Stereoisomerization of the $\dot{\mathrm{P}}(\mathrm{OCH_2CH_2})_3\mathrm{N^+BF_4^-}$ Radical: a Single-crystal E.S.R. Study

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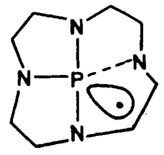
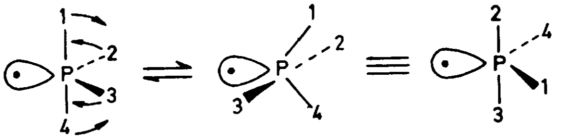
Summary The $\dot{\mathrm{P}}(\mathrm{OCH_2CH_2})_3\mathrm{N^+BF_4^-}$ radical with the unpaired electron in an apical position of the trigonal-bipyramidal (TBP) structure is generated by *X*-irradiation *via* an intermediate TBP structure in which the unpaired electron is located in an equatorial position.

The nature of the unpaired electron in phosphoranyl radicals has been the subject of extensive debate. Initially the unpaired electron was regarded as a fifth (phantom) ligand in an equatorial position of a trigonal-bipyramidal structure (TBP-*e*).[1] Subsequently it was thought to be delocalized in a σ^* orbital of the phosphorus–ligand linkages, either in a TBP (*e.g.* $^-\dot{\mathrm{O}}\mathrm{PCl_3}$)[2] or in a C_{3v} structure (*e.g.* $\mathrm{Ph_3\dot{P}Cl}$).[3] In contrast, we established recently the *ligand* nature of the unpaired electron in phosphoranyl radicals by correlation of single-crystal e.s.r. studies with *X*-ray results.[4,5]



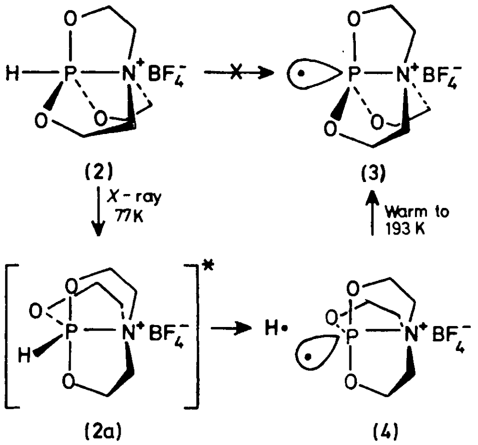
(1)

Moreover, the unpaired electron was shown to be capable of residing in either apical or equatorial positions of a TBP structure. Furthermore a striking example was provided by the dynamic behaviour of the phosphoranyl radical (**1**) in the solid state at low temperature, in which the ligands were shown to exchange uniquely *via* an M-1 Berry pseudorotation mechanism (Scheme 1), with the unpaired electron acting as the pivot.[6]



Scheme 1

We now report the temperature-dependent e.s.r. spectra of the radicals derived from (**2**) by *X*-irradiation. On *X*-irradiation of a single crystal of (**2**) at room temperature radical (**3**) was observed (Scheme 2).[5] Two orientations are present which are perpendicular. The anisotropic phosphorus coupling constants $a(\mathrm{P}_{\|})$ 888, $a(\mathrm{P}_{\perp})$ 753 G indicate a spin density of 0·21 in the phosphorus 3s orbital and 0·43 in its 3p orbital. Additional hyperfine coupling was observed due to ^{14}N, $a(\mathrm{N}_{\|})$ 21·2, $a(\mathrm{N}_{\perp})$ 22·7 G, the $a(\mathrm{N}_{\mathrm{iso}})$ = 22·2 G indicating a spin density of 0·05 in the 2s orbital of nitrogen. The small anisotropic contribution (0·5 G) can be attributed to dipole–dipole interaction. Alignment of the single crystal by means of the Laue back reflection method showed the maximum phosphorus hyperfine coupling constant to be oriented approximately along the initial P–H linkage, the N–P–• angle being 168°. Therefore, it is concluded that radical (**3**) possesses a TBP structure with the unpaired electron and nitrogen in the apical positions (TBP-*a*).



