

Electronic Structure of Phosphoranyl Radicals^{1a}Tomas Gillbro^{1b} and Ffranco Williams*^{1c}

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Abstract: Anisotropic esr studies are reported on the radical anion of phosphorus oxychloride. Two of the chlorine ligands are magnetically equivalent over a wide range of hyperfine anisotropy and the results are interpreted in terms of a trigonal-bipyramidal (C_{2v}) structure for POCl_3^- with the equivalent chlorines occupying the axial positions. The anisotropic hfs for the axial chlorines corresponds to a spin density of 0.29 in each of the two ligand $3p_\sigma$ orbitals while the isotropic ^{31}P hfs gives a $3s$ spin density of 0.38 on the central atom. The large spin densities in the $3p_\sigma$ orbitals of the axial chlorines are contrary to the predictions of valence-bond theory but accord well with the results of MO calculations on related radicals. These findings indicate that the unpaired electron in phosphoranyl radicals occupies an MO of a_1 (or a_1') symmetry whose main component can be represented as a Rundle three-center nonbonding orbital involving the axial ligand orbitals modified by mixing with the symmetry-allowed $3s$ and $3p$ orbitals of the phosphorus atom in an antibonding combination. This description also accounts for the previously unexplained observation of large isotropic hyperfine couplings for hydrogen ligands in the axial positions of organo-phosphoranyl radicals. The effects of ligand electronegativity in both axial and equatorial sites are discussed for a variety of phosphoranyl radicals and it is concluded that the change in the spin density distribution on the phosphorus atom can be explained without recourse to severe distortions from trigonal-bipyramidal geometry.

Phosphoranyl radicals such as PF_4 ,² PCl_4 ,³ POCl_3^- ,⁴ PO_4^{4-} ,⁵ and $\text{P}(\text{O}-t\text{-Bu})\text{R}_3$ ($\text{R} = \text{H}$, alkyl)⁶ present a challenge to theories of valence since nine electrons must be accommodated in the valence shell of the phosphorus atom. According to traditional valence-bond theory, the phosphorus atom in these radicals achieves quinquivalency by valence-shell expansion and the unpaired electron occupies one of the five sp^3d -hybridized orbitals which are directed from the central atom to the vertices of a trigonal bipyramid. On the other hand, MO calculations⁷ for the structurally related molecule SF_4 (trigonal bipyramidal geometry and C_{2v} symmetry) suggest that the unpaired electron in PF_4 and related radicals occupies a doubly noded $3a_1$ orbital with more than half the total spin density concentrated in the σ orbitals of the ligands in the axial positions. This $3a_1$ orbital is weakly antibonding between the axial ligands and the central atom, but otherwise it corresponds closely to the nonbonding orbital in Rundle's simple model of three-center bonding.⁸

Hitherto it has not been possible to adequately test

the different predictions of these rival theories against experiment since reliable esr data have been available only for the isotropic hyperfine splittings which are not a satisfactory guide to the overall spin density distribution for σ radicals. The well-known theoretical study of PF_4 by Higuchi⁹ showed that by assuming C_{2v} symmetry and the participation of phosphorus $3d$ orbitals the isotropic hyperfine splittings for phosphorus and the two pairs of equivalent fluorines could be accounted for by either valence-bond or MO approaches. Both theoretical treatments indicated that the fluorines with the larger isotropic hfs occupy the positions close to the axial arrangement in a slightly distorted trigonal bipyramidal structure. Thus it would seem from Higuchi's analysis that the isotropic hyperfine splittings are equivocal regarding the two different theoretical descriptions but this is not entirely surprising since the relatively large isotropic fluorine splittings arise from small spin densities (*ca.* 0.01–0.02) in the fluorine $2s$ orbitals and Higuchi was mainly concerned with the estimation of the splittings produced by direct interaction. However, the possibility of large spin densities in the $2p_\sigma$ orbitals of the axial fluorines was not discussed by Higuchi.⁹

Our interest in the general problem was aroused by the recent finding¹⁰ that the valence-isoelectronic species SO_2Cl_2^- could be properly described by MO theory as a trigonal bipyramidal structure rather than as a radical anion complex, the latter description having been proposed earlier¹¹ in order to explain the large anisotropy of the chlorine hfs which could not be reconciled with a conventional valence-bond model. In this contribution we report the spin density distribution obtained from anisotropic esr studies on the radical anion of phosphorus oxychloride. Our results are in much better agreement with the Rundle MO description than with valence-bond theory.

