detected in one precursor (7) affording a direct comparison of both types (7a), (7b). It appears that the  $a_{\text{P-iso}}$  of the TBP-a species is smaller than that obtained for the TBP-e type. This indicates that the 3s contribution in bonding in the apical axis is reduced compared with the equatorial sites. A similar trend is found for the analogous phosphoranes. However, the s contribution is still so large, that structure assignment purely on the basis of  $a_{\text{P}}$  value without knowledge of the direction of the orbital the unpaired electron resides in, remains questionable.



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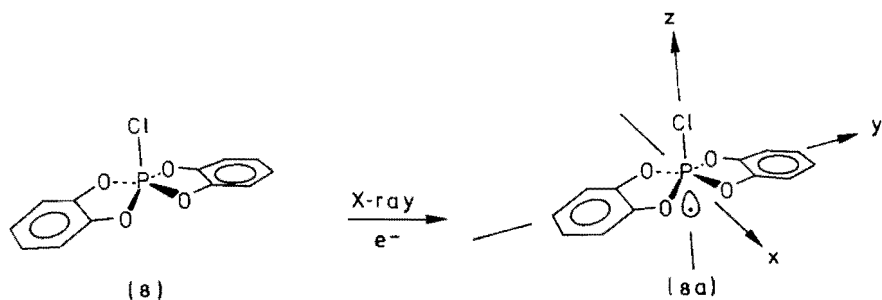
## CHAPTER III

### Phosphoranyl radicals in an octahedral configuration

#### III.1 Phosphorus in an octahedral $P^{VI}$ geometry with the unpaired electron in axial position

The 2-chloro-2,2'-spirobis(1,3,2-benzodioxaphosphol)-2-yl radical anion

A single crystal of 2-chloro-2,2'-spirobis(1,3,2-benzodioxaphosphole)<sup>1</sup> (8) was grown by slow crystallization from a mixture of benzene-hexane. It crystallizes in the monoclinic space group  $P2_1/n$  with four molecules in the unit cell (fig. XVI)<sup>2</sup> and has a non-crystallographic twofold axis along the P-Cl bond. Its structure is nearly square pyramidal with chlorine in the axial position. By means of the rotating crystal<sup>3</sup> method the crystallographic a-axis has been identified, using  $CuK_{\alpha}$  radiation. The radical was generated by X-irradiation at room temperature.



X-irradiation of (8) at room temperature gives rise to the ESR spectrum of radical (8a)<sup>4</sup>. On rotation of the crystal around the crystallographic a-axis, only one site is detected (fig. XVII). The angular variation of the  $^{31}P$  and  $^{35}Cl$  h.f.c. are shown in fig. XVIII. The ESR spectra show the maximum anisotropy of  $^{31}P$ ,  $a_{P//}$  to be perpendicular to this axis, indicating that the radical x-axis coincides

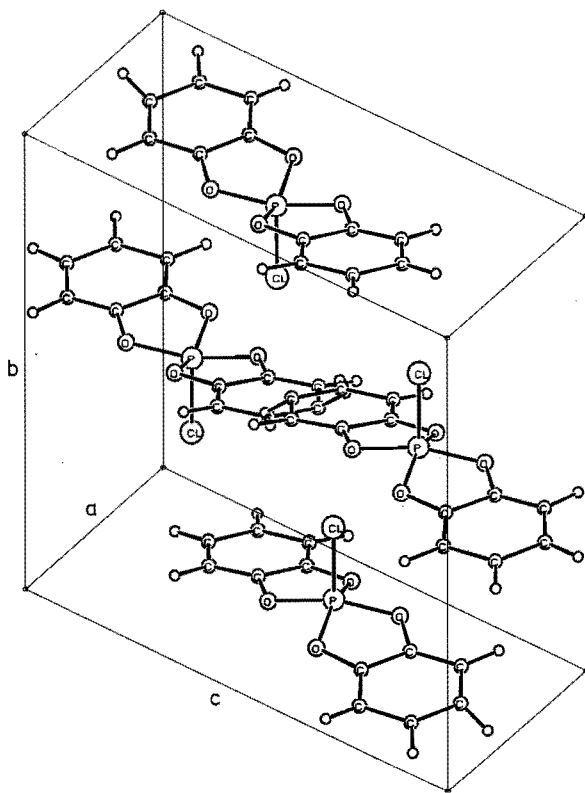


Fig. XVI. ORTEP drawing of the unit cell of (8)

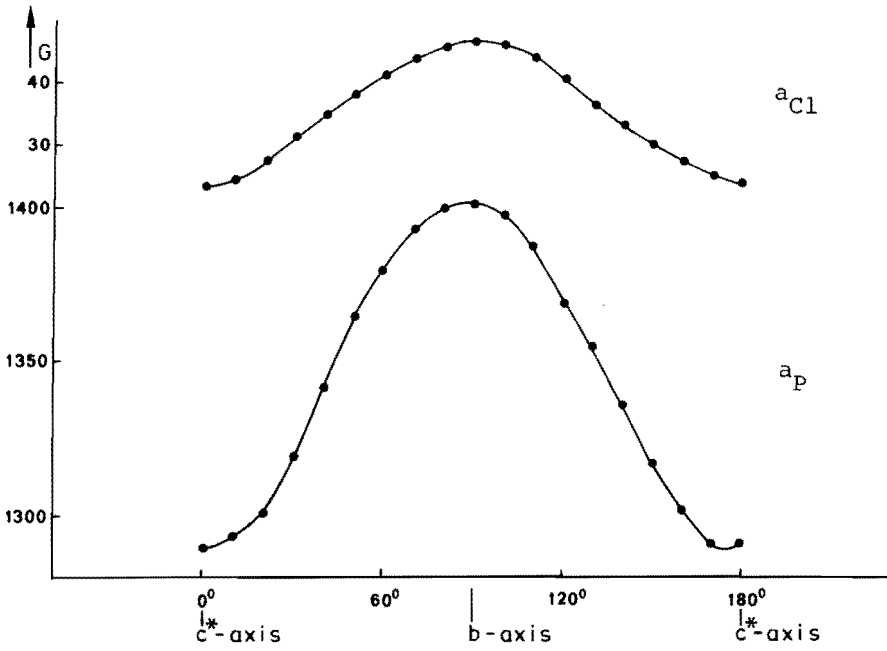


Fig. XVIII. Angular variations of  $a_{Cl}$  and  $a_P$ :  
rotation around the a-axis

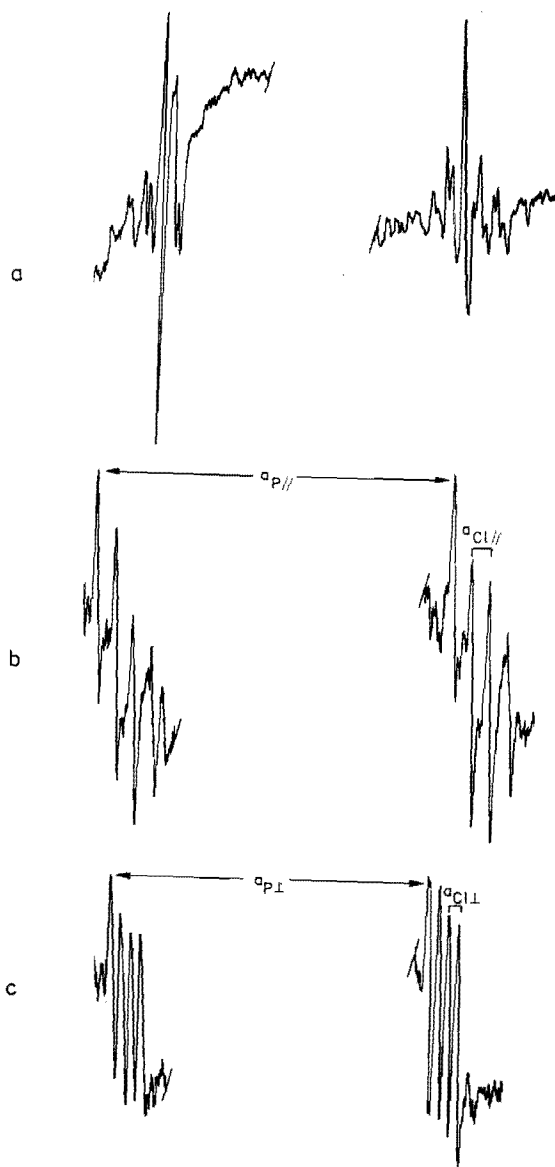


Fig. XVII. ESR spectra of (8a)

a. powder spectrum

b. single crystal spectrum,  $H_0 \parallel b$ -axis

c. single crystal spectrum,  $H_0 \parallel c$ -axis

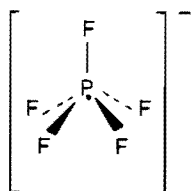
with the crystallographic a-axis. Furthermore the maximum in the anisotropy of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  appears to be parallel with  $a_{\text{P//}}$ , indicating that the direction of  $a_{\text{P//}}$  corresponds with the orientation of the P-Cl linkage, which is the crystallographic b-axis in its precursor. From the ESR spectrum of a powdered sample the principal values of  $a_{\text{P}}$  and  $a_{\text{Cl}}$  were obtained.