Scheme 2

Surprisingly, *X*-irradiation of a single crystal of (**2**) at liquid nitrogen temperature (77 K) led to the spectrum of radical (**4**) exclusively with $a(\mathrm{P}_{\|})$ 1120, $a(\mathrm{P}_{\perp})$ 930 G, while ^{14}N splitting was not resolved. From these values we calculated a value of $a(\mathrm{P}_{\mathrm{iso}})$ = 993 G, indicating that the phosphorus 3s spin density is 0·27, while the anisotropic contribution places 0·61 of the spin density in its 3p orbital, which gives a total spin density of 0·88 on phosphorus. Again on rotation about the crystallographic *c*-axis, two orientations are present, with an angle between their $a(\mathrm{P}_{\|})$ components of 70°. On raising the temperature, these signals start to disappear irreversibly at 193 K, and those of compound (**3**) become apparent.

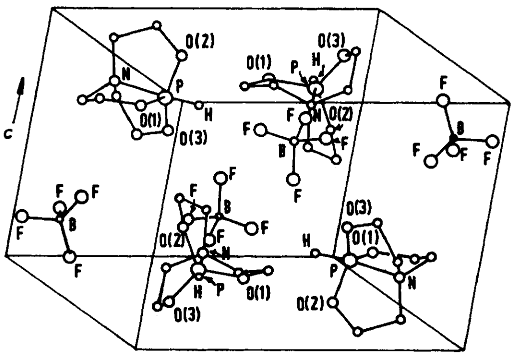
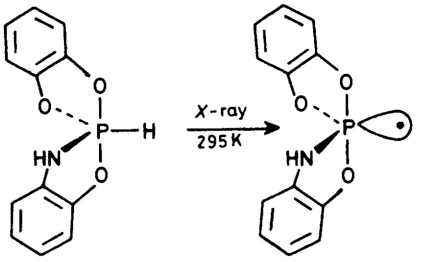


Figure. ORTEP drawing of the unit cell of (**2**).

In the plane perpendicular to the crystal mounting axis (c-axis) (*cf.* Figure) the directions of the $a(\mathrm{P}_{\parallel})$ components of (**3**) and (**4**) differ by 35° or the complementary angle 55°; this angle cannot be assigned uniquely owing to the presence of two orientations for both radicals in the unit cell.[7] Nevertheless, both angles apply to a TBP-*e*-like geometry. Furthermore, the a(P) values of (**4**) are consistent with those we found for the closely related phosphoranyl radical (**5**) generated by X-irradiation of compound (**6**) which is known to possess a nearly perfect TBP structure as inferred from X-ray analysis.[8] The radical (**5**) has $a(\mathrm{P}_{\parallel})$ 1061, $a(\mathrm{P}_{\perp})$ 869 G, while $a(\mathrm{N}) < 5$ G is not resolved; these values are reasonably close to those found for (**4**).



(6) (5)

The irreversible rearrangement of (**4**) to (**3**) at higher temperatures shows that (**3**) is the thermodynamically more stable. This may be explicable on the basis of release of ring strain by the five-membered ring in structure (**4**) which spans two equatorial positions. However, the driving force for the intermediate formation of structure (**4**) is less obvious. Its geometry can only be formed prior to P–H bond scission, *i.e.* (**2**) → (**2a**), since at the radical stage only the reverse reaction was observed. Most probably, during X-irradiation compound (**2**) absorbs energy photochemically to produce compound (**2a**)* in the excited state which subsequently undergoes P–H bond scission with retention of configuration to produce (**4**).

These processes may be understood on the basis of balancing electronic energy *vs.* strain energy. Apparently, the TBP structure of (**2a**) with the hydrogen atom in an equatorial position is electronically favoured over that of (**2**) with the hydrogen in an apical position. In contrast, the strain energy in structure (**2a**) is greater than that of (**2**). However, the latter factor may be less important in (**2a**)*, since in this excited state the bond lengths are increased. Therefore, in (**2a**)* the electronic factor has become dominant. In this way the irreversible retro-rearrangement of (**4**) to (**3**) is also consistent.

The work presented in this paper confirms our earlier results which established the ligand character of the unpaired electron in phosphoranyl radicals. Moreover, it is an unique example of stereoisomerization of a TBP-*e* to a TBP-*a* structure.

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