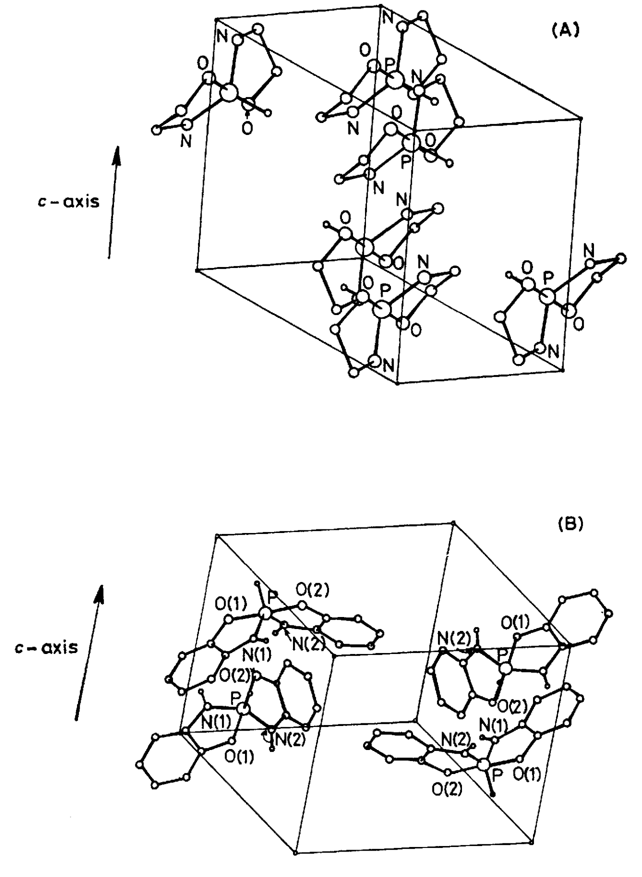
Single Crystal E.S.R. Study of the 1,6-Dioxa-4,9-diaza-5-phospha(v)spiro-[4.4]nonan-5-yl and the 1,6-Dioxa-4,9-diaza-2,3,7,8-dibenzo-5-phospha(v)spiro[4.4]nona-2,7-dien-5-yl Radicals

By JOEP H. H. HAMERLINCK,* PIETER SCHIPPER, and HENK M. BUCK
(*Eindhoven University of Technology, Department of Organic Chemistry, The Netherlands*)

Summary The unpaired electron in two oriented phosphoranyl radicals (title) with trigonal bipyramidal geometry is located in an equatorial position.

THE structure of phosphoranyl radicals in solution has usually been described as trigonal bipyramidal (TBP), with the unpaired electron in an equatorial position. This is based on the isotropic phosphorus hyperfine coupling constant (a_P) and theoretical predictions. However, from the very scarce studies concerning oriented phosphoranyl radicals, conflicting ideas arise about the location of the unpaired electron. Berclaz *et al.* have found a C_{3v} structure for $Ph_3\dot{P}Cl$ with the unpaired electron in an anti-bonding P–Cl orbital.[1] In contrast, for $\dot{P}F_4$ and $Cl_3\dot{P}O^-$ a TBP structure has been found with the unpaired electron located in the axial axis, suggesting a Rundle three-centre non-bonding orbital.[2,3] Furthermore, we recently observed, for the radical[4] $\dot{P}(OCH_2CH_2)_3N^+BF_4^-$, the unpaired electron to be located in an apical position.



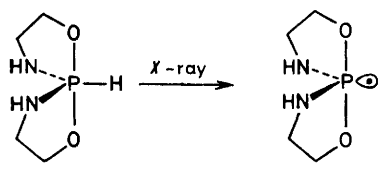
Figure

In order to get more insight into the location of the odd electron in TBP structures, we performed an e.s.r. study of X-ray-irradiated single crystals of (**1**) and (**2**). The data are collected in the Table.

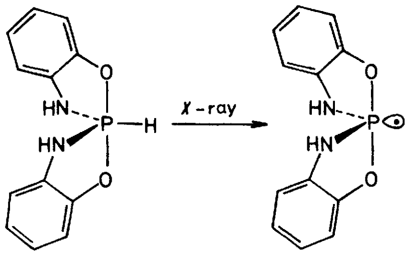
Table

Radical	(**1a**)	(**2a**)
$a_{P\perp}/G$	735	808
$a_{P\parallel}/G$	893	960
a_P^{iso}/G	788	859
B^P/G	53	50
ρ^P_{3s}	0·22	0·24
ρ^P_{3p}	0·49	0·47
p:s	2·2	2·0
$g_\perp$	2·005	2·008
$g_\parallel$	1·988	1·983

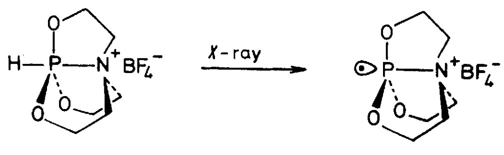
It appears that both systems have axial symmetry. Rotating the single crystal of (**1**) around the crystallographic c-axis revealed the maximum anisotropy ($a_{P\parallel}$) to be perpendicular to this axis. This corresponds with the direction of the P–H linkage in its precursor as determined by X-ray diffraction analysis[5] [Figure (A)]. Similarly, a correspondence was found for the orientation of the unpaired electron and the initial P–H linkage in (**2**). In this case, the angle between $a_{P\parallel}$ and the crystallographic c-axis turned out to be 35°. This is in excellent accordance with the angle of the P–H bond with the c-axis, which has been determined[5] to be 36° [Figure (B)]. From these findings, it was concluded that the unpaired electron resides in an sp^2 hybrid orbital directed along the initial P–H linkage for both (**1a**) and (**2a**).



(1) (1a)



(2) (2a)



(3) (3a)

Recently we obtained e.s.r. data for a phosphoranyl radical (**3**) in a TBP configuration in which the unpaired electron occupies an apical position (**3a**),[4] but in spite of this different orientation, its anisotropic a_P values are very similar to those found for (**1a**). In contrast, the nitrogen splittings (a_N) are characteristic of their positioning *i.e.* 22 G for apical (**3a**) and less than *ca.* 5 G‡ for equatorial nitrogen (**1a**). Therefore, reliable structural assignments may only be made on the basis of both a_P and a_N. The reported isotropic a_P (807 G) and a_N (6·1 G) values for a closely related spirophosphoranyl radical[6] in solution both agree well with those that we have now found in the single crystal study of (**1a**). This indicates that its geometry in both environments is similar.

---

† The ORTEP drawings of the unit cell of (**1**) and (**2**) were kindly provided by Dr. G. J. Visser (Computing Centre of the Eindhoven University of Technology, The Netherlands).

‡ Estimated from line width, nitrogen hyperfine couplings were not resolved.

This investigation has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Advancement of Pure Research (ZWO).

(*Received, 9th May* 1980; *Com.* 493.)

[1] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Lett.*, 1975, **36**, 677.
[2] A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Mol. Phys.*, 1975, **30**, 1367.
[3] T. Gillbro and F. Williams, *J. Am. Chem. Soc.*, 1974, **96**, 5032.
[4] J. H. H. Hamerlinck, P. Schipper, and H. M. Buck, *J. Am. Chem. Soc.*, 1980, **102**, 5679.
[5] P. F. Meunier, R. O. Day, J. R. Devillers, and R. R. Holmes, *Inorg. Chem.*, 1978, **17**, 3270.
[6] D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans.* 2, 1973, 1416.