From this it is concluded that radical (8) has been generated by electron capture rather than by rupture of the P-O linkage. In the latter case the  $a_{\text{Cl//}}$  and  $a_{\text{P//}}$  directions should have been expected to be perpendicular. From the ESR data it is derived that  $a_{\text{P-iso}} = 1317$  G, indicating a phosphorus 3s spin density of 0.36. A spin density of 0.40 is located in the phosphorus  $3p_z$  orbital as inferred from the anisotropy of  $a_{\text{P}}$ . This results in a total spin density of 0.76 on phosphorus. From the  $^{35}\text{Cl}$  h.f.c. one calculates  $a_{\text{Cl-iso}} = 31$  G, indicating<sup>5</sup> a 3s spin density of 0.02, while the anisotropic contribution (B) accounts for a spin density of 0.16 in a chlorine  $3p_z$  orbital which is directed along the P-Cl linkage. Similar spin densities are obtained from the  $^{37}\text{Cl}$  tensor. Therefore, the structure of (8a) is described as  $\text{C}_{4v}$  with 76% of the unpaired electron located in an axial  $sp_z$  hybrid orbital at the phosphorus nucleus and 16% in the  $3p_z$  of chlorine.

### III.2 Discussion

The  $\text{P}^{\text{VI}}$  structure derived for (8a) has been assigned previously to  $\dot{\text{P}}\text{F}_5^-$ , obtained by  $\gamma$ -irradiation of hexafluorophosphate<sup>6,7</sup>. Its history is rather curious since for many years this radical centre was thought to be  $\dot{\text{P}}\text{F}_4$ , which was assumed to rotate rapidly in the solid matrix, accounting for the existence of four equivalent anisotropic fluorines ( $a_{\text{F-iso}} = 196$  G) and the isotropic  $^{31}\text{P}$  h.f.c. ( $a_{\text{P-iso}} = 1346$  G)<sup>8</sup>. These values are close to those obtained for the single crystal of irradiated  $\text{PF}_3$  with anisotropic fluorines,  $a_{\text{F-iso}} = 306$  G (2F apical),  $a_{\text{F-iso}} = 61$  G (2F equatorial) and an anisotropic  $^{31}\text{P}$  h.f.c. ( $a_{\text{P-iso}} = 1310$  G), assigned

to  $\dot{\text{P}}\text{F}_4$  in a TBP-e structure<sup>9</sup>. However, on the basis of a near zero h.f.c. ascribed to a fifth fluorine ligand<sup>6</sup>, it was suggested that the radical centre in irradiated hexafluorophosphate should be  $\dot{\text{P}}\text{F}_5^-$  instead of  $\dot{\text{P}}\text{F}_4$ .



Furthermore it is believed that the fifth ligand in such  $\text{C}_{4v}$  geometries, e.g.  $\dot{\text{P}}\text{F}_5^-$ ,  $\dot{\text{S}}\text{F}_5^-$ ,  $\dot{\text{As}}\text{F}_5^-$  and  $\dot{\text{PCl}}_5^-$ , possesses an almost zero h.f.c. as a general rule<sup>7,10,11</sup>. However, the  $\text{Cl}\dot{\text{P}}(\text{O}_2\text{C}_6\text{H}_4)_2^-$  radical anion (8a) has been proven to possess a similar  $\text{C}_{4v}$  symmetry in which the odd electron and chlorine are located in axial positions, the chlorine having a rather large h.f.c. which is comparable to those found for apical chlorine in  $\text{P}^{\text{V}}$  phosphoranyl radicals<sup>12</sup>. Therefore it is suggested that the small coupling detected for the " $\dot{\text{P}}\text{F}_5^-$ " radical<sup>6</sup> is due to a neighbouring fluorine in the solid matrix, as was also the case in TBP-e  $\dot{\text{P}}\text{F}_4$ <sup>9</sup>. Also the fact that the phosphorus h.f.c. of the TBP-e  $\dot{\text{P}}\text{F}_4$  radical and that for the assumed  $\dot{\text{P}}\text{F}_5^-$  structure are almost identical, in spite of the higher coordination of the latter is indicative for a  $\text{P}^{\text{V}}$  phosphoranyl radical. Compared to  $\dot{\text{P}}(\text{O}_2\text{C}_6\text{H}_4)_2$  (4a) which has a TBP-e  $\text{P}^{\text{V}}$  structure with  $a_{\text{P-iso}} = 1005$  G, the introduction of one chlorine ligand raises the  $a_{\text{P-iso}}$  to 1317 G. On this basis the  $\dot{\text{P}}\text{F}_5^-$  radical becomes unbelievable, and here it is suggested that there are two possibilities, i.e. the centre is pseudo-rotating TBP-e  $\dot{\text{P}}\text{F}_4$ , or it is  $\dot{\text{P}}\text{F}_4$  with a square pyramidal structure (chapter IV)<sup>13</sup>.



*References and notes*

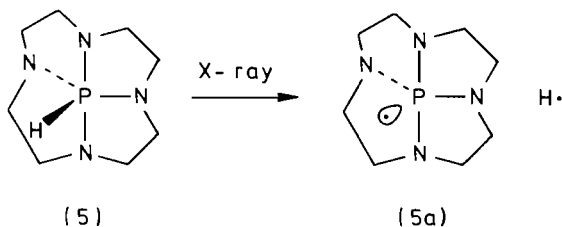
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# CHAPTER IV

## Intramolecular ligand reorganisation in phosphoranyl radicals

### IV.1 Pseudo-rotating TBP-e

The octahydro-2a,4a,6a,8a-tetra-aza-8b-phospha<sup>(V)</sup>pentaleno [1,6-cd] pentalen-8b-yl radical  
 Single crystals of octahydro-2a,4a,6a,8a-tetra-aza-8b-phospha<sup>(V)</sup>pentaleno [1,6-cd]pentalen(5)<sup>1</sup> were grown by slow crystallization from acetonitrile/hexane 1:1. The structure of (5) is TBP as revealed by X-ray diffraction analysis<sup>2</sup>. The radical was generated by X-irradiation at room temperature and studied between 295 K and 258 K. Below 253 K the single crystal became polycrystalline. Powder samples were UV or X-irradiated at 77 K and studied between 77 K and 295 K.



X-irradiation or UV irradiation (248 nm) of a powdered sample of (5) at 77 K generates the free hydrogen radical  $\text{H}\cdot$  ( $a_{\text{H}} = 509 \text{ G}$ )<sup>3</sup>. On annealing to 200 K a phosphoranyl radical is detected with  $a_{\text{P}\parallel} = 715$ ,  $a_{\text{P}\perp} = 606 \text{ G}$  and additional hyperfine coupling  $a_{\text{N}\parallel} = 26.3$ ,  $a_{\text{N}\perp} = 24.0 \text{ G}$  due to two nitrogen atoms. From these values one calculates<sup>4</sup> an  $a_{\text{P-iso}}$  of 642 G which indicates a phosphorus 3s spin density of 0.18, and a 3p spin density of 0.35, giving a total spin density of 0.53 on phosphorus. The nearly isotropic  $^{14}\text{N}$

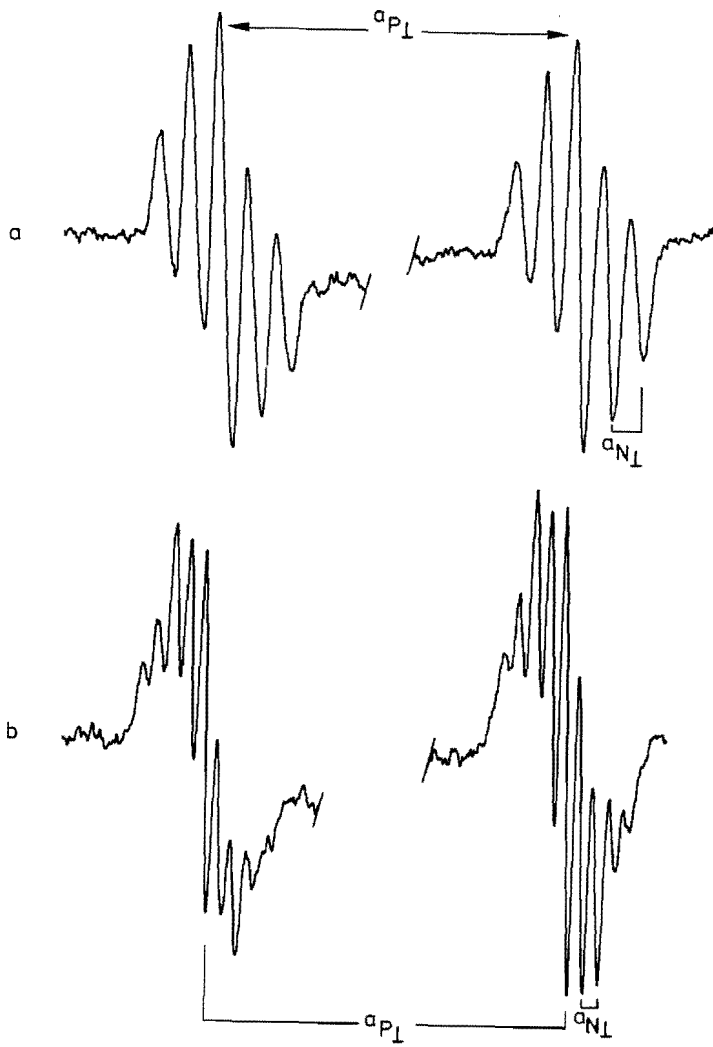


Fig. XIX. ESR spectra of (5a) single crystal  
 a. temperature 258 K  
 b. temperature 295 K

