Table IV. Early Rate Data for Equivalent Systems with some Aromatic Hydrocarbons

	initial composition, mmol			$10^4 \times$
ArH	$AlCl_3$	ArH	CH_3COCl	d[product]/dt
benzene	0.243	0.245	0.243	very slow
p-xylene	0.247	0.236	0.250	3.15
toluene	0.240	0.250	0.243	14.4
mesitylene	0.232	0.246	0.243	20.2

this study is the intermediate normally postulated in Friedel–Crafts acetylation.

There is always concern that conclusion from studies under a particular set of conditions may not be transferable to studies made under other conditions. To establish the generality of the preceding results, we also made comparitive rate studies with benzene, toluene, and mesitylene. The data are listed in Table IV. The differences in reactivity of toluene, p-xylene, and mesitylene are only slightly smaller than those listed for other aromatic substitutions.[15] The greater reactivity of toluene compared to p-xylene is unique, but a displacement of the position of mesitylene has been observed previously.[16] It thus appears that the present studies are within the range of values reported previously for other systems. The increase in rate constant from p-xylene to mesitylene is much less than the increase in equilibrium constant K_3. This implies that the more stable intermediate complex with mesitylene breaks down more slowly to give products than that of p-xylene. Therefore, the much larger range of values for the stability of σ complexes than for relative rates of reactions does not necessarily preclude σ complexes as intermediates in these reactions.[15]

Registry No. CH_3COCl, 75-36-5; $AlCl_3$, 7446-70-0; benzene, 71-43-2; p-xylene, 106-42-3; toluene, 108-88-3; mesitylene, 108-67-8.

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Phosphorus Hybridization in the Equatorial and Apical Directions of Trigonal Bipyramids. An Electron Spin Resonance Study

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The stereoisomers **1a** and **1b** open the possibility to determine the contribution of the 3s and 3p character of phosphorus in a trigonal-bipyramidal (TBP) configuration. The ESR experiments clearly show that there is a small excess of 3s spin density in the equatorial ligand in comparison with the apical one. Although this result does not conflict with the physical and chemical properties of phosphorus in a TBP, it refines the established idea that the sp^3d hybridization of phosphorus can be constructed from three equatorial sp^2 ligands and two apical pd ligands. This study was carried out by starting from the precursor **2**, present as a single crystal. By means of UV and X-ray irradiation the different stereoisomers could be obtained. The single-crystal experiments allowed us to obtain the directional information, i.e., location of the odd electron in the equatorial and apical location.

An important aspect of phosphorus five-coordination,[1] in contrast to four-coordination, is that the distribution of the ligands about the central atom cannot be spherically symmetrical; i.e., the ligands are not equivalent.[2,3] Two possible structural models are favored, as shown by X-ray analyses:[3-5] the trigonal bipyramid (TBP) and the tetragonal pyramid (TP). Usually, the TBP is encountered, although the energy difference between the TBP and TP is often very small.[2] In the TBP configuration, the apical bonds are longer and usually weaker than the equatorial bonds.[2,3,6,7] In addition, apical sites are preferred by electron-withdrawing ligands, whereas electron-donating ligands tend to occupy equatorial positions.[6-8] This polarity rule has been derived from many experimental data[9,10] and is supported by semiempirical calculations.[3-5,11-15] Furthermore, it has been found that small rings are easily accommodated in the TBP configuration if they span an apical and an equatorial position. This strain rule[16] is a result of the 90° angle between apical and equatorial bonds in the TBP. In fact, since the TBP is

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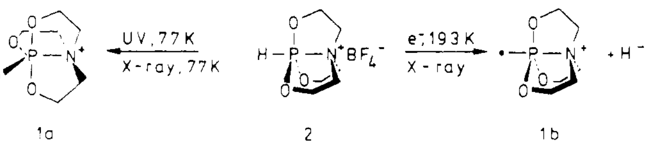
Table I. ESR Parameters of 1a and 1b

		parameter					
compd	atom	$a_\parallel$, G	$a_\perp$, G	a_{iso}, G	B, G	ρ_s	ρ_p
1a	^{31}P	1120	930	993	63	0.27	0.61
1b	^{31}P	888	753	798	45	0.21	0.43
1b	^{14}N	21.2	22.7	22.2	0.5	0.05	(1N)