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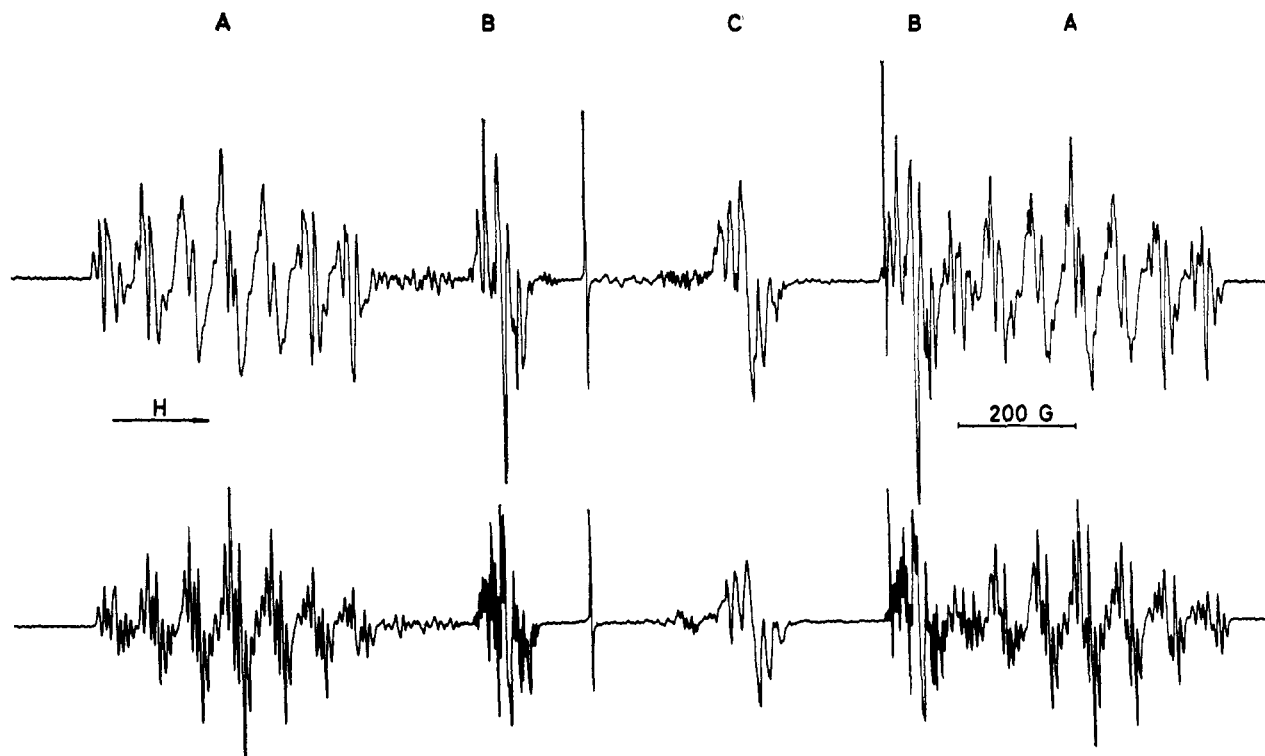


Figure 1. First-derivative esr spectra of a γ -irradiated single crystal of phosphorus oxychloride at -196° . The spectra refer to two directions of the magnetic field differing by 10° in the rotation plane perpendicular to the tube axis.

Experimental Section

Single crystals of POCl_3 were grown at -6° in Suprasil tubes using a technique previously described for single-crystal growth at subambient temperatures.¹² The samples remained transparent after immersion in liquid nitrogen, at which temperature they were γ irradiated (dose, ca. 1 Mrad) and transferred to the cavity of the esr spectrometer without being exposed to visible light. ESR spectra were recorded at X band with a Varian E-9 instrument. The microwave power was usually kept below 0.05 mW to minimize saturation effects. The angular dependence of the spectrum was studied by rotating the sample tube in turn about each of the three mutually perpendicular directions held at right angles to the magnetic field. The rotation about the tube (z) axis was performed using a conventional dewar arrangement at liquid nitrogen temperature in the rectangular E-231 cavity. Rotations about the x and y axes were carried out using a specially designed holder which fitted into the variable-temperature accessory (11-mm i.d.) of the large-access cylindrical E-235 cavity. The sample temperature was ca. -180° in this latter assembly. The hyperfine splittings and g factors were determined using the hydrogen atom doublet as an internal standard¹¹ and applying corrections according to the Breit-Rabi expression.

It might be noted here that contrary to the observations detailed below on the very marked anisotropy of the POCl_3^- spectrum, Begum and Symons^{4b} have reported that the esr spectrum of a single-crystal sample of γ -irradiated POCl_3 showed no orientation dependence although the resolution was noticeably improved over that of a powder sample. Such results indicate to us that their sample was not a single crystal but probably a polycrystal with some degree of preferential orientation. It has been frequently observed¹¹ that the esr spectra of such aligned crystals show resolution enhancement and positional invariance of the anisotropic spectral features with respect to sample orientation.