h.f.c.  $a_{N\text{-iso}}$  of 24.8 G indicates<sup>4</sup> a spin density of 0.05 in its 2s orbital. The small anisotropic contribution (0.8 G) can be attributed to dipole-dipole interaction. From this a TBP-e structure is derived with two apical nitrogen atoms accounting for the observed high h.f.c. and two equatorial nitrogens with small h.f.c. values ( $< 5$  G). On further raising of the temperature (to 295 K) an ESR spectrum was obtained which consisted of the same  $a_{P//}$  and  $a_{P\perp}$  values as found at low temperatures, and additional h.f.c. due to four equivalent nitrogen atoms  $a_{N//}$  14.4 and  $a_{N\perp}$  12.7 G. These changes in the ESR spectrum are reversible as indicated by the appearance of the initial spectrum on cooling. Therefore this phenomenon has to be attributed to a rapid pairwise interconversion of the nitrogen ligands. Additional evidence was obtained by a single crystal ESR study of (5a). The ESR spectra of an X-irradiated single crystal of (5) at room temperature show that two identical radicals with an angle between their  $a_{P//}$  components of  $34 \pm 2^\circ$  are present. These spectra were temperature dependent in the same way as found for the powder sample; at 295 K four equivalent nitrogens were observed, whereas on cooling to 258 K only two nitrogen couplings appeared, with the principal  $a_p$  values at exactly the same positions as found at 295 K (see fig. XIX and fig. XX). Unfortunately the single crystal became polycrystalline at 253 K, showing the features of the powdered sample with enhanced resolution.

Both the  $a_p$  principal values and their directions remain constant throughout temperature variation, indicating that the position of the orbital the unpaired electron resides in, is fixed in this process. Only the  $^{14}\text{N}$  h.f.c. varies from 13.3 (4N) to 24.8 G (2N), whereas the anisotropy in  $^{14}\text{N}$  h.f.c. is preserved. Furthermore the process is reversible. From this it is concluded that the nitrogen ligands exchange in a Berry pseudorotation<sup>5</sup> mechanism with the unpaired electron acting as the pivot ( $m-1$ ). At low temperature the pseudorotation proceeds more slowly than the measuring frequency of the  $^{14}\text{N}$  h.f.c. ( $\nu = 9 \times 10^7$  Hz),

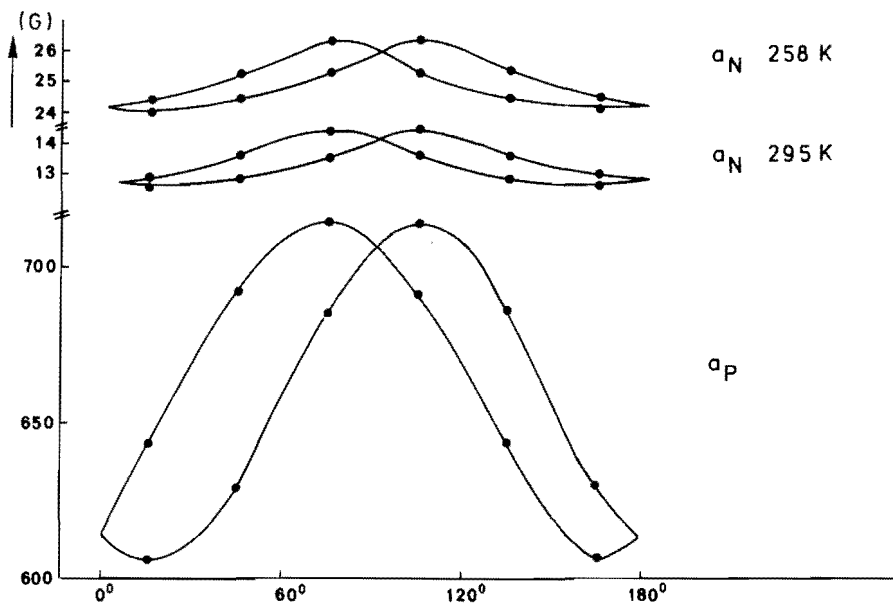


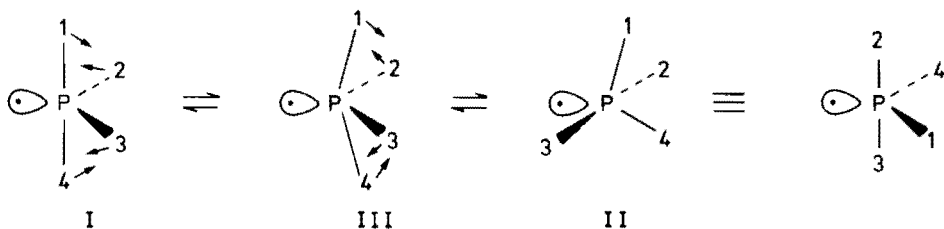
Fig. XX. Angular variations of  $a_N$  and  $a_P$

while at room temperature the exchange frequency equals this value, rendering the four nitrogens equivalent. From this one calculates with equation (1) (Eyring)

$$\nu = \left(\frac{kT}{h}\right) e^{-\left(\frac{\Delta G^\ddagger}{RT}\right)} \quad (1)$$

$\nu$  = unimolecular rate constant  
 $\Delta G^\ddagger$  = free energy of activation

that  $\Delta G^\ddagger$  amounts 6.0 kcal/mol, indicating that the intermediate structure III (square pyramidal) lies only slightly above the TBP-e structure.



This is the first example of a Berry pseudorotation which is established unequivocally. It is pointed out that the Berry Pseudorotation has been proposed many times especially in phosphoranes in solution on the basis of NMR measurements<sup>6</sup>. However, these results could be explained by the Turnstile mechanism (chapter I.2) also. Therefore radical (5a) constitutes a unique example since the Berry pseudorotation operates here in the solid state. This permits us to determine unambiguously the pivot in this process: the unpaired electron.

#### IV.2 X-ray structure determination

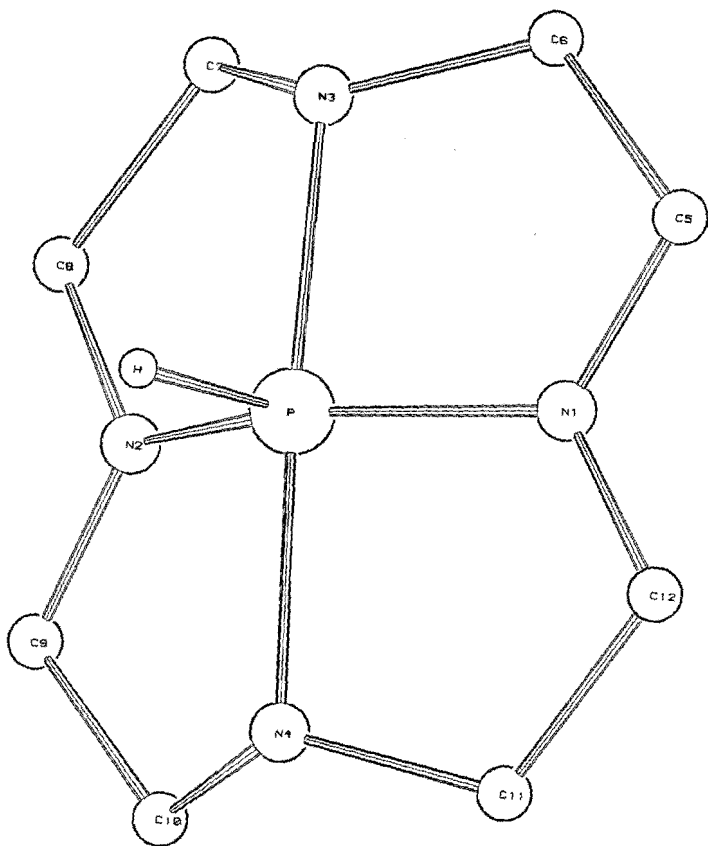
The crystals of (5) belong to the tetragonal crystal system with  $a = 6.102(7)$ ,  $c = 13.90(1)$  Å, numbers in parentheses referring to standard deviations in the last digit. The space group is  $P4_2/mnm$  and there are two molecules per unit cell. The calculated density is  $1.29 \text{ g cm}^{-3}$ . The structure was solved by direct methods using the MULTAN program on the basis of 353 unique reflections. The model could not be refined beyond an R-factor of 22 percent, however, since the crystals show disorder. The coordinates given in table IV.1 refer to a tetragonal cell in which there are four instead of two molecules, because of two possible orientations of the molecule. These two orientations are related by a mirror plane through the two-fold axis of the space group. Electron density maps point also to the possibility that the molecule may be rotated by  $90^\circ$ . Computer drawings are shown in fig. XXI. Intramolecular bond distances and angles are listed in table IV.2 and IV.3 respectively.