Scheme I



a rather crowded configuration with short nonbonded distances, the presence of rings stabilizes this configuration. As a result, the phosphorus atom is part of one or more rings in most of the known stable phosphoranes. The assumption that d orbitals participate in bonding in pentavalent phosphorus compounds provides a rationalization of their properties,[17-19] although the exact role of d orbitals is still a subject of controversy.[20-22] In four- and five-coordination, back-donation[6-8] from the lone pairs of the ligands into the empty d orbitals of phosphorus gives rise to p_π–d_π bonds. This back-donation constitutes a substantial contribution to the stability of the phosphoryl (P═O) bond. A TBP configuration can be realized by a hybridization of the p_z and d_{z^2} orbitals to account for the apical bonds, combined with three sp^2 orbitals in the equatorial plane.[17] The sp^3d hybridization scheme is consistent with the observed difference in length between apical and equatorial bonds, since pd hybrids are relatively diffuse, resulting in long apical bonds. Moreover, the polarity rule is explained by this hybridization: the apical pd orbitals interact strongly with electron-withdrawing ligands, whereas the equatorial sp^2 orbitals favor donation of electrons from the ligands. In addition, equatorial ligands are more capable of forming d_π–p_π bonds to phosphorus.[6-8] One of the consequences of the differences in bond strength in a TBP is that the leaving groups depart from an apical position.[14,16] Conversely, nucleophilic attack on four-coordinated phosphorus results in a TBP in which the nucleophile occupies an apical position,[14] as required by the principle of microscopic reversibility.[16] The present ESR study shows unambiguously that the contribution of the hybrids of phosphorus (sp^3d) in the equatorial (sp^2) and apical (pd) directions is oversimplified.

A definite answer for the different phosphorus hybrids in the equatorial and apical direction of the TBP can be offered by the generation of $\cdot P(OCH_2CH_2)_3N^+BF_4^-$ (**1a,b**) with the odd electron as the equatorial and apical ligand, respectively. For this purpose a single crystal of $HP(OCH_2CH_2)_3N^+BF_4^-$ (**2**) was grown by slow crystallization from anhydrous acetonitrile.[23] The structure of this precursor was definitely established as a TBP configuration. The two types of radicals were obtained under different irradiation conditions, either with X-ray or UV laser irradiation. The results of these irradiations are outlined in the Scheme I. The radicals were measured by means of ESR spectroscopy.

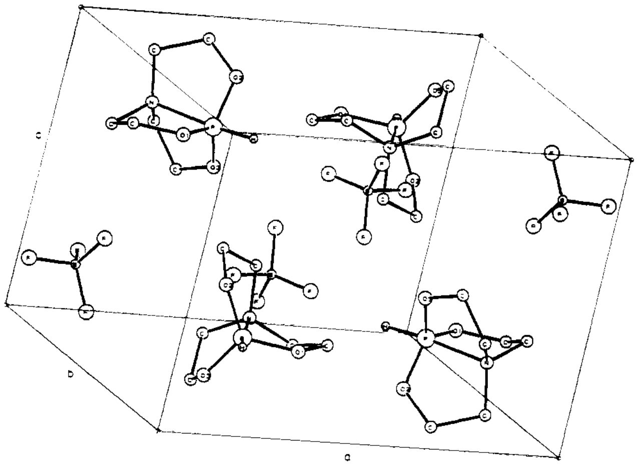


Figure 1. ORTEP drawing of the unit cell of 2.

Radical **1a** is obtained by X-ray irradiation at 77 K, yielding hyperfine couplings for phosphorus (a_p) which are observed when the magnetic field is parallel with the orbital in which the unpaired electron is located, $a_p(\parallel)$ = 1120 G and when it is perpendicular, $a_p(\perp)$ = 930 G. At 193 K **1a** disappears and **1b** is obtained. In both cases two differently oriented radicals are present, which is the result of two orientations of **2** in the unit cell (see Figure 1).

By means of the Laue back-reflection method[24] it could be established that $a_p(\parallel)$ of **1b** is oriented almost along the apical ligand with the N–P–· angle being 168°, thus resulting in a TBP configuration with the odd electron in the apical position.[25] The anisotropic phosphorus hyperfine couplings are $a_p(\parallel)$ = 888 G and $a_p(\perp)$ = 753 G. It has been ascertained that the directions of the $a_p(\parallel)$ components of **1a** and **1b** differ by 35° or the complementary angle of 55°, which infers a TBP configuration with the odd electron in the equatorial position (**1a**).[26] With the obtained phosphorus hyperfine couplings it is possible to evaluate the isotropic (3s) and anisotropic (3p) contributions. Since the discrimination between $3p_z$ and $3d_{z^2}$ orbital occupation in the phosphoranyl radicals is not possible, the anisotropies observed for phosphorus will be considered to arise from 3p contributions only. With the help of the isotropic hyperfine coupling a_p(iso) and the anisotropic contribution B which result from $a_{iso} = {}^1/_3(a_\parallel + 2a_\perp)$ and $B = {}^1/_2(a_\parallel - a_{iso})$, an estimate of the s and p character can be shown as the spin densities ρ_s and ρ_p, respectively: $\rho_s = a_{iso}/a_0$ and $\rho_p = B/B_0$. From calculations one derives for phosphorus a_0 = 3640 G and B_0 = 103 G.[27]

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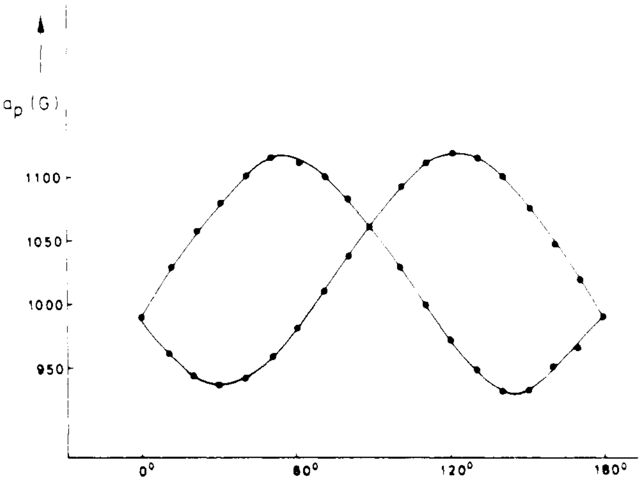

Figure 2. Rotation around the *c* axis for **1a**.

