

### 490. The Structure of the Phosphonitrilic Halides.

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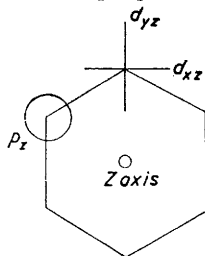
The electronic structures proposed by Craig for the cyclic polymers  $(AB)_n$ , of which the phosphonitrilic chlorides are typical examples, have been reconsidered. It is concluded that each phosphorus atom makes use of two  $d_\pi$ -orbitals in forming  $\pi$ -bonds and that these interact with the nitrogen  $p_\pi$ -orbital to give a system of weakly interacting three-centred  $\pi$ -bonds, embracing two phosphorus atoms and a central nitrogen atom.

The structure and properties of the phosphonitrilic halides are then briefly discussed in the light of this conclusion.

CRAIG and PADDOCK<sup>1</sup> have considered the electronic structures of the cyclic phosphonitrilic chlorides  $(PNCl_2)_n$  in some detail, and their ideas have been developed further by Craig<sup>2-5</sup> who concludes that these compounds are aromatic, interaction of the nitrogen  $p$ -orbitals and phosphorus  $d$ -orbitals giving rise to continuous  $d_\pi$ - $p_\pi$   $\pi$ -bonding round the ring. He also drew attention to certain differences between the annular  $\pi$ -orbitals in phosphonitrilic chlorides and those in conventional aromatic systems (*e.g.*, 1,3,5-triazine<sup>4</sup>) with  $p_\pi$ - $p_\pi$   $\pi$ -bonds. He concluded that in the former case aromatic character did not depend critically on the size of the ring, in contrast to conventional aromatic systems where the Hückel rule applies [*i.e.*, the requirement that an aromatic ring should contain  $(4n + 2)$   $\pi$ -electrons,  $n$  being an integer].

The  $\sigma$ -bonds in the phosphonitrilic chlorides are undoubtedly formed by  $sp^3$ -hybrid orbitals of phosphorus since the phosphorus atoms are four-co-ordinated, and  $X$ -ray analysis indicates that they are tetrahedral. A preliminary  $X$ -ray analysis<sup>6</sup> of the trimer suggested that the ring was planar, but a complete three-dimensional Fourier analysis has now shown<sup>7</sup> it to be puckered, having the chair conformation. The higher polymers must certainly also be puckered.<sup>7</sup>

FIG. 1. Site axes of the phosphorus  $d$ - and nitrogen  $p_z$ -orbitals.



The molecular symmetry of any cyclic polymer will therefore not be  $D_{nh}$ . The exact symmetry classification of any polymer will depend upon its puckering and may change, not only from one polymer to the next, but also within a given polymer system depending on the groups attached to the phosphorus. However, it is safe to conclude that the symmetry will be much lower, probably of the  $C_{nv}$  type.

Nevertheless, in order to discuss the probable interactions of the atomic orbitals, it is more convenient to assume that the molecules have  $D_n$  symmetry, and to treat subsequently the puckering of this planar ring as a perturbation. Use of the  $D_{nh}$  classification would throw no further light on the interactions.

The orbitals available for  $\pi$ -bonding in such a ring,  $(PNCl_2)_n$ , are the nitrogen  $p_z$ - and the phosphorus  $d_{xz}$ - and  $d_{yz}$ -orbitals (see Fig. 1).

Let the nitrogen atoms be numbered  $t = 1, 2, \dots, n$ , and the phosphorus atoms

<sup>1</sup> Craig and Paddock, *Nature*, 1958, **181**, 1052.

<sup>2</sup> Craig, *Chem. Soc. Special Publ.*, 1958, No. 12, 343.

<sup>3</sup> Craig in "Theoretical Organic Chemistry (Kekulé Symposium)," Butterworths, London, 1959, p. 20.

<sup>4</sup> Craig, *J.*, 1959, 997.

<sup>5</sup> Craig, *Chem. and Ind.*, 1958, 3.

<sup>6</sup> Wilson and Carrol, *Chem. and Ind.*, 1958, 158.

<sup>7</sup> Liquori, Pompa, and Ripamonti XVIIth Internat. Congr. Pure and Appl. Chem., Munich, 1959, Paper A1025.

$t = 3/2, 5/2, \dots (2n + 1)/2$ ; then the proper combinations of the atomic orbitals giving rise to molecular orbitals may be shown to be:<sup>2</sup>

$$P_l = n^{-\frac{1}{2}} \sum_{t=1}^n e^{2\pi i l t/n} \cdot p_t$$

$$D_l = n^{-\frac{1}{2}} \sum_{t=3/2}^n e^{2\pi i l (2t+1)/2n} \cdot d_{(2t+1)/2}$$

where  $p_t$  and  $d_{(2t+1)/2}$  are the atomic orbitals at the atom  $t$ , and  $l$  is the molecular quantum number with the allowed values  $0, \pm 1, \pm 2, \dots \pm (n-1)/2$  ( $n$  odd) and  $0, \pm 1, \dots n/2$  ( $n$  even).

