Reactions of Radical Anions. Part XVI.[1] Interpretation of the Hyperfine Coupling Constants of ^{31}P Nuclei in Phosphorus-containing Radical Anions

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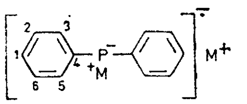
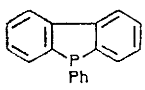
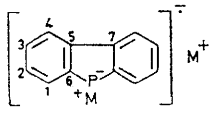
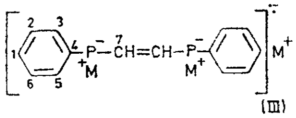
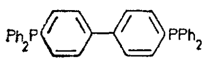
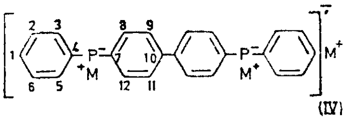
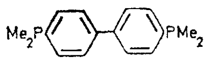
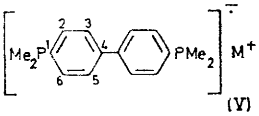
We have correlated the observed phosphorus coupling constants of five radical anions obtained from phosphine derivatives with the calculated spin densities, and find that $d\pi$–$p\pi$ interactions account satisfactorily for the results whereas $p\pi$–$p\pi$ interactions give results very different from those observed.

A NUMBER of papers have reported the e.s.r. spectra of the radical ions obtained when arylphosphines are treated with alkali metals in solvents such as tetrahydrofuran or dimethoxyethane.[2] In Table 1 we list five phosphorus-containing radical anions (I)—(V) together with the alkali metal and solvent used to generate them and the experimentally observed phosphorus and proton isotropic coupling constants. In this paper we have attempted to interpret the hyperfine coupling constants of ^{31}P nuclei in these radical anions. Although the e.s.r. spectra of a number of pentavalent phosphorus radical anions have also been reported[2e] we have confined our calculations to the five trivalent phosphorus-containing radical anions listed in Table 1.

TABLE 1

Hyperfine coupling constants for radical anions

Compound	Radical anion[b]	Metal	Solvent	Experimental coupling constant		Reference
				Position	A/G	
Ph$_3$P	 (I)	Li	DME[c]	1, 3, 5	2.30 ± 0.15	
		Na		2, 6	0.80	2(*a*), (*b*)
		K	THF[d]	P	8.36 ± 0.05	
		Cs		K	0.20	
	 (II)	Li		1, 3	2.40 ± 0.10	
		Na	THF	2		2*c*
		K		4		
		Cs		P	8.50 ± 0.10	
				M		
Ph$_2$PCH=CHPPh$_2$ (*cis* or *trans*)	 (III)			1, 3, 5	2.40 ± 0.05	
		Rb	THF	2, 6	0.90	
		Cs		7	3.55 ± 0.10[a]	1
				P	4.25 ± 0.10[a]	
				Cs	1.10	
	 (IV)	Li	THF	1, 3, 5, 8, 12	2.05[a]	
		Na	DME	2, 6	1.05[a]	
		K		9, 11	0.40[a]	2(*d*)
				P	3.05	
				M		
	 (V)	Na	THF	2, 6	2.20[a]	
		K		3, 5	0.44[a]	
				P	5.70	2*e*
				Me protons	0.0	
				M	0.88	

Most arylphosphines, *e.g.* Ph$_3$P, undergo cleavage reactions when treated with alkali metal, M, in THF or DME[2b] producing the arylphosphide and Ph$^-$M$^+$. Radical anion production is then effected by reduction of the arylphosphine by a further mole of the metal to give, *e.g.* $[Ph_2P^-M^+]^{-\cdot}\ M^+$.

[a] We have made these assignments on the basis of MO calculations. [b] Numbering systems have been adopted for ease in comparisons. [c] Dimethoxyethane. [d] Tetrahydrofuran.

RESULTS AND DISCUSSION

Proposed Model.—The e.s.r. results given in Table 1 show that the phosphorus atom is capable of transmitting unpaired electron spin density and thus must contribute an atomic orbital of suitable energy and symmetry to the system.