The complete results are given in the Table I.

Thus in **1a**, $\rho^{P}_{3s} = 0.27$ and $\rho^{P}_{3p} = 0.61$, whereas for **1b**, $\rho^{P}_{3s} = 0.21$ and $\rho^{P}_{3p} = 0.43$. *From these values for both stereoisomers it is clearly shown that the amount of s character in the apical bonds is reduced in comparison with the equatorial bonds.* It should be emphasized that the single-crystal experiments are necessary to obtain directional information. Moreover, rather complex ESR spectra may arise from powdered samples because of superimposed hyperfine couplings due to atoms linked to the central atom. In contrast, in single crystals the parallel and perpendicular features are separated on rotation.

Discussion

Both stereoisomers **1a** and **1b** offer the unique possibility to study the contribution of the 3s and 3p character of phosphorus in a TBP configuration for the different hybrids in the equatorial and apical direction. The difference in 3s spin density in favor of the odd electron in an equatorial ligand with respect to the corresponding one in the apical ligand is in agreement with the well-established fact that in the five-coordination of phosphorus the distribution of the ligands cannot be spherically symmetrical. *On the other hand, it must be emphasized that the remarkable degree of s character in the apical ligands enables the description of the phosphorus hybridization via the* p_z *and* d_{z^2} *orbitals to account for the apical ligands, and this combined with three* sp^2 *orbitals in the equatorial plane gives an illusive picture.* Discrimination between $3p_z$ and $3d_{z^2}$ orbital occupation in the phosphoranyl radicals is not possible. Therefore, the anisotropics observed for phosphorus will be considered to arise from 3p contributions only. The results obtained certainly support the physical and chemical properties of phosphorus in a TBP configuration. It discriminates between the equatorial and apical ligands in a subtile way by a small overbalance of s character in the equatorial position. For **1a** the spin density on phosphorus is 0.88. From the observed spin density in **1b** including the apical nitrogen one obtains 0.69. Apparently, the remaining spin density is distributed over the equatorial oxygen atoms. The mechanistic aspects for the formation of the radical products resulting from the primary processes induced by UV and high-energy quanta will not be discussed here in detail. It seems that excited **2** results in a TBP configuration with the P–H linkage in an equatorial position from which the radical **1a** is formed. Trapped electrons in the matrix, induced by X-ray irradiation, which return to **2** lead to **1b**.

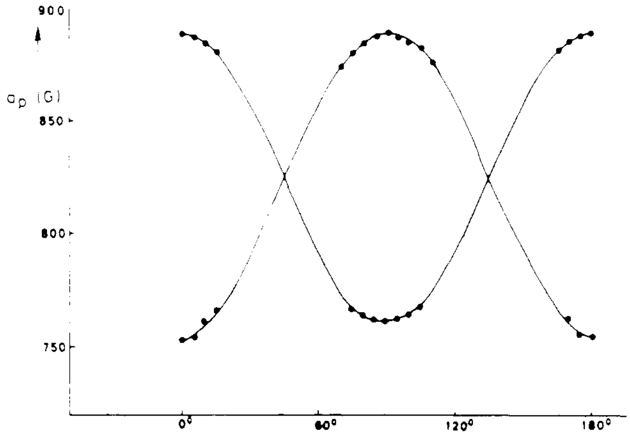

Figure 3. Rotation around the *c* axis for **1b**.

Experimental Section

The ESR spectra were recorded on a Varian E-4 spectrometer with variable-temperature auxiliary equipment. Irradiation experiments were carried out with X-ray or UV laser ($\lambda = 193$ or 248 nm) irradiation. The starting compound **2** was obtained via the procedure as outlined by Verkade et al.[23] A single crystal was obtained by slow crystallization from anhydrous acetonitrile. Crystal alignment was performed by the Laue back-reflection method by using Cu Kα radiation.[24] The rotating crystal method, which is very similar to the Debye–Scherrer method, is used for rotating the single crystal around the principle *c* axis (see Figure 1). For the radicals **1a** and **1b** the changes in the a_p value as a function of the rotations around the *c* axis are also given (see Figures 2 and 3).

Reflection spots are only expected when Debye-Scherrer 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 (0*kl*) 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 reflection. 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 Debey–Scherrer camera occupies the positions of the cylinders enclosing the cones, 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. 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 μ is obtained by $\tan \mu = h/r$. Thus the value of $a = n\lambda/\sin \mu$ is obtained if the crystal is rotated around the *a* axis. Similarly, rotation around the *b* or *c* axis gives the value of *b* or *c*, respectively.

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Registry No. **1a**/**1b**, 74304-90-8; **2**, 58418-99-8.