Results

Figure 1 shows esr spectra with extensive hyperfine structure indicative of at least three major species, two of which possess large ^{31}P doublet splittings. The inner lines (B) corresponding to the smaller ^{31}P doublet

were selectively removed on photobleaching. Here we are concerned only with the outer lines (A) which can be assigned to POCl_3^- from a detailed consideration of the anisotropic hyperfine structure, as described below. The correctness of this assignment is also substantiated by radiation-chemical experiments¹³ showing that the corresponding features in the polycrystalline spectrum are reproduced in the powder spectrum of a γ -irradiated solution of POCl_3 in a 2-methyltetrahydrofuran glass, the latter method of preparation being highly specific for products of electron attachment reactions.¹⁴

The outer lines in the upper spectrum of Figure 1 consist basically of a ^{31}P doublet of septets with a quartet substructure which is most clearly revealed for the low-field components of each septet. Additional fine structure in the lower spectrum recorded at a slightly different orientation has the effect of improving the septet resolution so that the intensity ratios are close to those expected (1:2:3:4:3:2:1 from the dominant $^{35}\text{Cl}^{35}\text{Cl}$ contribution) for hyperfine coupling to two equivalent chlorines. The substructure is attributable to a weaker interaction with a third chlorine, the additional lines in the lower spectrum probably resulting from the superimposition of forbidden transitions ($\Delta m_1 = \pm 2, \pm 1$) on the already complex first-order pattern which arises from permutations of the chlorine isotope combinations. In accord with theory for nuclei of spin $3/2$,¹⁵ previous esr studies of chlorine-containing radicals¹⁶ indicate that such forbidden transi-

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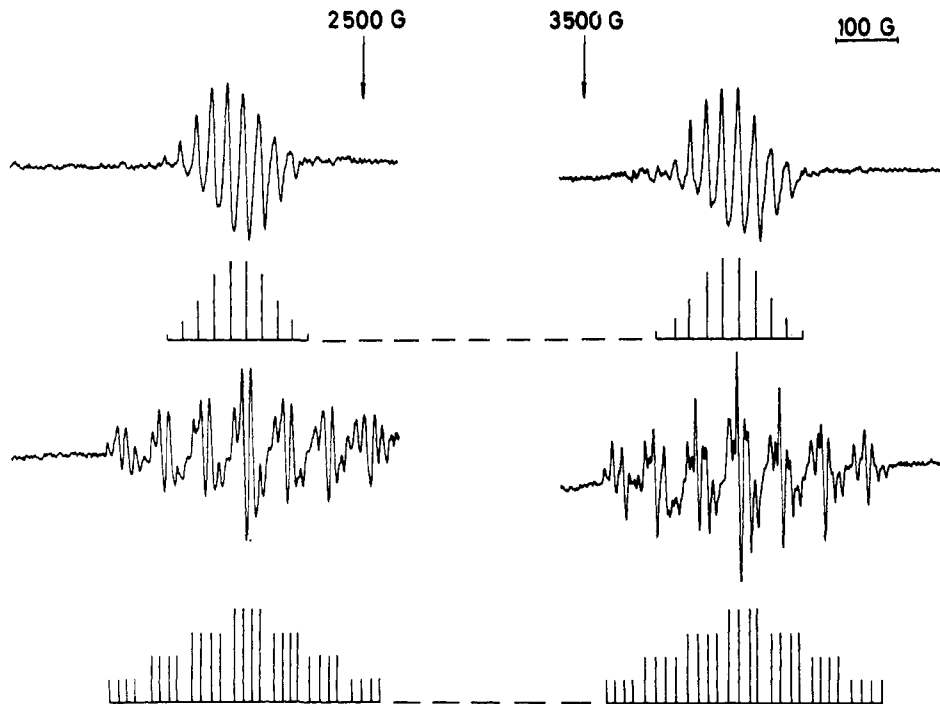


Figure 2. ESR spectra of POCl_3^- in a single crystal of phosphorus oxychloride showing anisotropy of chlorine hyperfine couplings. The upper spectrum ($g = 2.017$) shows equivalent couplings for three chlorines and was recorded with H parallel to the tube axis. The lower spectrum ($g = 2.008$) was taken with H perpendicular to the tube axis and corresponds to the largest value of the hfs for the two equivalent chlorines in this rotation plane.

tions are intense and show considerable angular dependence when the hfs tensor is comparable to the nuclear electric quadrupole resonance frequency, a situation which applies here to the third chlorine since the frequency $\frac{1}{2}e^2qQ$ is 28.98 MHz for ^{35}Cl in POCl_3 at -196° .¹⁷

The anisotropy of the chlorine hyperfine couplings was studied first by rotation in the xy plane perpendicular to the tube (z) axis, the x axis representing the direction of the magnetic field for which the hfs of the two equivalent chlorines, $A_x^{35}(2) = 70$ G, was a maximum in this plane. The hfs of the third chlorine in the x direction, $A_x^{35}(1)$, was 15 G. Although the spectrum taken along the y direction could not be analyzed into a simple first-order pattern, the total width of the chlorine multiplet ($6A_y^{35}(2) + 3A_y^{35}(1)$) was only ca. 255 G as compared to 465 G for the x direction, indicating considerable anisotropy in the xy plane. The sample tube was then remounted and rotated in the xz plane, whereupon the maximum hfs for the two equivalent chlorines was observed again along the x direction. Assuming that the hfs tensor is axially symmetric (see below), this suggests that the x component is the parallel principal value. In addition, a particularly simple spectrum was obtained with the magnetic field along the z axis (Figure 2), the chlorine multiplet structure consisting of a ten-line pattern with intensity ratios close to the 1:3:6:10:12:12:10:6:3:1 distribution for equal couplings to all three chlorines ($A_z^{35}(2) = A_z^{35}(1) = 25$ G).