In the case of analogous nitrogen compounds a $2p_z$ orbital is usually invoked to effect conjugation with p_π systems. In the case of phosphorus, however, vacant $3d$ orbitals are also available for this purpose. p_π–d_π

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[1] Part XV, A. G. Evans, J. C. Evans, and D. Sheppard, *J.C.S. Perkin II*, 1975, 643.

[2] (*a*) M. W. Hanna, *J. Chem. Phys.*, 1962, **37**, 685; A. D. Britt and E. T. Kaiser; (*b*) *J. Chem. Phys.*, 1965, **69**, 2775; (*c*) *J. Org. Chem.*, 1966, **31**, 112; (*d*) M. H. Hnoosh and R. A. Zingaro, *Canad. J. Chem.*, 1969, **47**, 4679; (*e*) A. H. Cowley and M. H. Hnoosh, *J. Amer. Chem. Soc.*, 1966, **88**, 2595; (*f*) M. H. Hnoosh and R. A. Zingaro, *ibid.*, 1970, **92**, 4388; (*g*) F. Gerson, G. Plattner, and H. Bock, *Helv. Chim. Acta*, 1970, **53**, 1629.

Bonding has been invoked in the case of the phosphonitrilic chlorides,[3] and by Dewar *et al.*[4] To determine which of these two approaches conforms more to the results we have carried out two sets of calculations, one in which the eigenfunction for the odd electron was chosen assuming that each phosphorus atom contributed a lone pair of electrons and the other in which each phosphorus atom contributed an empty orbital.

Preliminary Molecular Orbital Calculations.—Simple Hückel molecular orbital (HMO)[5] and McLachlan[6] self-consistent field calculations were performed through a very large range of phosphorus coulomb and resonance integral parameters for radicals (I)—(V) (Table 1). The $3p_z$ orbital model was tested by including the lone pair electrons. Every combination of molecular orbital parameters used was found to give a grossly inaccurate picture of the spin density distribution for every radical for both the HMO and McLachlan calculations. Even an approximate agreement with the experimental results was unobtainable when the $3p_z$ model was used.

The $3d$ model was tested by leaving out the lone pair electrons, and performing the calculation over the same range of coulomb and resonance integrals. In this case the calculated spin density distribution in the $(m + 1)$ orbital matched exactly the distribution found experimentally, for a number of combinations of resonance and coulomb integrals. This agreement extended through all five radical anions and thus, for this series at least, the d orbital approach gives a good correlation with experiment.

Because of these results, we carried out more detailed calculations using the d orbital model exclusively.

The ^{31}P *Isotropic Coupling Constant.*—The d orbital model proposed in the previous section, allows for the delocalization of any unpaired electron spin density into a phosphorus $3d$ orbital giving rise to a spin density population at this atom. This kind of delocalisation, however, is unable to account for the ^{31}P hyperfine coupling, $A^{^{31}\mathrm{P}}$ since only orbitals of an s character have non-vanishing values at the nucleus, a condition essential to the observation of electron–nuclear hyperfine interactions.[7] We can bring about finite spin densities in the phosphorus $1s$, $2s$, and $3s$ AOs, which alone are responsible for $A^{^{31}\mathrm{P}}$, by 'spin polarization.' Application of the Karplus–Fraenkel theory[8] together with a number of modifications, leads to equations (1) and (2) relating spin densities to the experimental

$$A^{^{31}\mathrm{P}} = [Q^{\pi\mathrm{P}}_{1s} + Q^{\pi\mathrm{P}}_{2s} + Q^{\pi\mathrm{P}}_{\mathrm{LP}} + Q^{\pi\mathrm{P}}_{\mathrm{PM}} + 2Q^{\pi\mathrm{P}}_{\mathrm{PC}}]\rho^{\pi}_{\mathrm{P}} + Q^{\pi\mathrm{C}}_{\mathrm{PC}}[\rho^{\pi}_{\mathrm{C}_i} + \rho^{\pi}_{\mathrm{C}_j}] \quad (1)$$

