

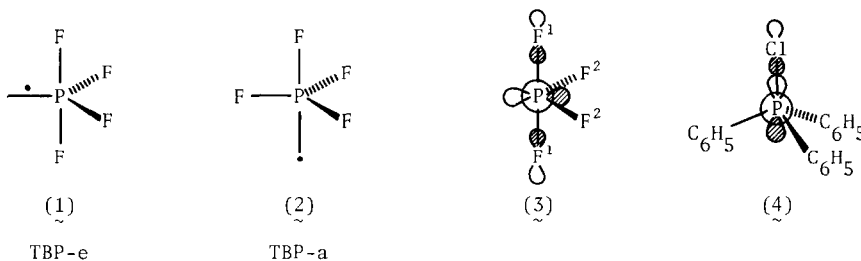
COMMENTS ON THE STRUCTURES OF PHOSPHORANYL RADICALS

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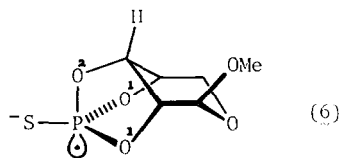
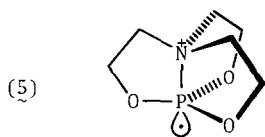
It is argued that the recent reports by Hamerlinck *et al.* of phosphoranyl radicals described as having TBP-a structures are misleading and that conclusions based on these assignments are unsubstantiated.

Since they were first proposed as transient reaction intermediates in 1957,¹ phosphoranyl radicals $X_4P\cdot$ have been investigated extensively by a number of research groups.^{2,3} Starting from a regular trigonal bipyramidal (TBP) phosphorane (*e.g.* F_5P), phosphoranyl radicals with C_{2v} or C_{3v} symmetry would be formed by 'instantaneous' homolytic cleavage of an equatorial or an apical P-F bond, respectively. These structures, shown in (1) and (2), have been labelled TBP-e and TBP-a by Howell and Olsen,⁴ because the unpaired electron may be thought of as *formally* occupying an orbital directed towards the missing ligand.



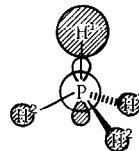
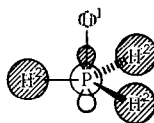
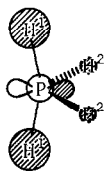
The E.S.R. spectrum of $F_4P\cdot$ trapped in a single crystal of F_3P shows clearly that this radical has a C_{2v} structure (3), in which the F^1PF^1 angle is close to 180° .⁵ The direction of maximum hyperfine coupling to F^1 is perpendicular to that of maximum phosphorus coupling and the atomic orbitals that make the major contribution to the SOMO are indicated in (3). This TBP-e type structure is also adopted by $Cl_3P\dot{O}$ ⁶ and by $Cl_2(RO)P\dot{O}$ ⁷ and in both these radicals the $Cl_{ap}PCl_{ap}$ angle is close to 180° . In contrast, the chlorotriphenylphosphoranyl radical adopts the structure (4), with local C_{3v} symmetry at phosphorus.^{8,9} The directions of maximum chlorine and phosphorus couplings are parallel and the SOMO is basically a 2-centre P-Cl σ^* orbital as indicated. Which of these structural extremes or whichever of the infinite number of intermediate geometries a particular phosphoranyl radical prefers will depend on the nature of the ligands attached to phosphorus.¹⁰

In recent papers by Hamerlinck *et al.*¹¹⁻¹³ E.S.R. spectroscopy has been used to study two phosphoranyl radicals which have been assigned the TBP-a structures shown in (5) and (6).



It was asserted that these radicals have geometries and electronic configurations that are novel and basically different from those of the species (3) and (4). It was proposed that the angles between bonds to apical and basal (equatorial) ligands in (5) and (6) are close to 90°. In their most recent paper,¹³ Hamerlinck *et al.* make the following statement: "we presume that the σ^* model, which concerns the excited state of the radical, will be less stable than a TBP-a structure".

One purpose of this note is to discuss the differences, imagined and real, between the various descriptions of structures with local C_{3v} symmetry at phosphorus and to propose alternative interpretations for the results reported by Hamerlinck. The general patterns^{2,3} of bonding in phosphoranyl radicals are illustrated by the results of MNDO-UHF calculations for $H_4P\cdot$.¹⁴ Calculations for the optimised C_{2v} structure reported by Howell and Olsen⁴ show that the SOMO is predominantly the 3-centre anti-bonding orbital shown in (7). This structure illustrates the important characteristics of TBP-e radicals, namely relatively long P-Ligand_{ap} bonds and large spin populations on, and hence large hyperfine coupling with, apical ligand atoms.



$d(P-H^1)$	= 1.641 Å	1.426 Å	1.591 Å
$d(P-H^2)$	= 1.423 Å	1.591 Å	1.426 Å
$H^1\hat{P}H^1$	= 172°	$H^1\hat{P}H^2 = 90°$	117°
$H^2\hat{P}H^2$	= 97°	120°	101°

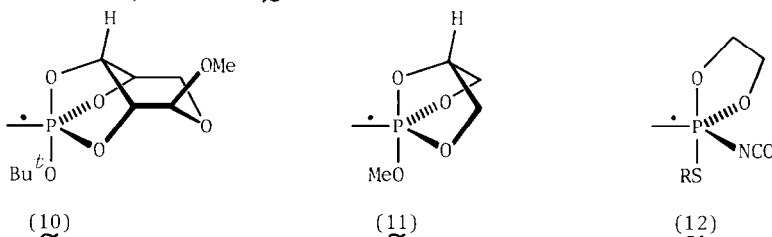
In contrast, the SOMO for Howell and Olsen's TBP-a (C_{3v}) structure (8) is a 4-centre orbital which is antibonding between the basal atoms; the unpaired electron is concentrated on phosphorus and the basal ligands. This appears to be the type of structure envisaged by Hamerlinck *et al.* for (6), since they state¹² that "the O^2PS angle probably will decrease from 121° (in the parent sulphide) to 90°" and¹³ "the remaining spin density will be distributed over the equatorial ligands".