Since the above results demonstrate that two of the chlorines are magnetically equivalent over a wide range of hyperfine anisotropy, these ligands must occupy the axial positions in a trigonal bipyramidal structure for

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POCl_3^- and the hfs tensor is expected to have approximately cylindrical symmetry. Accordingly, if we take $A^{35}(2)$ in the x and z directions to be the parallel and perpendicular values, respectively, with positive signs, the anisotropic component $B_{\parallel}^{35}(2) = 30$ G and a spin density of 0.29 is calculated¹⁸ to reside in a 3p orbital on each of the two chlorine atoms in the axial positions. These ligand spin populations are much too large to be interpretable solely in terms of spin-polarization effects resulting from the presence of the unpaired electron in an orbital on the phosphorus atom. Consequently, the only reasonable conclusion is that direct population of the chlorine p orbitals directed along the Cl-P-Cl axis must be involved. Regarding the third chlorine, the smaller magnitude of the coupling and anisotropy are consistent with its location in an equatorial position with a p-orbital spin density of less than 0.1, at least part of which could arise indirectly from spin densities in neighboring orbitals.

Turning now to the results for the central atom, the ^{31}P hfs of 1434 G in the xz plane was isotropic within experimental error (± 10 G) and the Breit-Rabi corrected value is 1371 G which corresponds¹⁹ to a spin density of 0.38 in the phosphorus 3s orbital. The anisotropy of the ^{31}P hfs also appeared to be quite small in the xy and yz planes. These results are consistent with interpretations of the polycrystalline spectrum⁴ in terms of an isotropic ^{31}P coupling, but caution is necessary here because relatively small ^{31}P anisotropies are not clearly revealed in powder spectra where there is hyperfine coupling to other nuclei as in the

(18) Calculated assuming $B_{\parallel} = 105$ G for unit spin density in a 3p orbital of ^{35}Cl : D. Schoemaker, *Phys. Rev.*, **149**, 693 (1966).

(19) Calculated assuming $A_{\text{iso}} = 3640$ G for unit spin density in a 3s orbital of ^{31}P : P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967, p 21.

present case. Moreover, we must also recognize that ^{31}P anisotropy can go undetected even in single-crystal spectra when first-order interpretations are not possible at certain orientations owing to the general complexity of the hyperfine pattern. Nevertheless, the negative results obtained here do suggest that the ^{31}P anisotropy is much too small to be consistent with valence-bond models in which the unpaired electron occupies an sp^2 (equatorial) or sp^3d orbital on the central atom.

The sum of the experimental spin densities for the axial chlorine ligand orbitals ($0.29 \times 2 = 0.58$) and the phosphorus $3s$ orbital (0.38) is 0.96 or close to unity so it is interesting to compare these results with the spin density distribution suggested by MO theory. A trigonal bipyramidal structure for POCl_3^- has C_s point symmetry and a qualitative MO treatment places the unpaired electron in the $4a'$ orbital. The composition of this orbital is expected to be qualitatively similar to the $3a_1$ HOMO in SF_4 ^{7,20} and the $2a_1'$ HOMO in PF_5 ⁷ or PH_5 ²¹ the most important contribution coming from the axial ligand orbitals which participate in the σ bonding. This is illustrated by the VESCF calculations for the $3a_1$ orbital in SF_4 ,⁷ the orbital composition corresponding to a spin density of 0.35 in the $2p_\sigma$ orbital for each of the two axial fluorines in SF_4^+ . Therefore, there is good qualitative agreement between these MO calculations and the experimental data for POCl_3^- regarding the important contribution of the axial ligand orbitals. As might be expected for such a rough analogy, the extent of agreement is less satisfactory for the contribution made by the $3s$ orbital of the central atom, the VESCF calculations indicating a spin density of 0.06 for SF_4^+ as compared to the experimental value of 0.38 for POCl_3^- . However, much closer accord with experimental data for the $3s$ contribution of the central atom is seen in the results of recent CNDO/2 calculations on PF_4 and PCl_4 .²² Significantly, these latter calculations also predict a relatively large spin density (ca. 0.20) in each of the axial ligand p_σ orbitals.

Discussion

The present results for POCl_3^- parallel those obtained previously for the closely related 33 valence-electron species SO_2Cl_2^- ^{10,11} in showing the presence of two anisotropically equivalent chlorines which must necessarily occupy the axial positions in a trigonal-bipyramidal structure. As far as we are aware, this study provides the first direct demonstration of ligand hyperfine anisotropy in the esr spectrum of a phosphoranyl radical. It also illustrates the obvious superiority of the single-crystal approach as compared to the indirect determination of anisotropy from a powder spectrum. In fact, the polycrystalline esr spectrum of POCl_3^- does not reveal anisotropic features and was analyzed simply in terms of isotropic chlorine couplings⁴ although the line widths are typical of solid-state spec-

tra. However, it now becomes clear that the apparently isotropic hfs of ca. 67 G deduced from the powder spectrum closely reflects the parallel value of 70 G obtained here. The absence of distinguishable perpendicular features is not altogether surprising in view of the negative results obtained with Cl_2^- and SO_2Cl_2^- ,¹¹ each of these species also possessing two equivalent chlorines with an axially symmetric hfs tensor. Essentially, this situation comes about because the chlorine quadrupole interactions are stronger in the direction normal to the bond axis¹⁵ resulting in deviations from the first-order pattern and the loss of well-defined features for this perpendicular orientation. Thus we conclude that the isotropic line shape of the chlorine septets in the powder spectrum of POCl_3^- is an accidental result brought about by a combination of the above effect with the additional broadening induced by the relatively small ^{31}P hfs anisotropy.