$$A^{^{31}\mathrm{P}} = [Q^{\pi\mathrm{P}}_{1s} + Q^{\pi\mathrm{P}}_{2s} + Q^{\pi\mathrm{P}}_{\mathrm{LP}} + Q^{\pi\mathrm{P}}_{\mathrm{PC}} + 2Q^{\pi\mathrm{P}}_{\mathrm{PC'}}]\rho^{\pi}_{\mathrm{P}} + Q^{\pi\mathrm{C}}_{\mathrm{PC}}\rho^{\pi}_{\mathrm{C}_i} \quad (2)$$

coupling constants. Thus in our notation, for radicals (I)—(IV) we have equation (1) whilst for radical (V) we have (2). ρ^{π}_{P} and $\rho^{\pi}_{\mathrm{C}_i}$ or $\rho^{\pi}_{\mathrm{C}_j}$ represent the spin density on the phosphorus atom and the sp^2 hybridized carbon atoms bonded to it, respectively. E.s.r. measurements indicate that the unpaired π electron spin density on the carbon atoms of the methyl groups in radical (V) is *ca.* 0.0, and hence their effect has been neglected in the above equation. The parameters $Q^{\pi\mathrm{P}}_{1s}$ and $Q^{\pi\mathrm{P}}_{2s}$ allow for the π-$1s$ and π-$2s$ interactions respectively. $Q^{\pi\mathrm{P}}_{\mathrm{LP}}$ and $Q^{\pi\mathrm{P}}_{\mathrm{PM}}$ similarly account for the polarization of the electrons in the lone pair orbital and the phosphorus–metal bond, whilst the terms $Q^{\pi\mathrm{P}}_{\mathrm{PC}}$ and $Q^{\pi\mathrm{P}}_{\mathrm{PC}}$ allow for the spin polarization of the phosphorus–carbon bonding electrons. Finally $Q^{\pi\mathrm{C}}_{\mathrm{PC}}$ accounts for the spin polarization of the electrons in the phosphorus–carbon bonds by the unpaired π electron spin density on the neighbouring carbon atom.

Fortunately, substantial simplification is possible for both equations (1) and (2). First, the sum $Q^{\pi\mathrm{P}}_{1s} + Q^{\pi\mathrm{P}}_{2s} + Q^{\pi\mathrm{P}}_{\mathrm{LP}} + Q^{\pi\mathrm{P}}_{\mathrm{PM}} + 2Q^{\pi\mathrm{P}}_{\mathrm{PC}}$ can be replaced by a single constant, $Q^{\pi\mathrm{P}}_{(\mathrm{i})-(\mathrm{iv})}$ for radicals (I)—(IV), and equation (1) can then be rewritten as (3). Similarly, for the

$$A^{^{31}\mathrm{P}} = Q^{\pi\mathrm{P}}_{(\mathrm{i})-(\mathrm{iv})}\rho^{\pi}_{\mathrm{P}} + Q^{\pi\mathrm{C}}_{\mathrm{PC}}[\rho^{\pi}_{\mathrm{C}_i} + \rho^{\pi}_{\mathrm{C}_j}] \quad (3)$$

equation relating to radical (V), we may replace the sum $Q^{\pi\mathrm{P}}_{1s} + Q^{\pi\mathrm{P}}_{2s} + Q^{\pi\mathrm{P}}_{\mathrm{LP}} + Q^{\pi\mathrm{P}}_{\mathrm{PC}} + 2Q^{\pi\mathrm{P}}_{\mathrm{PC'}}$ by the single constant, $Q^{\pi\mathrm{P}}_{(\mathrm{v})}$, so that equation (2) now reads as (4). Finally,

$$A^{^{31}\mathrm{P}} = Q^{\pi\mathrm{P}}_{\mathrm{V}}\rho^{\pi}_{\mathrm{P}} + Q^{\pi\mathrm{C}}_{\mathrm{PC}}\rho^{\pi}_{\mathrm{PC}i} \quad (4)$$