The  $N(1)-P-N(2)$ ,  $N(3)-P-N(4)$ , and  $N(1)-P-N(3)$  angles in table IV.3 clearly prove that the configuration of phosphorus is a TBP. It is noticed that the equatorial  $N(2)-P-N(1)$  angle of  $145^\circ$  obtained for (5) is the largest one that has been reported for phosphoranes with a TBP structure.

		ATOMIC COORDINATES OF (5)		
atoms <sup>a</sup>	x	y	z	
P	0.43(1) <sup>b</sup>	0.43(1)	0	
N(1)	0.68(1)	0.30(1)	0	
N(3)	0.44(1)	0.44(1)	0.135(10)	
C(5)	0.77(1)	0.23(1)	0.08(1)	
C(6)	0.65(1)	0.35(1)	0.16(1)	

a Atom numbering corresponds to fig. XXI

b Standard deviations in the last digit are given in parentheses



*Fig. XXI. ORTEP drawing of (5)*



atoms <sup>a</sup>	distance/Å
P-N(1)	1.72(8) <sup>b</sup>
P-N(3)	1.88(14)
N(1)-C(5)	1.31(12)
N(3)-C(6)	1.44(9)
C(5)-C(6)	1.48(8)

a Atom numbering corresponds to fig. XXI

b Standard deviations are given in parentheses

atoms <sup>a</sup>	angle/degrees
N(1)-P-N(2)	145(6) <sup>b</sup>
N(1)-P-N(3)	89(3)
N(3)-P-N(4)	175(5)
N(3)-C(6)-C(5)	116(11)
N(1)-C(5)-C(6)	105(6)
P-N(1)-C(5)	121(4)
P-N(3)-C(6)	105(8)
C(5)-N(1)-C(12)	116(9)
C(6)-N(3)-C(7)	129(9)

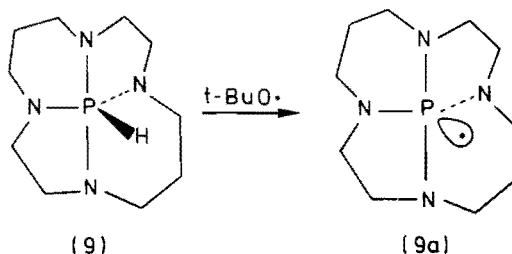
a Atom numbering corresponds to fig. XXI

b Standard deviations are given in parentheses

The X-ray data were collected at the University of Utrecht by prof. dr. J.C. Schoone.

### IV.3 Discussion

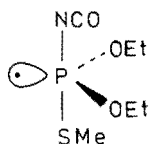
From the single crystal ESR analysis of (5a) it appears that ligand exchange in phosphoranyl radicals proceeds extremely rapidly in the solid state and that even at low temperature this interconversion takes place. However, if the exchange frequency becomes lower than  $9 \times 10^7$  Hz this phenomenon is easily overlooked. This is nicely illustrated with the related radical (9a), which is generated at 155 K in cyclopropane by UV photolysis of di-*t*-butylperoxide in the presence of precursor (9)<sup>1</sup>.



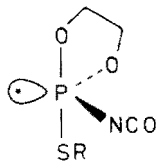
The ESR spectrum of (9a) in the liquid phase reveals the presence of an isotropic  $^{31}\text{P}$  h.f.c. of 713 G, with h.f.c. due to two nitrogens with  $a_{\text{N}} = 27.5$  G (2N), indicating a similar TBP-e structure as obtained for (5a). On warming, the radical (9a) disappears irreversibly without rendering the four nitrogens equivalent. As a consequence one might have considered this radical (9a) as a rigid TBP-e structure.

Unfortunately the dynamic properties of the phosphoranyl radicals are neglected frequently in the literature. For example, radical (10a) has been characterized as TBP-e with the NCO ligand in apical position on the basis of the relatively large  $^{14}\text{N}$  h.f.c. of 17.4 G, and an  $a_{\text{P-iso}}$  of 810 G in liquid phase<sup>7</sup>. Comparison with cyclic analogues<sup>8</sup> which have been reported to possess  $a_{\text{N}} = 26$  G for an apically located N and  $a_{\text{N}} = 6.5$  G for a nitrogen in equa-

torial position, gives an averaged value of  $^{14}\text{N}$  h.f.c. of 16 G which value is close to the observed h.f.c. On this basis it is suggested that this radical (10a) pseudo-rotates rapidly.



(10a)



(11a)

In addition, the assignment of a TBP-e structure to (11a) is far from unambiguous, since the alternative TBP-a structure with the SR ligand in equatorial position and the unpaired electron apically, which structure is close to that of the well-established radical (6a), is not taken into account in reference <sup>7</sup>. Therefore the conclusion which was tentatively drawn, that the apicophilicity of the sulphur ligand is larger than that of an alkoxy or trimethylsiloxy group appears to be unjustified. As a consequence the basis on which the mechanism of ligand permutation in phosphoranyl radicals is proposed by these authors needs a more careful reinvestigation. Moreover, the dynamic properties revealed here for radical (5a) in the single crystal clearly demonstrate the ligand nature of the unpaired electron: it serves as the pivot in the Berry pseudorotation. Therefore, the  $\sigma^*$  intermediate which is frequently suggested in the ligand exchange process of phosphoranyl radicals is not acceptable any more <sup>9</sup>.

As we have suggested before it is plausible that the  $\dot{\text{P}}\text{F}_4$  radical observed in irradiated hexafluorophosphate <sup>10</sup> undergoes very rapid pseudorotation rendering the four fluorines equivalent due to the fact that the radical is acyclic. Cooling of the sample to liquid helium temperature may reveal its TBP-e structure. Another possibility is that it adopts a  $\text{P}^{\text{V}}$  square pyramidal  $\text{C}_{4\text{v}}$  (SP) geometry with the unpaired electron localized in axial position, since it is

inferred from the single crystal ESR study of (5a) that the SP structure is only slightly less stable (6.0 kcal/mol) than the TBP-e structure. A ligand exchange process accounts possibly also for the observed isotropic  $^{31}\text{P}$  h.f.c. of  $^-\dot{\text{O}}\text{PCl}_3$  in a single crystal of  $\gamma$ -irradiated  $\text{OPCl}_3$ .<sup>11</sup> It is apparent that the isotropic  $^{31}\text{P}$  h.f.c. remains incompatible with the results obtained here on phosphoranyl radicals. Therefore it is suggested that the  $\text{Cl}_3\dot{\text{P}}\text{O}^-$  radical undergoes ligand exchange in such mode that the unpaired electron is not the pivot. Since it is evident from the analysis of the single crystal spectra of (5a) that the anisotropies of the ligand h.f.c. remain unaffected by the pseudorotation process, the alignment of the anisotropic chlorine h.f.c. due to two apical chlorines does not simply implicate that the Cl-P-Cl angle is  $180^\circ$ , but may deviate dramatically from this value. The same applies for the TBP-e radical  $\dot{\text{P}}\text{F}_4$  in irradiated  $\text{PF}_3$  where a similar conclusion was made about the axial F-P-F angle<sup>12</sup>. This is clear from inspection of the angular dependence of the h.f.c. of the equatorial fluorines of which the principal h.f.c. are in disagreement with the proposed TBP-e structure which implies an angle between  $a_{\text{F}\parallel}$  and  $a_{\text{P}\parallel}$  of  $60^\circ$ .

*References and notes*

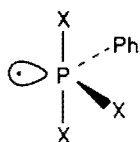
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## CHAPTER V

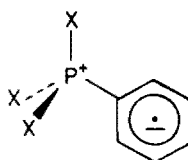
### Intramolecular electron transfer in phosphoranyl radicals

#### V.1 Introduction

ESR studies on phenyl substituted phosphoranyl radicals in liquid phase show that the electronic nature of the other ligands prescribes the valence state of phosphorus in these radicals <sup>1,2,3</sup>. If one of these ligands is H, Cl, OCH<sub>2</sub>CF<sub>3</sub> or MeS a large  $a_p$  value (600-1000 G) is observed indicating a P<sup>V</sup> structure with the unpaired electron mainly located on phosphorus ( $\sigma$ -radical). In contrast, in the presence of Me<sub>2</sub>N or MeO ligands the unpaired electron is stored in the phenyl ring, resulting in a tetrahedral (T) configuration for phosphorus with a low  $a_p$  value (< 40 G) ( $\pi$ -radical).