The clarification of the chlorine hfs anisotropy afforded by this single-crystal study ($A_{\parallel}^{35}(2) = 70$ G; $A_{\perp}^{35}(2) = 25$ G) leads to a value of 40 G for $A_{\text{iso}}^{35}(2) = \frac{1}{3}(A_{\parallel}^{35}(2) + 2A_{\perp}^{35}(2))$, the isotropic hfs for the two equivalent chlorines in POCl_3^- . This result falls within the range of 31 to 47 G for the isotropic chlorine splittings obtained directly from the solution esr spectra of a variety of organic chlorophosphoranyl radicals²³ and therefore confirms the suggestion made by Griller and Roberts²³ that the chlorine ligands (either one or two) in these radicals are held rigidly in the axial positions. Indeed, it was the disagreement with the larger value of ca. 67 G previously reported⁴ for the apparently isotropic hfs of the axial chlorines in POCl_3^- which led these authors to consider the alternative possibility that the observed coupling in the chlorophosphoranyl radicals is an average value resulting from the fast exchange of the chlorine ligands between the axial and equatorial positions, although kinetic and thermodynamic considerations argued strongly against this proposition. Furthermore, the compatibility now demonstrated between the single-crystal and the solution esr spectra reinforces the main conclusion²³ regarding the apicophilicity of the chlorine ligands in the chlorophosphoranyl radicals. This tendency for the more electronegative ligands to assume the axial (apical) sites is a basic prediction of MO theory^{8,21} because of the high electron density at these sites.

Turning now to consider the spin distribution in phosphoranyl radicals, the novel finding presented here is the large spin density of 0.29 in each of the two $3p_\sigma$ orbitals belonging to the axial chlorine ligands of POCl_3^- . We note immediately the similarity of this result to the corresponding spin density of 0.31 for the isostructural species SO_2Cl_2^- .^{10,11} More pertinent to this discussion, however, is the apparent agreement shown in Table I between the above values and the hydrogen $1s$ spin density of the strongly coupled proton in phosphoranyl radicals containing one or more hydrogen ligands. These radicals were prepared by the addition of *tert*-butoxyl radicals to phosphine, methylphosphine, and dimethylphosphine, and their esr spectra could be consistently interpreted^{6a} by assigning one of the hydrogen ligands to an axial position, the other being occupied by the more electronegative *tert*-but-

(20) R. D. Willett, *Theor. Chim. Acta*, **2**, 393 (1964). In the qualitative MO treatment by Willett, the $3a_1$ orbital of SF_4 is described as essentially an sp^2 hybrid on the central atom. As we suggested earlier on the basis of our experimental results for SO_2Cl_2^- ,¹⁰ Willett's ordering seems to be incorrect here and his descriptions of the $2a_1$ and $3a_1$ orbitals should be interchanged to bring them into line with the results of Brown and Peel.⁷

(21) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

(22) D. Kilcast and C. Thomson, *J. Chem. Soc., Faraday Trans. 2*, **68**, 435 (1972).

(23) D. Griller and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1339 (1973).

Table I. Experimental Hyperfine Parameters (G) and Spin Density Distributions^a for Phosphoranyl and Related Radicals

Radicals	Central atom	Axial ligand(s)			Equatorial ligand(s)				
		A_{iso}	ρ_{3s}	A_{iso}	B_{\parallel}	ρ_{ns}	A_{iso}	ρ_{ns}	
PF ₃ ^b	³¹ P	1330	0.365	¹⁹ F(2)	282	0.016	¹⁹ F(2)	59	0.003
SOF ₂ ^c	³³ S	263	0.270	¹⁹ F(2)	252	0.015	¹⁹ F(1)	51	0.003
POCl ₃ ^{-d}	³¹ P	1371	0.376	³⁵ Cl(2)	40	0.024	³⁵ Cl(1)	ca. 18	0.011
SO ₂ Cl ₂ ^{-e}	³³ S	ca. 215	0.22	³⁵ Cl(2)	30.9	0.018	O(2)		
(C ₂ H ₅ O)PCl ₂ (O- <i>t</i> -Bu) ^f	³¹ P	1145	0.315	³⁵ Cl(2)	34.1	0.020			
(C ₂ H ₅) ₂ PCl(O- <i>t</i> -Bu) ^f	³¹ P	794	0.218	³⁵ Cl(1)	38.9	0.023	C ₂ H ₅ (2)		
PH ₃ (O- <i>t</i> -Bu) ^g	³¹ P	626.7	0.172	¹ H(1)	139.6	0.275 ^h	¹ H(2)	10.8	0.021
CH ₃ PH ₂ (O- <i>t</i> -Bu) ^g	³¹ P	631.5	0.174	¹ H(1)	139.6	0.275 ^h	¹ H(1)	9.8	0.019
(CH ₃) ₂ PH(O- <i>t</i> -Bu) ^g	³¹ P	631.4	0.174	¹ H(1)	142.9	0.282 ^h	CH ₃ (2)		