many of the investigations for second row elements have found $Q^{\pi\mathrm{X}}_{\mathrm{X}} \gg Q^{\pi\mathrm{C}}_{\mathrm{XC}}$ such that the hyperfine splittings observed from nucleus X can equally well be described by an equation of the form (5). The usefulness of both

$$A^{\mathrm{X}} = Q^{\pi\mathrm{X}}_{\mathrm{X}}\rho^{\pi}_{\mathrm{X}} \quad (5)$$

approaches in predicting the isotropic hyperfine coupling constants of the phosphorus nucleus have been investigated in this work.

Molecular Orbital Calculations.—We have calculated the spin densities using the HMO method together with the corrections obtained by applying the approximate configuration interaction method of McLachlan, the relevant equation being (6) where ρ^{π}_{R} is the π spin

$$\rho^{\pi}_{\mathrm{R}} = C^2_{m+1,\mathrm{R}} - \lambda\sum_{\mathrm{S}}\pi_{\mathrm{RS}}C^2_{m+1,\mathrm{S}} \quad (6)$$

density on atom R, $C_{m+1,\mathrm{R}}$ and $C_{m+1,\mathrm{S}}$ are the coefficients of the atomic orbitals for atoms R and S respectively in the eigenfunction for the $(m + 1)$ molecular orbital, π_{RS} represents the atom–atom polarizability, and λ is a constant. The d orbital model has been used exclusively for the reasons outlined previously.

The coulomb and resonance integrals of α_{P} and β_{PC} of the phosphorus atom and the phosphorus–carbon bond respectively are expressed in equations (7) and (8).

$$\alpha_{\mathrm{P}} = \alpha_{\mathrm{C}} + h_{\mathrm{P}}\beta_{\mathrm{CC}} \quad (7)$$

$$\beta_{\mathrm{PC}} = k_{\mathrm{PC}}\beta_{\mathrm{CC}} \quad (8)$$

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[3] D. P. Craig and N. L. Paddock, *Nature*, 1958, **181**, 1052.

[4] M. J. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 1960, 2423.

[5] E. Hückel, *Z. Phys.*, 1931, **70**, 204.

[6] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

[7] E. Fermi, *Z. Phys.*, 1930, **60**, 320.

[8] M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **35**, 1312.

A further parameter δ, was tentatively introduced such that equation (9) applies where $\alpha_{C(P)}$ represents the

$$\alpha_{C(P)} = \alpha_C + \delta h_P \beta_{CC} \qquad (9)$$

coulomb integral of the carbon atom bonded to phosphorus. This parameter should then allow for any inductive effect operating in the C–P bond due to the difference in electronegativity between phosphorus and carbon. A value of $\delta = +0.1$ was found to be quite reasonable.

The molecular orbital calculation for radical (V) was performed by treating the whole dimethylphosphinyl group as a heteroatom X. Such a procedure has been adopted elsewhere for other similar calculations [9,10] and seems justified in this case since the e.s.r. spectrum of the radical indicates little or no methyl proton splitting.[2e]

A computer program was developed which calculated the relevant spin densities for every combination of the following ranges of parameter: $\alpha_P = 0.00$ to -1.60, $\beta_{PC} = 0.10$—1.50, in any predetermined increment, Δ. The McLachlan correction was applied to the HMO values obtained from each combination of α_P and β_{PC} and the values of λ altered through the acceptable range of 1.00—1.20 in increments of $\Delta = 0.05$.