The symmetries of the combinations of  $p_z$ ,  $d_{xz}$ , and  $d_{yz}$  for the ring systems  $(\text{PNCl}_2)_n$ , where  $n = 3$  to  $n = 6$ , are shown in Table I. The symmetry requirements thus favour the

TABLE I.

Orbital		$n = 3$	$n = 4$	$n = 5$	$n = 6$
$d_{xz}$ .....	0	$D_3$	$D_4$	$D_6$	$D_6$
	$\pm 1$	$A_1$	$A_1$	$A_1$	$A_1$
	$\pm 2$	$E$	$E$	$E_1$	$E_1$
	$\pm 3$		$B_1$	$E_2$	$E_2$
$d_{yz}$ .....	0	$A_2$	$A_2$	$A_2$	$A_2$
	$\pm 1$	$E$	$E$	$E_1$	$E_1$
	$\pm 2$		$B_2$	$E_2$	$E_2$
	$\pm 3$				$B_2$
$p_z$ .....	0	$A_2$	$A_2$	$A_2$	$A_2$
	$\pm 1$	$E$	$E$	$E_1$	$E_1$
	$\pm 2$		$B_2$	$E_2$	$E_2$
	$\pm 3$				$B_2$

$A$  = Symmetrical representation;  $B$  = antisymmetrical representation;  $E$  = doubly degenerate representation.

$d_{yz}$ -orbital for interaction with the  $p_z$ -orbital since the  $d_{xz}$ -orbital cannot interact with the  $p_z$ -orbital in the totally symmetrical state.

Craig<sup>2</sup> pointed out that the dimensions and energies of the phosphorus  $d$ -orbitals will be affected by the adjacent ligands; since these are not all the same, the sizes and energies of the  $d_{xz}$ - and  $d_{yz}$ -orbitals may differ. Craig believed that the resulting changes in Coulomb and resonance integrals are such as to make interactions between the  $d_{xz}$ -orbital and the  $p$ -orbitals of the adjacent nitrogen atoms much more important than the corresponding interactions of the  $d_{yz}$ -orbital; he therefore neglected the latter interactions in his treatment.

This assumption seemed to us unjustified. Since we also felt that the experimental evidence did not support the idea of aromatic resonance in the phosphonitrilic chlorides, we suspected that the prediction of such resonance by Craig's treatment was an artefact, due to neglect of the  $d_{yz}$ -interactions; and that when these were included the  $\pi$ -electron system would be seen not to be continuous around the ring.

Methane provides a simple analogy. The conventional L.C.A.O.-M.O. treatment, based on the carbon  $2s$ - and  $2p$ -orbitals and four hydrogen  $1s$ -orbitals, leads to a chemically unrealistic representation in which all the valency electrons are delocalised over all five atoms. This can, however, be transformed<sup>8</sup> into an entirely equivalent representation in which the electrons are essentially localised in two-centre  $\sigma$ -bonds. We suspected that the set of  $\pi$ -orbitals for the phosphonitrilic chlorides could likewise be transformed into a set of weakly interacting fragments, provided that *all* the relevant orbitals ( $d_{yz}$  as well as  $d_{xz}$ ) were included in the calculation.

The equivalent orbital picture of methane can be reached in a simpler manner. In any L.C.A.O.-M.O. treatment, it is legitimate first to combine any of the atomic orbitals into an

<sup>8</sup> Hall and Lennard-Jones, *Proc. Roy. Soc.*, 1950, *A*, **205**, 357.

orthogonal set of linear combinations, and then to use these in place of the original atomic orbitals in the L.C.A.O.-M.O. treatment; a particular case of this is one where the atomic orbitals of different atoms are first combined into molecular orbitals (the L.C.M.O. treatment<sup>9</sup>), as when the  $\pi$ -molecular orbitals of benzene are constructed from three pairs of ethylenic molecular orbitals instead of from six atomic orbitals. The results of this procedure cannot differ from those given by the conventional L.C.A.O.-M.O. treatment. In the case of methane, the carbon orbitals can first be combined into a set of four  $sp^3$ -hybrids. Each of these overlaps efficiently with just *one* of the hydrogen 1s-atomic orbitals; combination of the hybrid carbon orbitals with the appropriate hydrogen orbitals gives a set of four pairs of two-centre  $\sigma$ -bond molecular orbitals (one bonding, one antibonding in each case). These could be used as a basis for the final variation (L.C.M.O.) treatment; but since they overlap very inefficiently, it is evident that the set of four