^a Calculated using the compilation of magnetic resonance parameters for atomic orbitals given in ref 18 and 19. ^b Reference 2c. ^c J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973). ^d This work. ^e References 10 and 11. ^f Reference 23. ^g Reference 6a. ^h Calculated using $A_{\text{iso}} = 506.9$ G for the hydrogen atom.

oxyl group. In contrast to the 1s spin density of 0.28 for the axial hydrogen, the coupling to the equatorial hydrogen(s) corresponds to a spin density of only ca. 0.02. Similarly, the total 3s and 3p spin density for the equatorial chlorine ligands in POCl₃⁻ is estimated to be less than 0.1, a value which probably represents an upper limit for polarization effects resulting from unpaired spin in the orbitals of the phosphorus atom. So we reach the significant conclusion in accord with the application of Rundle's MO theory^{7,8,20,21} that the unpaired electron is largely distributed over the σ orbitals of the axial but not of the equatorial ligands, irrespective of the electronegativities of these ligands. It will be interesting to see if the closeness of the agreement between the hydrogen and chlorine σ spin densities in the axial positions carries over to other ligand atoms or groups, but to obtain this information will require single-crystal studies on additional radicals of this type.

Assuming the generality of the results presented here, the larger isotropic splitting constants for the axial as compared to the equatorial fluorines in PF₃ are readily rationalized in terms of an intraatomic indirect interaction involving the larger spin populations resident in the axial ligand p_{σ} orbitals. Although Higuchi noted⁹ (see ref 16 of his paper) that a contribution to the isotropic fluorine splitting would be expected from intraatomic and interatomic indirect interactions, *i.e.*, spin-polarization effects from the unpaired electron in fluorine 2p and phosphorus orbitals, his calculations are concerned with the direct interaction. Of course, both the direct and indirect effects would contribute to the larger axial splittings if the small proportion of 2s admixture into the σ orbitals of the axial and equatorial fluorines is the same for both sets of ligands or is greater for the axial pair. This is a difficult problem which cannot be resolved here but we feel that this short discussion illustrates the possible ambiguities inherent in the structural interpretation of isotropic splittings for ligands other than hydrogen.

Although we are mainly concerned in this paper with the interpretation of ligand hyperfine couplings, the isotropic ³¹P hfs of phosphoranyl radicals is known to depend strongly on the nature of the ligands, and the change in the 3s spin density on the central atom as a function of ligand electronegativity has been discussed previously^{3,6b} in terms of an electrostatic effect. According to this interpretation which seems to be based on the VSEPR principle,²⁴ a lower electronegativity re-

duces the repulsion between the ligands leading to a distortion of the trigonal-bipyramidal structure toward a more closed square-pyramidal (C_{4v}) configuration with a consequent decrease in the s character of the orbital of the unpaired electron. However, this type of distortion does not explain why the appreciable spin density in the σ orbitals of the axial substituents (Table I) seems to be unaffected nor does it account for the marked difference between the couplings (and therefore the σ spin densities) of the axial and equatorial hydrogens in the spectra of the phosphoranyl radicals derived from the phosphines.

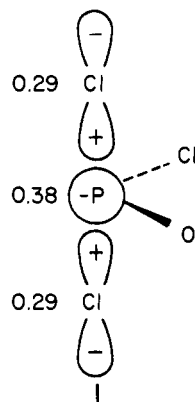
A more reasonable explanation of the electronegativity effect for the axial ligands can be based on the MO description adopted earlier. Since the unpaired electron occupies an antibonding orbital between the central atom and the axial ligands, an increase in the electronegativity of the ligand should force more spin density into the phosphorus 3s orbital, as observed. The only difficulty here is that it is not immediately obvious why there should be a larger combined spin density in the phosphorus 3s and axial ligand σ orbitals when these ligands are more electronegative. In this connection, the results in Table I show a deficiency of ca. 0.3 in the total spin density for the organic phosphoranyl radical derived from phosphine so there is a need for anisotropic esr data to ascertain whether the remaining spin density resides in the 3p orbital of the central atom which can contribute to the 3a₁ MO in radicals of C_{2v} symmetry. An indication that the spin density deficiency is located in this particular orbital is provided by the observation of ³¹P anisotropy in the powder spectrum of the radical CH₃P(OCH₃)₃ produced in a γ -irradiated trimethyl phosphite glass.²⁵ For this radical $A_{\parallel}^{31} = 885$ G and $A_{\perp}^{31} = 725$ G giving $2B^{31} = 107$ G and $A_{\text{iso}}^{31} = 778$ G, the latter being in satisfactory agreement with the value of 783 G reported for the same radical in solution.^{6b} These results correspond to spin densities of ca. 0.5 and 0.21 in the phosphorus 3p and 3s orbitals, respectively. Thus we may tentatively conclude from rather limited data that increasing the electronegativities of the axial ligands has the net effect of withdrawing spin density from the 3p into the 3s orbital of phosphorus, the spin densities in the σ orbitals of the axial ligands remaining approximately constant.