As a typical approach to each calculation, consider the case of the radical anion (III). An inspection of the proton coupling constants given in Table 1, shows that for this radical anion, an acceptable calculation must simultaneously provide that $\rho_1/\rho_{3,5} = R = 1.00$, and $\rho_7/\rho_1 = R' = 1.46$, where ρ_1, $\rho_{3,5}$, and ρ_7 are the unpaired π spin densities at positions 1; 3,5; and 7 respectively. Furthermore the values of these spin densities must fall within a range governed by the generally accepted limits of the McConnell σ–π parameter: Q^{H}_{CH} -20.0 to -30.0 G. Thus the calculated spin densities at the *ortho*- and *para*-carbon atoms in the phenyl groups attached to the phosphorus in this radical must lie between 0.120 0 (Q^{H}_{CH} -20.0 G) and 0.080 0 (Q^{H}_{CH} -30.0 G) to give the required proton splitting of 2.40 G. Similarly the calculated π spin densities of the carbon atoms of the ethylene group must lie between 0.175 0 (Q^{H}_{CH} -20.0 G) and 0.113 (Q^{H}_{CH} -30.0 G) to give the observed proton splitting of 3.50 G.

The simple Hückel calculation failed to give reasonable approximation to these criteria for any combinations of the parameters, so the more exact McLachlan method was adopted.

For radical anion (III) a value of $\lambda = 1.20$ was found to be most satisfactory. Figure 1 shows the computer drawn plot of the ratio $R = \rho_1/\rho_{3,5}$ (where ρ now represent McLachlan spin densities) for various coulomb and resonance integrals α_P and β_{PC} respectively. (Figure 1 shows only a few of the plots so as not to confuse the picture. In practice the increment of Δ, added to the coulomb integral was much smaller than 0.20.) For coulomb integrals between -1.60 and -0.80 (inclusive) the values of the spin densities fell well outside the acceptable range, even though the ratio R sometimes equalled 1. These values were consequently discarded. Between the values $\alpha_P = -0.70$ and 0.00, however, both criteria of range and ratio were approximately realised. In some cases two values of β_{PC} gave $R = 1.00$ for a particular coulomb integral (for example β_{PC} has two such values when $\alpha_P = -0.60$, see Figure 1). In each case where this occurred, however, only the larger value of β_{PC} gave spin densities which fell within the range requirements. These resonance integrals were then plotted against the corresponding coulomb integrals as shown by plot (i) in Figure 2. All values of α_P and β_{PC} lying on this line give $R = 1.00$ and also fall within reasonable range limits. Plot (ii) in Figure 2 was similarly constructed from values of α_P and β_{PC} which gave $R' = 1.46$ and again fell approximately within the range requirements. Where the two lines intersect, $R = 1.00$ and $R' = 1.46$ are simultaneously satisfied, and the relevant spin densities fall within approximate range requirements. The results obtained utilising this procedure are shown in Table 2. These spin densities would require Q^{H}_{HO} -31.7 G. This is somewhat higher than the normal value and the same occurred for all the radicals studied.

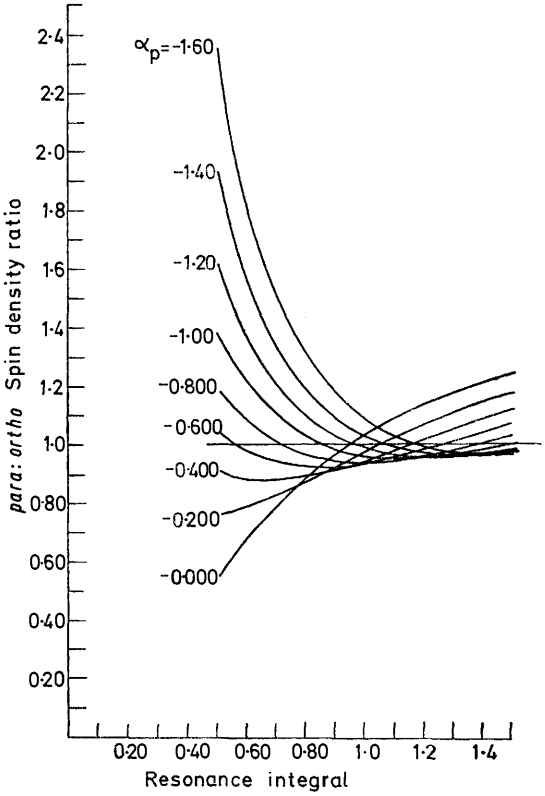

FIGURE 1 Dependence of *para* : *ortho* spin density ratio (R) on the coulomb and resonance integrals

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F. Gerson, J. Heinzer, and H. Bock, *Mol. Phys.*, 1970, **18**, 461.