$\sigma$ -radical



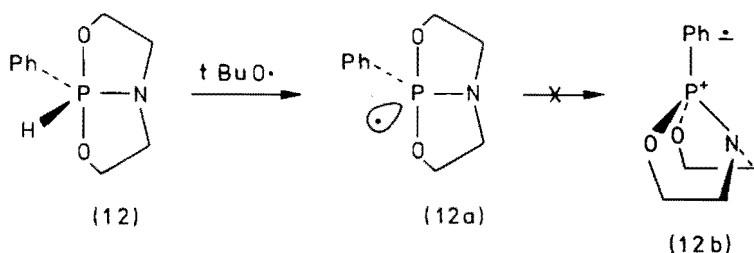
$\pi$ -radical

It was suggested that in phenylphosphoranyl radicals the electron withdrawing character of the other ligands accounts for the ultimate structure, highly electron withdrawing substituents causing the TBP structure, while in the absence of these ligands the tetrahedral form T is favoured.

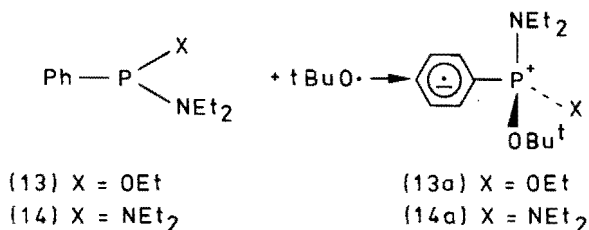
#### V.2 Results and discussion

1. The 5-phenyl-4,6-dioxa-1-aza-5-phospha<sup>(V)</sup>bicyclo[3.3.0]octan-5-yl radical

The phosphorane 5-phenyl-4,6-dioxo-1-aza-5-phospha<sup>(V)</sup> bicyclo[3.3.0]octane (12) was prepared according to the method described in reference<sup>4</sup>. Its structure has been deduced to be TBP with nitrogen, hydrogen and the phenyl group in the equatorial positions. The radical (12a) was generated in anhydrous toluene at 203 K by UV photolysis of di-*t*-butylperoxide in the presence of (12). The UV irradiation was carried out with the aid of a Philips SP 500 W lamp. The di-*t*-butylperoxide was dried by distillation under reduced pressure from calciumhydride.



Irradiation of a solution of (12) in toluene/di-*t*-butylperoxide gives rise to the ESR spectrum ascribed to (12a), consisting of one isotropic  $^{31}\text{P}$  doublet with  $a_{\text{P}} = 763 \text{ G}^5$ . No further hyperfine splittings could be observed. Irradiation of phenylphosphonite (13) in the presence of di-*t*-butylperoxide however, generates the acyclic analogous radical  $\text{Ph}\dot{\text{P}}(\text{OEt})(\text{NEt}_2)\text{OBU}^{\text{t}}$  (13a) with  $a_{\text{P}} = 10.9 \text{ G}$ ,  $a_{\text{P-H}} = 14.4 \text{ G}$  (1H),  $a_{\text{O-H}} = 5.9 \text{ G}$  (2H) and  $a_{\text{m-H}} = 1.4 \text{ G}$  (2H).



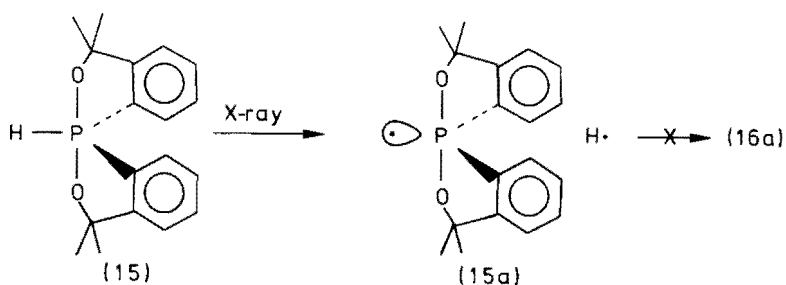
In a similar way the related radical  $\text{Ph}\dot{\text{P}}(\text{NEt}_2)_2\text{OBU}^{\text{t}}$  (14a) with  $a_{\text{P}} = 10.5 \text{ G}$ ,  $a_{\text{P-H}} = 10.5 \text{ G}$  (1H),  $a_{\text{O-H}} = 5.0 \text{ G}$  (2H) and  $a_{\text{m-H}} = \text{ca. } 0 \text{ G}$  has been obtained. At higher tempera-

ture (235 K) the t-butylradical has been observed. The phosphorus h.f.c. of (12a) together with the TBP structure of its precursor indicates a TBP-e structure for (12a) with the unpaired electron on phosphorus in equatorial position. From the linewidth,  $a_N$  is estimated less than 5 G. In contrast the h.f.c. values observed for the acyclic analogous radicals indicate the unpaired electron to be delocalized on the phenylring, indicating a tetrahedral configuration of phosphorus as was earlier observed for  $\text{Ph}\dot{\text{P}}(\text{OMe})_2\text{Bu}^\dagger$ . Apparently the initially formed TBP structure underwent stereoisomerization to the tetrahedral form<sup>6</sup>. The TBP-e structure of (12a) is stabilized by the two five-membered rings, which span apical-equatorial positions. Thus the energy of (12a) is lowered with respect to its acyclic analogue. On the other hand, the rings will increase the energy of the phosphonium structure (12b) by enhanced ring strain and crowding in comparison with the acyclic species<sup>7</sup>. This results in the formation of a stable TBP-e structure. Therefore it is demonstrated with (12a) that the valence state  $\text{P}^{\text{V}}$  on phosphoranyl radicals in solution can be imposed by incorporation of phosphorus within a suitably chosen framework.

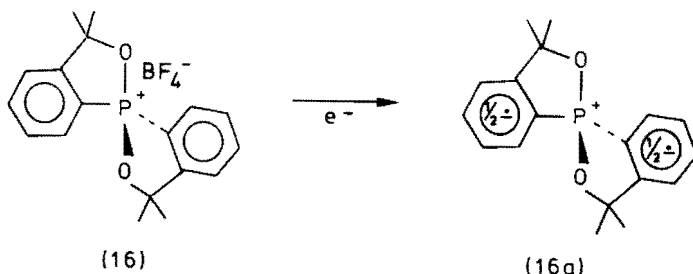
## 2. The 3,3,3',3'-tetramethyl-1,1'-spirobi(3H-2,1-benzoxaphosph<sup>V</sup>ole)-1-yl radical

The phosphorane 3,3,3',3'-tetramethyl-1,1'-spirobi(3H-2,1-benzoxaphosphole) (15) was prepared according to the method described in reference<sup>8</sup>. Its structure is inferred as TBP with hydrogen and the phenyl rings located equatorially. UV irradiation was performed in toluene at 203 K in the presence of di-t-butylperoxide. A powdered sample of (15) was X-irradiated at 77 K. The phosphonium tetrafluoroborate (16) was obtained in a similar way to that given in reference<sup>9</sup> for the analogous phosphoniumtrifluoromethanesulphonate salt by using an 50% solution of fluoroboric acid in water instead of trifluoromethane sulphonic acid. Electrolysis of the phosphonium salt was achieved at 228 K in a flat cell using an acetonitrile solution.





X-irradiation of a powdered sample of (15) generates radical (15a) with  $a_{\text{P}||} = 730$  G and  $a_{\text{P}\perp} = 603$  G, from which values an  $a_{\text{P-iso}}$  of 645 G is calculated. In toluene at 203 K photolysis of (15) in the presence of di-*t*-butylperoxide gives rise to the isotropic ESR spectrum assigned to (15a) showing an  $a_{\text{P-iso}}$  of 652 G, close to the value obtained for the powdered sample. This phosphorus splitting together with the TBP structure of the precursor characterizes the structure of (15a) as TBP-e with the unpaired electron located on phosphorus in equatorial position<sup>10</sup>.



Cathodic reduction of the phosphonium salt (16) in acetonitrile at 228 K results in the isotropic ESR spectrum of (16a) with  $a_{\text{P}} = 8.4$  G,  $a_{\text{P-H}} = 5.6$  G (2H),  $a_{\text{O-H}} = 3.0$  G (2H) and  $a_{\text{m-H}} = \text{ca. } 0$  G indicating that the unpaired electron is mainly located in both phenyl rings with phosphorus in a T configuration.

The structure of (15a) is TBP-e with the unpaired electron centered on phosphorus. From the anisotropic values  $a_{\text{P-iso}}$  is derived to be 645 G indicating a  $\rho_{3s}^{\text{P}}$  of 0.18 and  $B = 42$

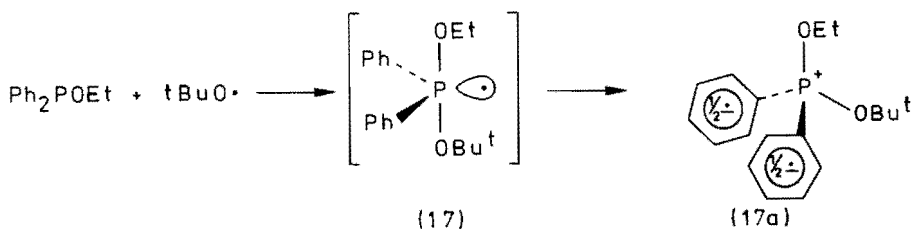
G indicating a  $\rho_{3p}^P$  of 0.39, resulting in 0.57 spin density on phosphorus<sup>11</sup>.