Regarding the role played by the electronegativities of the equatorial substituents in determining the 3s spin

(24) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).(25) T. Gillbro, C. M. L. Kerr, and F. Williams, *Mol. Phys.*, in press.

density on the phosphorus, this is clearly a secondary effect in terms of the qualitative MO approach adopted here since there is negligible spin density in the σ bonding orbitals of the equatorial ligands. Nevertheless, the availability of the phosphorus 3s orbital to the unpaired electron is expected to be influenced by the composition of the sp hybrid orbitals used by phosphorus for equatorial bonding. By a simple argument due to Pauling,²⁶ p orbitals are utilized preferentially in sp² bonding from the central atom to a more electronegative atom or group thereby releasing more of the s orbital for occupation by the unpaired electron. This reasoning accounts for the well-established trend whereby A_{iso}^{31} increases with the greater electronegativity of the equatorial ligand,^{3,6,23} as it also does for the correlation between A_{iso}^{31} in the phosphoranyl radicals and the spin-spin coupling constant $^1J_{\text{P-H}}$ in their parent hydrides.²⁷ As pointed out to us by a referee, POCl_3^- constitutes an apparent exception to this rule in that a decrease in the electronegativity of an equatorial substituent (O^- vs. Cl) leads to an increase of 150 G in A_{iso}^{31} as compared to the value for PCl_4 . However, the replacement of the two equatorial chlorines in PCl_4 by the alkoxy groups as in *t*-BuO(EtO)PCl₂ results only in the relatively small decrease of A_{iso}^{31} from 1217 to 1145 G,^{3,23} suggesting that the electronegativity difference between chlorine and oxyl substituents in the equatorial positions has a relatively minor effect and that this consideration may be outweighed by other factors in the case of POCl_3^- . In marked contrast, the further replacement of the two axial chlorines in *t*-BuO(EtO)PCl₂ by ethoxyl groups leads to a reduction of A_{iso}^{31} from 1145 to 890 G.^{6b,23} Summarizing, electronegativity differences for both axial and equatorial substituents are seen to change the spin distribution between the 3s and 3p orbitals of phosphorus but there are indications that the spin densities in the axial ligand orbitals are not greatly affected. These observations can be rationalized without invoking the need for distortions from the trigonal bipyramidal geometry.

Essentially the present work furnishes experimental evidence that the unpaired electron in phosphoranyl radicals occupies a molecular orbital which can be represented as a Rundle three-center nonbonding orbital involving the axial ligand orbitals modified by mixing with the 3s orbitals of the central atom in an antibonding combination, as illustrated in structure I.

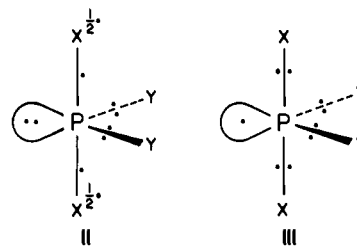


The unmodified Rundle description corresponds to

(26) L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).

(27) A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, *Mol. Phys.*, **25**, 989 (1973).

structure II for PY_2X_2 which can be usefully thought of



(compare ref 21) as constituted from PY_2 (a π radical) and two X ligands placed in the axial positions. In this extreme representation which preserves the octet of electrons around the phosphorus by forming a three-center two-electron bond along the X-P-X axis, the unpaired electron is distributed equally between the axial ligands with no contribution on the central atom. This structure should be compared with the usual valence-bond representation^{3,6} (III) in which the unpaired electron occupies a central atom sp^{3d} or sp² orbital with its axis in the equatorial plane. While both pictorial descriptions could be said to have some validity in terms of the experimental spin distribution, the valence-bond model is wrong not only in neglecting the ligand orbitals but also in always requiring a disproportionately large contribution from the p orbitals of the central atom. More seriously, the model is incorrigible. On the other hand, we have alluded already to the fact that the Rundle description is amenable through a more complete MO treatment^{7,20,21} to the inclusion of contributions from the symmetry-allowed 3s, 3p (two orbitals for C_s and one for C_{2v} symmetry), and 3d_{2z} orbitals of the central atom in the a₁ or a' orbital containing the unpaired electron.