[10] A. G. Evans, B. Jerome, and N. H. Rees, *J.C.S. Perkin II*, 1973, 2091.

In some cases several sets of α_P and β_{PO} values gave good fits to the criteria required of the calculated spin density values. Examination of Table 1 shows that the splitting constants of the protons bonded to the carbon atoms in the *ortho*- and *para*-positions in a phenyl group are approximately the same in each radical, *i.e.* 2.2 ± 0.20 G. Consequently, combinations of α_P and β_{PO} were chosen so that the spin densities in the *ortho*- and *para*-positions were approximately the same for each radical provided that they also gave reasonable agreement with the relevant ratio requirements.

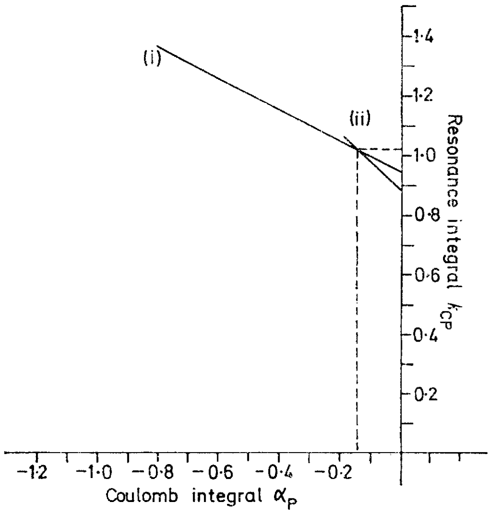

FIGURE 2 Computer plot of relationship between coulomb integral and resonance integral: (i) all values of α_P and β_{PO} give $R = 1.00$; (ii) all values of α_P and β_{PO} give $R' = 1.46$

Plotting the experimental proton hyperfine coupling constants against the corresponding spin densities calculated by this procedure according to the McLachlan relationship gave a good straight line. A least squares fit to the data gave Q^{H}_{CH} −26.75 G, a value which falls well within the generally accepted range of this parameter. Table 3 shows the best fit calculated spin densities, the ' experimental ' spin densities (using Q^{H}_{CH} as above) for such radicals, together with the molecular orbital parameters used. The corresponding values from the HMO calculations have also been included which show the poor agreement obtained using this method alone. Excellent agreement with experiment was found with λ values ranging between 1.0 and 1.2, and there was no need to revert to lower values (1.00 and 0.40) to increase the experimental–calculated correlation as has been done for similar calculations involving third row elements.[9,10]

Calculation of the σ–π Parameters.—(a) *Using the Karplus–Fraenkel relationship*. The calculated spin densities on the phosphorus and neighbouring atoms together with the experimentally obtained ^{31}P coupling constants may now be used to calculate the values of $Q^{\pi P}_{A}$, $Q^{\pi P}_{B}$, and $Q^{\pi C}_{PC}$ in equations (3) and (4). Substitution of the relevant values from Table 3 into equation (3) gives expressions (10)—(13) for the calculated ^{31}P splitting constants $A^{^{31}P}$ (calc) for radicals

$$A^{^{31}P}\ (\text{calc})\ (\text{I}) = Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}\, 0.6086 - Q^{\pi C}_{PO}\, 0.0807 \qquad (10)$$

$$A^{^{31}P}\ (\text{calc})\ (\text{II}) = Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}\, 0.6126 - Q^{\pi C}_{PO}\, 0.0700 \qquad (11)$$

$$A^{^{31}P}\ (\text{calc})\ (\text{III})\ Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}\, 0.1928 + Q^{\pi C}_{PO}\, 0.1124 \qquad (12)$$

$$A^{^{31}P}\ (\text{calc})\ (\text{IV}) = Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}\, 0.2326 - Q^{\pi C}_{PO}\, 0.0517 \qquad (13)$$