If the bond lengths in (8) are reversed and the H^1PH^2 angle is optimised within C_{3v} symmetry this leads to structure (9). The spin population has been transferred from the basal hydrogens to the apical ligand and the unpaired electron now resides in what is essentially a 2-centre P-H σ^* orbital.

Hamerlinck *et al.*^{1,3} assert that "one of the most interesting observations of the single-crystal E.S.R. studies was the determination of a TBP-a structure for (5) and (6)". We believe that no convincing evidence has been offered to support the conclusion that (5) is other than a C_{3v} species analogous to (4) and (9), with the unpaired electron concentrated in a P-N σ^* orbital and an NPO angle substantially greater than 90° .^{10,15} The nitrogen splitting (22.2 G) for (5) is similar to that found for TBP-e type radicals in which the nitrogen ligands are in apical sites² and is not as expected if the unpaired electron resides on phosphorus and the three basal oxygens in an orbital analogous to the SOMO of (8)

Turning to (6), if we accept that the O^2P -angle is close to 162° it is a *complete assumption* to set the O^2PS angle equal to 90° . Instead of decreasing from " 121° to 90° " this angle could equally well increase after electron addition to the parent sulphide. In phosphoranyl radicals of low symmetry there is no reason why the direction of maximum ^{31}P hyperfine coupling should coincide with or make any particular angle with the molecular framework or with the direction of maximum ligand hyperfine coupling.^{16,17} However, it is still helpful to classify a radical with respect to the nearest regular geometry and electronic configuration.

We suggest that the O^2PS angle is not 90° , as shown in (6), but significantly larger and that this radical can be regarded as intermediate^{16,17} in structure between a $\sigma^*(P-S)$ and a TBP-e species in which O^2 and S^- are quasi-apical substituents. If (6) were a TBP-a radical, with large spin populations on the three basal ligands, it would appear unlikely that the splitting from the single quasi-apical ring proton (5 G) should be so close to the values shown by the TBP-e type species (10)¹² and (11)¹⁸ (7 and 5.1 G, respectively), since a splitting of



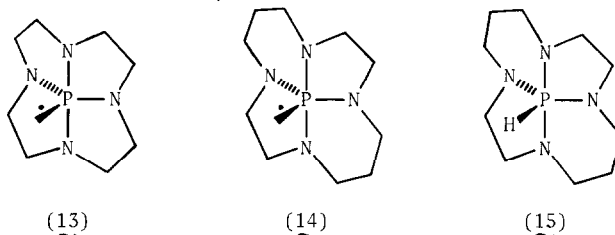
this magnitude is indicative of significant spin density on the oxygen attached to C-H group. At first sight the presence of the S^- substituent might be thought to militate against our proposed structure, because of the formal negative charge on this ligand and the general preference of electropositive substituents for equatorial sites in TBP-e species. However, factors other than substituent electronegativity are important in determining apicophilicity and the counter-cation, whatever its nature, is probably close to the S^- group. Indeed, there is no evidence that the substituent is not an SX group.

Similar distortion from TBP-e (RS and NCO apical) towards $\sigma^*(P-S)$ has been suggested to account for the low value of $\alpha(N)$ shown by $(EtO)_2\dot{P}(NCO)SMe$.¹⁰ This low value was commented on by Hamerlinck *et al.*,^{1,3} although they chose to ignore our explanation. In the same paragraph, they suggest that (12; R = Me or Bu^tCO) might adopt a TBP-a structure (with RS basal) by analogy with the "well-established" structure (6). We leave the reader to judge how well-established is the TBP-a structure (6).

Finally, we wish to comment on the rapid apical-equatorial ligand exchange that is often observed for TBP-e type phosphoranyl radicals.² We have proposed¹⁰ that this exchange takes place *via* an intermediate with local C_{3v} symmetry at phosphorus and such a mechanism is consistent

with the observed mode 4² ligand exchange reported for a monocyclic radical:¹⁰ the isoenergetic Berry pseudorotation (mode 1) with the 'unpaired electron' as pivot was not detected. This C_{3v} intermediate could be of the general type (8) or (9) and we have proposed that it is the 2-centre σ* species (9), because this type of electronic configuration is well-authenticated^{8, 9, 16, 17} rather than (8) in which the unpaired electron is concentrated on phosphorus and the three basal ligands.

Hamerlinck *et al.* have reported¹³ line shape effects in the E.S.R. spectrum of (13), trapped in a rigid matrix, which are attributable to apical-equatorial nitrogen ligand exchange. Mode 4 ligand exchange is not possible for (13), because of the constraints imposed by the tetracyclic



ligand system, and mode 1 exchange was observed in this special case. It is surprising that no solution spectra were reported for (13), since such spectra assigned to (14) were described in the same paper.¹³ The radical (14) was apparently generated by photolysis of di-*t*-butyl peroxide in the presence of (15), but we note that 18% of the P(III) tautomer of (15) (which should be very reactive towards addition of Bu^tO·) would be present along with the phosphorane at ambient temperature.¹⁹ The radical (14) is reported¹³ to "disappear *irreversibly*" as the temperature is raised "without rendering the four nitrogens equivalent". How can this *irreversible* loss of the spectrum mean anything other than that (14) is no longer being formed (presumably because of reagent depletion) when the temperature is subsequently lowered? It is not a property of the radical itself.

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