Finally, a straightforward application of the three-center bond model to the SF_5 radical leads to the prediction of a C_{4v} square-pyramidal configuration analogous to that of ClF_5 ,²⁸ the sulfur atom and the two mutually perpendicular three-center nonbonding orbitals lying in or close to the basal plane containing the four fluorines. Adopting this geometry, a full MO treatment indicates that the unpaired electron in SF_5 occupies a 3a₁ orbital which may be analyzed into two localized components.²⁹ The first of these is a basal orbital derived by mixing all the 2p_σ orbitals of the four basal fluorines with the 3s orbital of the sulfur atom in an antibonding way, while the second component is perpendicular to the basal plane and represents the antibonding combination of the appropriate 3p_σ sulfur orbital and the 2p_σ orbital of the apical fluorine. The coefficients of the HOMO for ClF_5 indicate⁷ that these two components are of about equal importance but preliminary CNDO calculations on SF_5 ³⁰ suggest that most of the spin density is concentrated in the basal component which is the biaxial counterpart of the modified three-center orbital for phosphoranyl radicals. Thus with the same assumption about spin polarization as for the axial fluorines in PF_4 , we are immediately led to expect four strongly coupled equivalent fluorines in the esr spectrum of SF_5 . This is observed,³¹ the isotropic

(28) G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

(29) Compare the illustration of the LUMO (3a₁) orbital of PH_5 with C_{4v} symmetry.²¹

(30) K. Nishikida and F. Williams, unpublished work.

(31) J. R. Morton and K. F. Preston, *Chem. Phys. Lett.*, **18**, 98 (1973).

hfs of the four (basal) fluorines being 143 G whereas the coupling to the fifth (apical) fluorine is undetectable. In comparison, the valence-bond description of SF₅ involves an sp³d² octahedral configuration with the unpaired electron occupying one of the six equivalent hybrid orbitals. However, this model provides no obvious explanation of the small coupling to the fluorine ligand situated trans to the orbital of the unpaired electron.³¹ Thus it seems that MO treatments involving

multicenter bonding provide a better understanding of ligand hyperfine interactions in the esr of hypervalent (electron rich) phosphorus and sulfur radicals.

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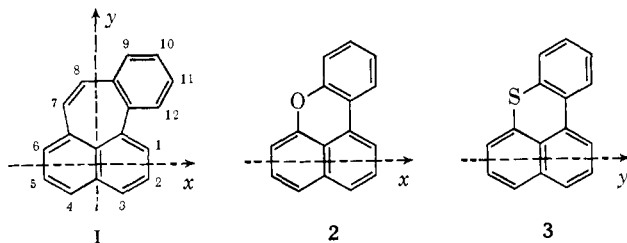
Excited States of Benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene and Its Heterocyclic Analogs. Polarization Directions and Magnetic Circular Dichroism

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Abstract: The combination of low-temperature absorption, polarized emission, and linear dichroism in stretched polyethylene and room-temperature magnetic circular dichroism has been used to obtain information about excited states of **1**. Assignments and comparison with related hydrocarbons and the heterocyclic analogs **2** and **3** are based on semiempirical π -electron calculations (PPP). The polarization directions of several lowest electronic transitions in **1**, which can in principle lie anywhere in the molecular plane, have been determined by a method which should be applicable to other molecules of low symmetry and are in good agreement with calculations. Signs of *B* terms in the MCD spectrum agree well with calculated signs for at least the lowest four transitions. In view of the low symmetry of **1**, this study represents one of the most stringent tests of the PPP model for hydrocarbons performed to date.

We have recently described² the synthesis of the nonalternant hydrocarbon benzo[4,5]cyclohepta[1,2,3-*de*]naphthalene (**1**) (benzo[*a*]pleiadiene) and now wish to report its spectral properties and compare them with those of related hydrocarbons and of the known isoconjugate analogs, benzo[*k*l]xanthene³ (**2**) and benzo[*k*l]thioxanthene (**3**) (in the form of its 6-methyl derivative⁴). The electronic absorption spectra of



1–3 are complex but bear a certain mutual resemblance (Figure 1). In each, three distinct absorption regions are immediately apparent: (I) 23,800–29,400 cm⁻¹ (log $\epsilon \cong 4$), (II) 31,200–35,700 cm⁻¹ (log $\epsilon \cong 3.8$), (III) near

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(2) J. F. Muller, D. Cagniant, and P. Cagniant, *Bull. Soc. Chim. Fr.*, 4364 (1972).

(3) M. Orchin, *J. Amer. Chem. Soc.*, **70**, 495 (1948).

(4) J. F. Muller and P. Cagniant, *C. R. Acad. Sci.*, **266**, 1072 (1968).

42,000 cm⁻¹ (log $\epsilon \cong 4.6$, with a shoulder at lower wave numbers). Our discussion of the similarity between the three compounds will be based on results of Pariser–Parr–Pople (PPP) type calculations.

Because of the low symmetry of **1**, its π – π^* transition moments can lie anywhere in the molecular plane. Both the experimental determination and quantum mechanical calculation of these directions represent a considerable challenge. Such measurement has only been made for very few conjugated hydrocarbons of C_s symmetry and then usually only for the lowest energy transition. The calculation is likely to be sensitive to the quality of the approximate wave functions used, whereas in the case of more highly symmetrical hydrocarbons it only depends on their symmetry. For molecules of C_s symmetry, little is known about the ability of the common π -electron methods to reproduce transition moment directions. This is not surprising considering the lack of experimental data with which comparison could be made.

We shall use a combination of the stretched sheet and polarized emission methods to determine the experimental polarization directions and the PPP method with a varying extent of configuration interaction for the calculated directions. Problems with parameters ought to be minimized in the case of hydrocarbons (such as **1**).