The structure of (16a) is tetrahedral with the electron located on the phenyl rings as inferred from the McConnell relation<sup>11,12</sup>:

$$a_H = Q\rho_C$$

where  $\rho_C$  is the unpaired electron density in the carbon  $2p_z$  orbital and  $Q$  is the value of  $a_H$  (H adjacent) when there is a full electron on the carbon (approximately -23 G), resulting in a total spin density of 0.74 on ortho and para positions of the phenyl rings, while spin density on phosphorus will be confined to a  $P_{3p}$  orbital.

The TBP-e structure obtained for (15a) is in sharp contrast with the behaviour of the analogous acyclic radical  $\text{Ph}_2\dot{\text{P}}(\text{OEt})\text{OBu}^t$  possessing iso-electronic ligands which only shows a low  $a_p$  value of 23 G with the unpaired electron located on the phenyl rings<sup>2</sup>. This  $a_p$  value is indicative for a T configuration. Apparently the initial TBP structure (17) isomerizes immediately to (17a). The behaviour of (17) is consistent with other acyclic radicals such as  $\text{Ph}\dot{\text{P}}(\text{OEt})_2\text{OBu}^t$  and  $\text{Ph}_3\dot{\text{P}}\text{OBu}^t$  which also occur in a T configuration.



Obviously, the different behaviour of (15a) cannot be ascribed to electronic factors, but is correlated with the incorporation of its ligands in the five-membered rings. It is conceivable that the five-membered rings increase the energy of the tetrahedral phosphonium structure (16a) by enhanced ring strain and crowding in comparison

with the acyclic analogous radical (17a)<sup>5</sup>. For structure (16a), however, strain effects are probably not dominant, since this radical could be generated by cathodic reduction of phosphonium salt (16) in acetonitrile at 228 K. It is known that the stability of P<sup>V</sup> TBP structures is greatly enhanced by bridging apical and equatorial positions. So precursor (15) is surprisingly stable and furthermore shows no pseudorotation at room temperature<sup>8</sup>, which behaviour is in sharp contrast with acyclic analogues. Similarly, the barrier of stereo-isomerization of (15a) to (16a) is increased compared with the analogous acyclic phenylphosphoranyl radical (17) to (17a). Apparently, the factors which determine pseudorotation of the P<sup>V</sup> phosphoranes (Muetterties' rules)<sup>7</sup> are similar to those determining the stereo-isomerization of the corresponding TPB phenylphosphoranyl radicals (15a) and (17). Moreover this observation is consistent with the high  $a_p$  value (600 - 1000 G)<sup>2</sup> for acyclic phenylphosphoranyl radicals on introduction of halogen, CF<sub>3</sub>CH<sub>2</sub>O, H or MeS ligands, which are highly apicophilic, i.e. these ligands preferentially occupy apical sites in the TBP P<sup>V</sup> structure, thus suppressing pseudorotation and consequently electron transfer<sup>10</sup>. The question remains open whether these acyclic phosphoranyl P<sup>V</sup> intermediates are TBP-e or TBP-a structures.

*References and notes.*

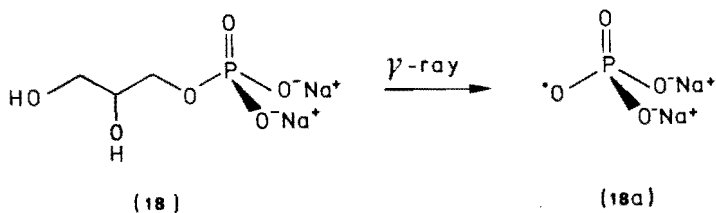
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## CHAPTER VI

### Biochemical aspects

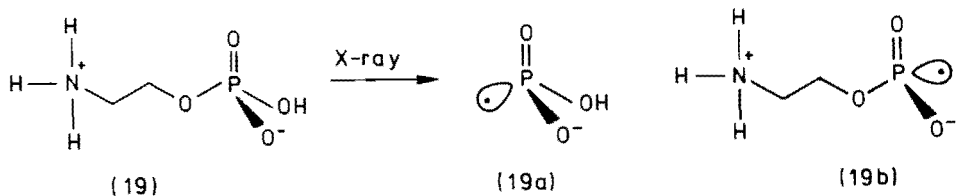
#### VI.1 Introduction

The effects of ionizing radiation on DNA have been the subject of many recent publications<sup>1</sup>. One approach has been to investigate free radical products and reactions in nucleic acid constituents which are irradiated in the solid state in order to understand the radiation chemistry of nucleic acid polymers<sup>2</sup>. The deoxynucleotides are of interest since they contain all principal elements of DNA: base, sugar and phosphate groups. It appears that irradiation of nucleotides gives rise to base-centered radicals and alkyl and alkoxy sugar radicals. The same was observed for irradiated DNA<sup>3</sup>. It has been assumed that phosphorus might serve as an electron trap, but no proof that phosphorus is actually involved in reduction processes, could be offered hitherto.

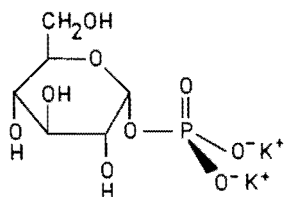


In a model study on  $\gamma$ -irradiated  $\alpha$ -glycerolphosphate (18), the  $\text{PO}_4^{2-}$  radical has been assigned, which results from C-O bond rupture with  $a_{\text{P-iso}} = 30$  G, indicating an oxygen-centered radical<sup>4</sup>. In a single crystal ESR study of X-irradiated o-phosphorylethanolamine (19), phosphonyl  $\text{P}^{\text{IV}}$  radicals have been detected which are obviously formed by P-O bond

cleavage<sup>5</sup>.



It is not clear whether this process is induced by electron capture at the ester bond resulting in dissociation, or that  $\dot{\text{H}}$  radicals are involved.

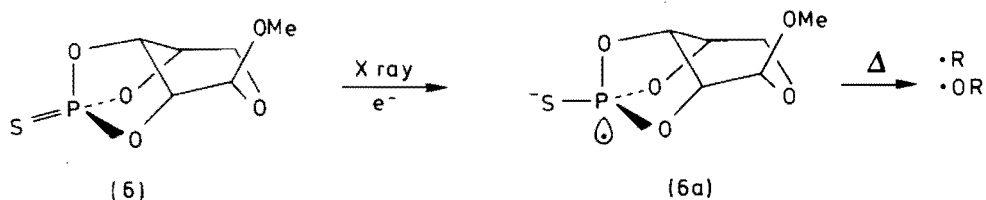


(20)

Also X-irradiated glucose-1-phosphate (20) did not show electron capture at phosphorus; alkoxy and alkyl radicals were assigned<sup>6</sup>.

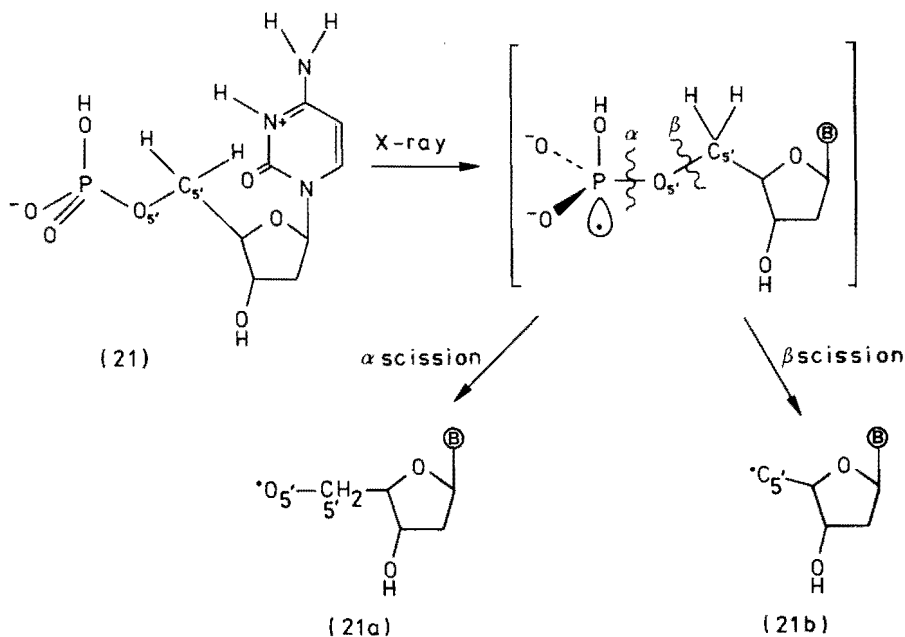
## VI.2 Results and discussion

In this connection the transient phosphoranyl radical (6a) which is generated upon X-irradiation and UV at low temperature (chapter II.2) is of interest since it contains a (thio)phosphate moiety and a sugar group<sup>7</sup>.