(I)—(IV). Similar substitution into equation (4) gives (14) for radical (V).

$$A^{^{31}P}\ (\text{calc})\ (\text{V}) = Q^{\pi P}_{(\text{v})}\, 0.3364 - Q^{\pi C}_{PO}\, 0.0363 \qquad (14)$$

The solution of equations (10)—(13) for radicals (I)—(IV) was effected by a least squares method. A computer programme was used to calculate $A^{^{31}P}$ (calc) (i) [(i) = (I)—(IV)] when the values of $Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}$ and $Q^{\pi C}_{PO}$ were varied through the ranges 0.0—30.0 and −30.0—30.0 G respectively, and in any pre-determined increments. $A^{^{31}P}$ (calc) (i) was then found for all combinations of $Q^{\pi P}_{(\text{i})\text{-}(\text{iv})}$ and $Q^{\pi C}_{PC}$ and the ' best ' values of these parameters taken as those which satisfied the least squares condition: $\sum_i [A^{^{31}P}\ (\text{calc})\ (\text{i}) - A^{^{31}P}\ (\text{exp})\ (\text{i})]^2 = \text{minimum}$. Such a procedure yielded the following values for the σ–π interaction parameters: $Q^{\pi P}_{(\text{i})\text{-}(\text{iv})} = 15.0 \pm 0.2$, $Q^{C}_{PC} = 10.6 \pm 0.40$ G, and substitution of Q^{C}_{PC} into equation (14) for radical (V) gave $Q^{\pi P}_{(\text{v})}$ 18.11 G.

(b) *Neglecting the contribution to* A$^{^{31}P}$ (exp) (i) *from the π spin density on neighbouring atoms*. The calculated π spin densities on the phosphorus atoms, together with the experimentally observed $A^{^{31}P}$ coupling constants were used to obtain a least squares fit to equation (5). This procedure yielded $Q^{\pi P}_{P}$ 14.43 G.

Comparison of the Calculations.—The results obtained by methods (a) and (b) were used to obtain values of $A^{^{31}P}$ (calc) (i) [(i) = (I)—(V)], which were then plotted against $A^{^{31}P}$ (exp) (i) [(i) = (I)—(V)]. Table 4 gives the experimental and calculated values for both the Karplus–Fraenkel and the unrefined calculations, whilst Figure 3 shows the experimental–calculated plots for both. (The line represents perfect correlation between theory and experiment *i.e.* slope = 1.0.)

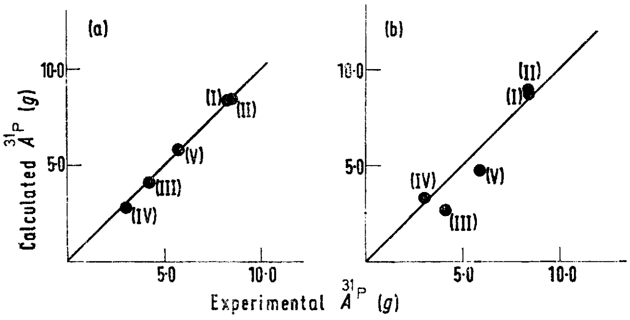

FIGURE 3 Plot of experimental against calculated coupling constants for phosphorus: (a) experimental–calculated plot; Karplus–Fraenkel relationship; (b) experimental–calculated plot; unrefined model

TABLE 2

Perfect correlation values for radical anion (III)

Position *	Calculated spin density (McLachlan)	R	R'	α_P	β_{PC}	λ	Other parameters
1, 3, 5	0.0956						
2, 6	−0.0299						
4	−0.0208	1.00	1.46	−0.17	1.04	1.20	$\delta = 0.10$
8	0.1115						
P	0.2443						

* See Table 1 for numbering system.

