

Phosphorus σ - π Spin Polarization Parameters

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Summary Experimental values of the σ - π spin polarisation parameters for phosphorus have been determined from a comparison of calculated spin densities and observed hyperfine coupling constants in several free radicals and ions containing phosphorus.

ALTHOUGH much work has been performed on estimating σ - π polarization (Q) parameters for magnetic nuclei such as ^{13}C , ^{14}N , ^{19}F *etc.* by comparison of experimental spin densities with calculated spin densities, lack of experimental data and useful theoretical calculations on phosphorus radicals have precluded estimation of the ^{31}P parameters. We have prepared the anions and cations of several heterocyclics containing phosphorus and in conjunction with theoretical calculations have estimated the Q parameters for phosphorus in these compounds.

and $\text{Pb}(\text{OAc})_4/\text{dimethoxyethane}$ oxidation]; all six were stable at room temperature. The anions of two phospholes [1-methyl-2,5-diphenylphosphole (D) and 1,2,5-triphenylphosphole (E)] were prepared² by Na/dimethoxyethane reduction at -60° . Comparison of the carbon $2p_z$ spin densities obtained from the experimental spectra of the phosphorin anions and cations with those calculated by the McLachlan method showed excellent agreement; the agreement in the phosphole anions was not quite as good.

Use of the one-parameter equation

$$A_{\text{F}}^{\text{exp}} = |Q_{\text{eff}}^{\text{P}}| \rho_{\text{P}}^{\text{calc}} \quad (1)$$

gave the values of $Q_{\text{eff}}^{\text{P}}$ in Table 1, where the average values are also given.

Although the errors in the calculated ρ_{P} values may be

TABLE 1

| System | | $\dagger A_{\text{F}}^{\text{exp}}$ | $\rho_{\text{P}}^{\text{calc}}$ | $ Q_{\text{eff}}^{\text{P}} $ | $ Q_{\text{eff}}^{\text{P}} _{\text{av}}$ |
|--------------------|-----|-------------------------------------|---------------------------------|-------------------------------|---|
| Phosphorin cations | (A) | 26.7 | 0.329 | 81.1 | |
| | (B) | 24.1 | 0.228 | 105.9 | 97.9 |
| | (C) | 24.2 | 0.227 | 106.6 | |
| Phosphorin anions | (A) | 26.9 | 1.067 | 25.2 | |
| | (B) | 30.4 | 0.779 | 39.0 | 31.7 |
| | (C) | 32.9 | 1.063 | 30.9 | |
| Phosphole anions | (D) | 23.5 | -0.035 | 671.4 | 725.4 |
| | (E) | 26.5 | -0.034 | 779.4 | |

\dagger Values in gauss.

The anions and cations of three phosphorins [2,4,6-tri-*t*-butylphosphorin (A), 2,6-di-*t*-butyl-4-phenylphosphorin (B), and 2,4,6-triphenylphosphorin (C)] were prepared by the method of Dimroth *et al.*¹ [K/dimethoxyethane reduction

rather large, the results do suggest that the average value of $Q_{\text{eff}}^{\text{P}+}$ is significantly higher than $Q_{\text{eff}}^{\text{P}-}$, which indicates a possible excess charge effect. The data of Cowley and Hnoosh⁵ on a series of phosphine anions confirm that the

high value obtained for $Q_{\text{eff}}^{\text{P}^-}$ for the phosphole anions is probably in error, presumably because of the very low negative values calculated for ρ_{P} . Using the data of ref. 3 and equation 1 with Hückel spin densities gives $|Q_{\text{eff}}^{\text{P}^-}| = 28.2\text{G}$, in good agreement with the value obtained for the phosphorin anions.

It was not possible to find evidence for an excess charge effect using a two-parameter equation.

$$A_{\text{F}}^{\text{exp}} = Q_{\text{FP}}^{\text{P}} \rho_{\text{F}}^{\text{calc}} + Q_{\text{CP}}^{\text{P}} \rho_{\text{C}}^{\text{calc}} \quad (2)$$

because of near-dependence of the equations. Solution of the equations for each phosphorin, giving "mean" values between the anion and cation, results in

$$|Q_{\text{FP}}^{\text{P}}| = 39\text{G}, \quad |Q_{\text{CP}}^{\text{P}}| = 28.6\text{G} \text{ (same sign),}$$

indicating a substantial adjacent atom effect.

Spin densities have also been calculated² by the CNDO method for the π -radicals PH_2 , PF_2 , and PCl_2 , and $Q_{\text{eff}}^{\text{P}}$ values obtained for these neutral radicals (Table 2).

¹ K. Dimroth, N. Greif, H. Perst, and F. W. Steuber, *Angew. Chem. Internat. Edn.*, 1967, **6**, 85; K. Dimroth and F. W. Steuber, *ibid.*, p. 445; K. Dimroth, N. Greif, W. Städe, and F. W. Steuber, *ibid.*, p. 711.

² C. Thomson and D. Kilcast, to be published.

³ A. H. Cowley and M. H. Hnoosh, *J. Amer. Chem. Soc.*, 1966, **88**, 2595.

(Owing to the low adjacent atom π spin densities, these are, in effect, Q_{FP}^{P} values). The values are consistent, and comparison with the corresponding values for the phosphorins indicates a substantial charge effect.

TABLE 2

| Radical | $\dagger A_{\text{P}}$ | ρ_{P} | $Q_{\text{eff}}^{\text{P}}$ |
|----------------|------------------------|-------------------|-----------------------------|
| PH_2 | +80.0 | 1.0 | +80.0 |
| PF_2 | +84.6 | 0.937 | +90.2 |
| PCl_2 | +70.0 | 0.718 | +97.5 |

\dagger Values in Gauss.

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