Clearly this radical (6a) is formed by electron capture at phosphorus. Its TBP-a structure is stabilized compared to

acyclic analogues by the introduction of the five-membered rings, spanning apical-equatorial positions, while electronically the negative sulphur ligand favours an equatorial position in this rigid frame-work. On warming, the ESR signals of (6a) disappear at 245 K giving rise to  $\alpha$  or  $\beta$  scission products, i.e. thermodynamically stable sugar radicals, analogous to those reported for irradiated glucose-1-phosphate (20) <sup>6</sup>. In the absence of  $P^V$  stabilizing factors  $\alpha$  or  $\beta$  scission may occur at such a rate that the  $P^V$  structure is not detected. For example in irradiated deoxycytidine-5'-phosphate (21) both radicals (21a) and (21b) are observed <sup>8</sup>.



From the relative concentrations it is derived that  $C_{5'}-O_{5'}$  bond rupture is about twice as probable than  $O_{5'}-P$  bond cleavage. Besides these alkyl and alkoxy radicals (21a) and (21b), base centered radicals are observed frequently <sup>9,10</sup>, which are also the product of an electron addition process. It has been found that in irradiated single crystals at low temperature, electrons are trapped in intermolecular sites, e.g. glucose-1-phosphate (20) by polarization forces

arising from nearby hydroxy groups<sup>6</sup>. At warming their ESR signals disappear irreversibly. It is suggested now that as a result, the phosphate moiety may be attacked by electrons released from suitably situated holes, generating a phosphoranyl radical anion which decomposes rapidly by  $\alpha$  and/or  $\beta$  scission in the absence of stabilizing factors (i.e. five-membered rings, suitably chosen ligands), resulting in the usually detected alkyl and alkoxy radicals. This mechanism, which is supported by the results obtained for (6a), has to be checked on nucleotides, and this may be achieved by 'fast response ESR'. In this way the ESR spectra are recorded several microseconds after a UV laser pulse<sup>11</sup>. With this technique it should be possible to detect the transient phosphoranyl P<sup>V</sup> radical before it is destroyed by cleavage processes.



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## Appendix

### *1. Optical examination of an orthorhombic crystal*

Light which vibrates in a plane perpendicular to the direction of propagation, is plane polarized light. A polarizing microscope enables us to examine crystals in plane polarized light and to observe the effect, the crystal has on the plane of polarization. The analyzer and polarizer of the microscope each have the ability to polarize light which passes through them. The analyzer usually has its polarization direction perpendicular to that of the polarizer, and when a crystal is observed in this way, the crystal is said to be observed between crossed polars. Light which enters an optically anisotropic crystal is resolved into two components vibrating in mutually perpendicular planes, i.e. double refraction occurs. If an anisotropic crystal is rotated on the microscope stage between crossed polars, the light passing through it is only extinguished in certain special orientations, each position of extinction being separated by an angle of  $90^\circ$  from the adjacent extinction positions. A relationship can be deduced between the positions at which a crystal extinguishes and the optic axes of the crystal. An optic axis is a direction in the crystal in which there is no double refraction. Orthorhombic crystals have two optic axes from which the directions of the crystallographic axes are deduced. Identification of these axes is then easily performed by the rotating crystal method.

### *2. The rotating crystal method*

This technique is very similar to the Debye-Scherrer (D-S) method, in fact the same camera and monochromatic radiation

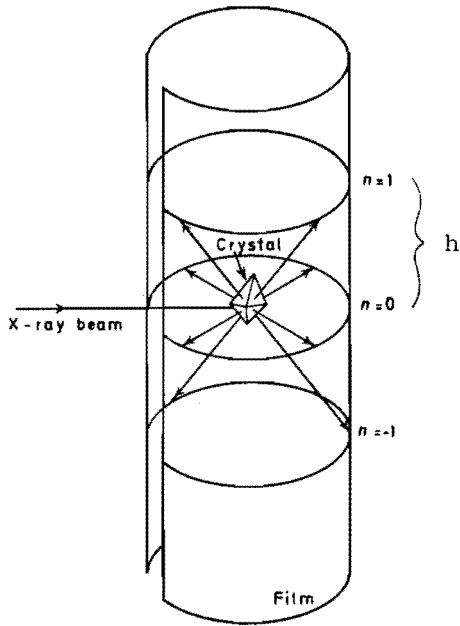


Fig. A.1.

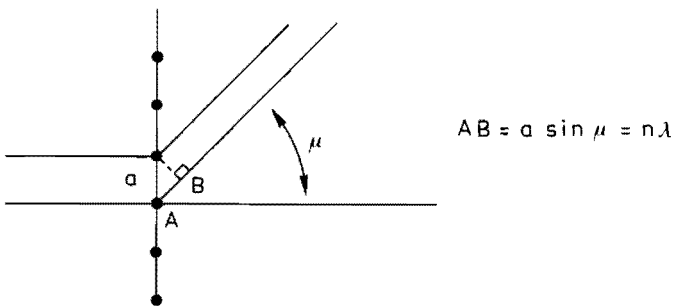


Fig. A.2.

is used. However, now a single crystal is rotated around a principal axis. A diffracted ray is shown in fig. A.1. Reflection spots are only expected where D-S rings would have been observed if the sample were a powder; of all the possible orientations in the powder, only one is left. As the crystal rotates around the a-axis, the family of  $[0kl]$  planes will produce the zero layer reflections ( $n=0$ ) since successive sets of planes are brought into positions which satisfy the Bragg equation  $n\lambda = 2d \sin \theta$ . Other planes not parallel to this axis of rotation will also be satisfying the Bragg equation, resulting in the production of cones of reflections. Each cone has a different value of  $n$  in the Bragg equation and is produced by a family of planes  $[nkl]$ . The film in the D-S camera occupies the positions of the cylinders enclosing the cones as shown in fig. A.1, and each cone will therefore appear as a straight line of diffraction spots on the film. A spot appears on the cone  $n$  whenever a set of planes  $[nkl]$  satisfies Bragg's equation (fig. A.2).

By measuring the height ( $h$ ) of a layer line from the zero layer line on the film, and knowing the camera radius ( $r$ ), the value of  $\mu$  is obtained by  $\tan \mu = \frac{h}{r}$ . Thus the value of  $a = \frac{n\lambda}{\sin \mu}$  is obtained if the crystal is rotated around the a-axis. Similarly, rotation around the b and c axis give the value of b and c respectively.

TABLE, SHOWING THE ESR PARAMETERS OF RADICAL (1a) - (8a)

Comp.nr.	$a_{//}$ (G)	$a_{\perp}$ (G)	$a_{iso}$ (G)	B (G)	$\rho_s$	$\rho_p$	$g_{//}$	$g_{\perp}$
1a	$^{31}\text{P}$ 893	735	788	53	0.22	0.49	1.988	2.005
2a	$^{31}\text{P}$ 960	808	859	50	0.24	0.47	1.983	2.008
3a	$^{31}\text{P}$ 1061	869	933	64	0.26	0.60		
4a	$^{31}\text{P}$ 1167	1005	1059	54	0.29	0.51		
5a	$^{31}\text{P}$ 715 $^{14}\text{N}$ 26.3	606 24.0	642 24.8	36 0.8	0.18 0.05	0.35 (2N)		
6a	$^{31}\text{P}$ 886 $^1\text{H}$ 5	776 5	813 5	37	0.22 0.01	0.35 (1H)	1.988	2.005
7a	$^{31}\text{P}$ 1120	930	993	63	0.27	0.61		
7b	$^{31}\text{P}$ 888 $^{14}\text{N}$ 21.2	753 22.7	798 22.2	45 0.5	0.21 0.05	0.43 (1N)	1.988	2.005
8a	$^{31}\text{P}$ 1400 $^{35}\text{Cl}$ 47 $^{37}\text{Cl}$ 43	1289,1263 23,24 22,22	1317 31 29	42 8 7	0.36 0.02 0.02	0.40 0.16(1Cl) 0.16	1.988	2008,2011

Reference values used for calculation of  $\rho_s$  and  $\rho_p$

	$a_o$ (G)	$B_o$ (G)	spin (I)
$^{31}\text{P}$	3640	103	1/2
$^1\text{H}$	508		1/2
$^{14}\text{N}$	552	17	1
$^{35}\text{Cl}$	1680	50	3/2
$^{37}\text{Cl}$	1395	42	3/2

## Summary

This thesis deals with the structure and the dynamic behaviour of phosphoranyl radicals. These radicals result from the interaction of ionizing radiation and organophosphorus compounds, in which process selective homolytic bond cleavage or electron addition takes place. When single crystals are irradiated, it appears that the radicals retain the original orientation of the parent molecules. In this way centres are formed which are ideally arranged for Electron Spin Resonance (ESR) spectroscopy. The anisotropic ESR spectra contain information about the 3s and 3p character of phosphorus and the direction of the hybrid orbital in which the unpaired electron is located.