TABLE 3

Experimental and calculated spin densities for radical anions (I)—(V)

Radical anion	Position [a]	Experimental spin density (Q^H_H 26.75 G)	Calculated spin densities (McLachlan)	Calculated spin densities (Hückel)	$h_{^{31}P}$	k_{PC}	λ	Other parameters
(I)	1	0.0916	0.0996	0.0850				
	2	0.0299	−0.0337	0.00086				
	3	0.0916	0.0995	0.0816				$\delta = 0.10$
	4		−0.0354	0.0075	−0.40	0.80	1.00	
	5	0.0916	0.0995	0.0816				
	6	0.0299	−0.0337	0.00086				
	P		0.6086	0.4858				
(II)	1	0.0897	0.0858	0.0832				
	2		−0.0190	0.0109				
	3	0.0897	0.0854	0.0803				$\delta = 0.10$
	4		−0.0248	0.0140	−0.18	0.85	1.10	
	5		0.1014	0.0771				
	6		−0.0350	0.0082				$\beta_{5-7} = 0.80$ [b]
	P		0.6126	0.4529				
(III)	1	0.0897	0.0859	0.07535				
	2	0.0328	−0.0323	0.0017				
	3	0.0897	0.0859	0.0659				$\delta = 0.10$
	4		−0.0195	0.0143	−0.40	1.20	1.20	
	5	0.0897	0.0859	0.0659				
	6	0.0328	−0.0323	0.0017				
	7	0.1308	0.1319	0.1550				
	P		0.1928	0.1232				
(IV)	1	0.0766	0.0675	0.0582				
	2	0.0393	−0.0261	0.0001				
	3	0.0766	0.0718	0.0517				
	4		−0.0305	0.0005				
	5	0.0766	0.0718	0.0517				$\delta = 0.10$
	6	0.0393	−0.0261	0.0001	−0.10	1.10	1.20	
	7		−0.0212	0.0074				
	8	0.0766	0.0649	0.0498				
	9	0.0149	−0.0108	0.0102				
	10		0.0519	0.0468				
	P		0.2326	0.1697				
(V)	1		−0.0363	0.0098				
	2	0.0822	0.0844	0.0727				
	3	0.0164	−0.0169	0.0144	−0.14	1.10	1.15	$\delta = 0.10$
	4		0.0648	0.0677				
	P		0.3364	0.2484				

[a] See Table 1 for numbering systems. [b] Resonance integral for the C(5)–C(7) bond reduced to 0.8 to account for the twist in the rings induced by the *ortho*-substitution. Assuming $\beta = \beta_0\cos\theta$, where $\beta_0 = 1.0$, then calculation gives $\theta = 36° 48'$.

TABLE 4

Experimental and calculated phosphorus hyperfine coupling constants

Radical anion	Experimental phosphorus hyperfine coupling constant (G)	Calculated values (G)	
		Karplus–Fraenkel	Unrefined model
(I)	8.36 ± 0.05	8.36	8.78
(II)	8.40 ± 0.10	8.44	8.84
(III)	4.10 ± 0.10	4.08	2.78
(IV)	3.05	2.84	3.35
(V)	5.70	5.70	4.85

Using $Q^{\pi P}_{(i)-(iv)} = 15.0 \pm 0.2$, $Q^{\pi C}_{PC} = 10.6 \pm 0.4$, $Q^{\pi P}_{(v)} = 18.11$, $Q^{\pi P}_{P} = 14.43$ G.

Conclusions.—A comparison of the calculated and ' experimental ' spin densities shown in Table **3** illustrates the excellent agreement obtained when a *d* orbital model is used for the calculation. Although the actual nature of the bonding orbitals used may be a point for some discussion these results enable us to discount the possibility of p_π–p_π conjunction *via* participation of the lone pair orbital for this series of radicals.

The molecular orbital parameters used to obtain the ' best fit ' certainly fall within acceptable limits when compared to other ' heteroatom ' calculations.[11] In particular, the negative value of the phosphorus coulomb integral would be expected on electronegativity grounds. It should also be noted that the fact that the variation in α_P and β_{PC} is small for the five radicals reflects their structural similarity.

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[11] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.