The main characteristic of the unpaired electron is its ligand nature: it can occupy an equatorial (e) as well as an apical (a) site in the trigonal bipyramidal (TBP) structure of phosphorus. Since both the TBP-e and TBP-a configuration are formed in one sample of  $\overline{\text{HP}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\text{BF}_4^-}$  upon X-irradiation, comparison of the two stereo-isomers is possible. It appears that the amount of s character in the apical bonds is reduced in comparison with the equatorial bonds, in accordance with the observed differences in reactivity between apical and equatorial sites in the TBP structure. Besides these TBP-a and TBP-e structures, the octahedral geometry of  $\text{Cl}\dot{\text{P}}(\text{O}_2\text{C}_6\text{H}_4)_2$  is established here, with the unpaired electron and chlorine in the axial axis. Intramolecular ligand reorganization in phosphoranyl radicals is studied in a single crystal, which reveals the exact mode of permutation: a Berry pseudorotation with the unpaired electron acting as the pivot. It is found that the intermediate square pyramidal (SP) geometry in this process

lies only slightly above the TBP-e structure. Furthermore it is demonstrated that the factors which determine pseudorotation are similar to those determining intramolecular electron transfer. In this process the initial  $\sigma$ -radical undergoes stereo-isomerization to a  $\pi$ -radical. Electron addition to phosphorus in the thiophosphate 0,0,0-triester of  $\beta$ -D-ribopyranoside upon UV or X-irradiation generates the radical anion in which phosphorus appears to be in a TBP-a configuration. According to the behaviour of this model compound a new mechanism is proposed for strand break in DNA upon irradiation: initial electron attack at phosphorus generates a phosphoranyl radical which subsequently produces alkyl and alkoxy radicals by  $\beta$  and/or  $\alpha$  scission processes. This mechanism accounts for the reaction products which are usually observed in irradiated nucleotides, i.e. alkyl and alkoxy radicals.



## Samenvatting

In dit proefschrift worden de structuur en het dynamisch gedrag van fosforanylradicalen beschreven. Deze radicalen worden gevormd door de interactie van ioniserende straling met organofosforverbindingen, waarbij selectief bindingen verbroken worden of electronadditie optreedt. Bij bestraling van éénkristallen blijkt, dat de radicalen de oorspronkelijke oriëntatie behouden van de moleculen waaruit ze zijn ontstaan. De op deze manier gerangschikte radicalen zijn met electronenspinresonantie (ESR) spectroscopie bestudeerd. De anisotrope ESR spectra leveren informatie op over zowel de richting als de hybridisatie van de orbital die het ongepaarde electron bevat.

Kenmerkend voor het ongepaarde electron is het ligand karakter ervan: het kan een equatoriale (e) of apicale (a) positie innemen in de trigonale bipyramidale (TBP) structuur van fosfor. Aangezien beide vormen, TBP-e en TBP-a voorkomen in  $\overline{\text{HP}(\text{OCH}_2\text{CH}_2)_3\text{N}^+\text{BF}_4^-}$  bij röntgenbestraling, is het mogelijk de twee stereo-isomeren met elkaar te vergelijken. Het blijkt dat de 3s bijdrage in de apicale binding geringer is dan die in de equatoriale binding. Dit komt overeen met de verschillen in reactiviteit tussen de apicale en equatoriale plaatsen in fosforanen. Behalve deze TBP-e en TBP-a configuraties is de structuur van  $\text{Cl}\overset{\cdot}{\text{P}}(\text{O}_2\text{C}_6\text{H}_4)_2$  bepaald. Hierin is fosfor 6-waardig met het chlooratoom en het ongepaarde electron in de as van de octaëder.

Intramoleculaire liganduitwisseling in fosforanylradicalen is bestudeerd in een éénkristal, waardoor de permutatie precies kon worden vastgesteld: een Berry pseudorotatie met het ongepaarde electron als pivot. Het blijkt dat het

intermediair in dit proces, een vierkant piramidale structuur met het ongepaarde electron apicaal, in energie slechts weinig boven de TBP-e structuur ligt. Verder wordt aangetoond dat de factoren welke pseudorotatie bepalen, ook intramoleculaire electronenoverdracht bewerkstelligen. In dit proces vindt stereo-isomerizatie plaats van een  $\sigma$ -radicaal naar een  $\pi$ -radicaal. Bij UV of röntgenbestraling van de thiofosfaat 0,0,0-triëster van  $\beta$ -D-ribopyranoside vindt electronadditie plaats aan fosfor, waarbij het radicaal anion wordt gevormd. De structuur hiervan is TBP-a. Aan de hand van het gedrag van dit modelsysteem is een nieuw mechanisme opgesteld voor ketenbreuk in DNA onder invloed van ioniserende straling: electronadditie aan fosfor genereert een fosforanylradicaal dat vervolgens disocieert met als reactieproducten alkyl en alkoxy radicalen. Met dit mechanisme kunnen de reactieproducten welke ontstaan bij bestraling van nucleotiden verklaard worden.

## **Curriculum vitae**

De auteur van dit proefschrift werd geboren op 17 juli 1952 te Bandung (Indonesië). Na het behalen van het diploma gymnasium- $\beta$  aan het Sint Michiellyceum te Geleen in 1970, werd in hetzelfde jaar begonnen met de studie aan de Technische Hogeschool te Eindhoven. Het afstudeerwerk werd verricht bij de vakgroep Organische Chemie onder leiding van prof. dr. H.M. Buck en dr. ir. W.G. Voncken. In januari 1976 werd het ingenieursexamen met lof afgelegd.

Na het vervullen van de militaire dienstplicht werd vanaf mei 1978 tot mei 1982 in dienst van de Nederlandse Stichting voor Zuiver Wetenschappelijk Onderzoek het onderzoek, beschreven in dit proefschrift, uitgevoerd onder leiding van prof. dr. H.M. Buck.

## **Dankwoord**

Gedurende het onderzoek heb ik van velen positieve impulsen ontvangen ter stimulering van mijn onderzoek. Zowel voor de morele als technische ondersteuning dank ik eenieder die aan de totstandkoming van dit proefschrift heeft bijgedragen.

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STELLINGEN

behorend bij het proefschrift van

J.H.H. Hamerlinck

Eindhoven, 14 mei 1982

1. Het model van Wang et al. voor de overgang van B- naar Z-DNA wordt niet gesteund door de NMR resultaten van Early et al.

A.H.J. Wang, G.J. Quigley, F.J. Kolpak, J.L. Crawford, J.H. van Boom, G. van der Marel, A. Rich, *Nature*, 1979, 282, 680.

T.A. Early, D.R. Kearns, W. Hillen, R.D. Wells, *Biochemistry*, 1981, 20, 3764.

2. De bewering van Roberts et al. dat ligand permutatie in fosforanylradicalen via een  $\sigma^*$  structuur analoog is aan die welke via een piramidale structuur plaatsvindt in fosforanen, is onjuist.

J.R.M. Giles, B.P. Roberts, *J. Chem. Soc., Perkin Trans II*, 1981, 1217.

3. De resultaten van de INDO II methode verkregen voor het  $\dot{\text{S}}\text{F}_5$  radicaal, worden ten onrechte beschouwd als misleidend.

A.R. Gregory, *Chem. Phys. Letters*, 1974, 28, 552.

4. Het door Kevan et al. voorgestelde mechanisme voor vesicle-tumbling is niet in overeenstemming met de door hen beschreven electron spin echo experimenten aan lecithine vesicles.

K. Madden, L. Kevan, P.D. Morse II, R.N. Schwartz, *J. Am. Chem. Soc.*, 1982, 104, 10.

5. De theoretische beschrijving van de fotochemische uitwisseling van methoxide in nitro-methoxybenzenen houdt slechts rekening met de energie-verschil term in de uitdrukking voor de koppeling tussen de energieprofielen voor grond en aangeslagen toestand.

H.C.H.A. van Riel, G. Lodder, E. Havinga, *J. Am. Chem. Soc.*, 1981, 103, 7257.

6. Het meten van de  $^{14}\text{N}$   $T_1$  waarden en de  $J_{\text{CN}}$  koppeling is niet voldoende om de verandering in de aggregatietoestand van cholinefosfolipiden te volgen, aangezien geen rekening wordt gehouden met het  $^1\text{H} - ^{13}\text{C}$  ontkoppelvermogen.  
R. Murari, W.J. Baumann, J. Am. Chem. Soc.,  
1981, 103, 1238.
7. Het gebruik van de term microgolf indien straling met een golflengte van enkele centimeters bedoeld wordt, is misleidend.
8. Het feit dat wolken organisch materiaal in de melkweg voorkomen met een massa die de totale massa van de aarde verre overtreft, en de ontdekking van celstructuren in meteorieten welke ouder zijn dan de aarde, laat toe te veronderstellen dat het leven niet op aarde is ontstaan.
9. Het gebruiken van een bindingsstreepje om de positie van het ongepaarde electron in de structuurformule van fosforanylradicalen aan te geven dient ten stelligste te worden afgeraden.  
B.P. Roberts, J.C. Scaiano, J. Chem. Soc.,  
Perkin Trans II, 1981, 905.
10. Het verdient aanbeveling om op auto's te vermelden dat gebruik ervan schadelijk is voor de gezondheid.
11. In het kader van de in te voeren trimesterindeling aan universiteiten en hogescholen verdient het aanbeveling behalve de datum van opening van het academisch jaar ook de sluiting ervan aan te geven.