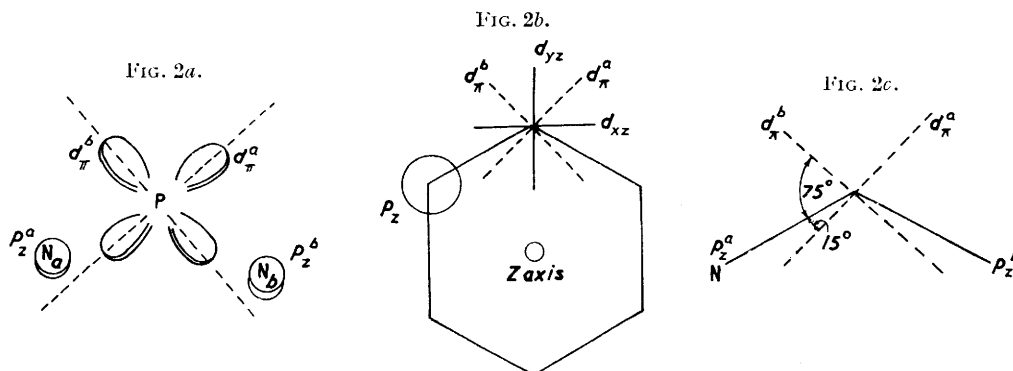


FIG. 2a. Overlap of  $d_{\pi^a}$ - and  $d_{\pi^b}$ -orbitals with nitrogen  $p$ -orbitals.

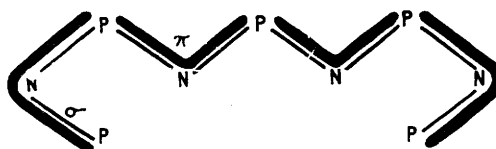
FIG. 2b. Relation of the orthogonal  $d_{\pi^a}$ - and  $d_{\pi^b}$ - to the original phosphorus  $d_{xz}$ - and  $d_{yz}$ - and the nitrogen  $p_z$ -orbitals in which the lines denote orbital axes.

FIG. 2c. Relation between the resonance integrals  $\beta$  and  $\gamma$  in the case of  $(\text{PNCl}_2)_3$ .

$$\gamma = \text{Interaction } p_z^a d_{\pi^b}, \quad \beta = \text{Interaction } d_{\pi^a} p_z^a.$$

Therefore,  $\gamma = \beta \cos 75^\circ / \cos 15^\circ$ .

FIG. 3. Breakdown of phosphonitric  $\pi$ -orbitals into three-centre  $\pi$ -bonds.



localised CH bond orbitals is already a good approximation to the structure of methane. It is evidently very similar to the equivalent orbital representation.

A similar procedure is possible for the phosphonitric chlorides. We can first replace each pair of phosphorus  $d$ -orbitals by a pair of linear combinations  $d_{\pi^a}$ ,  $d_{\pi^b}$ , given by:

$$d_{\pi^a} = \frac{1}{\sqrt{2}} (d_{xz} + d_{yz}); \quad d_{\pi^b} = \frac{1}{\sqrt{2}} (d_{xz} - d_{yz})$$

Fig. 2 indicates that each of these orbitals will overlap efficiently with the  $2p$ -orbitals of just *one* of the two adjacent nitrogen atoms. We now combine the  $d$ - and  $p$ -orbitals into sets of three-centre  $\pi$ -molecular orbitals, as indicated by the heavy lines in Fig. 3. These three-centre orbitals overlap only weakly with one another; consequently we already have a good representation of the  $\pi$ -orbitals of the parent phosphonitric chloride in terms of them. In other words, the  $\pi$ -electrons of the phosphonitric chlorides are effectively localised in definite three-centre  $\pi$ -bonds, in the same sense that the valency electrons in

<sup>9</sup> Dewar, *Proc. Cambridge Phil. Soc.*, 1949, **45**, 639.

methane are localised in two-centre  $\sigma$ -bonds. This is an entirely different situation from that holding in aromatic systems where no transformation into localised equivalent orbitals is possible.<sup>8</sup> This argument confirms our suspicion that Craig was led to an erroneous conclusion by his neglect of the phosphorus  $d_{yz}$ -orbitals.

Each three-centre  $\pi$ -bond is formally analogous to the  $\pi$ -bond in the allyl cation; in both cases there are just two electrons to be accommodated. The total energy from these is less than that of the electron pair occupying an analogous two-centre  $\pi$ -bond; in this sense the phosphonitrilic chlorides should be strongly resonance-stabilised even though they are not aromatic, just as the allyl cation is strongly resonance-stabilised. The resonance stabilisation should be directly proportional to the number of three-centre  $\pi$ -bonds, *i.e.*, to the degree of polymerisation; the heats of formation per  $\text{PNCl}_2$  unit should therefore be independent of ring size. Even the linear polymers should show the same stabilisation, apart from end-group effects.

The break in conjugation at each phosphorus atom implies that adjacent three-centre  $\pi$ -bonds need not be coplanar; puckering of the molecule should have little effect on the resonance energy. The actual puckered configurations should be largely determined by the same conformational  $\sigma$ -bond interactions that operate in cycloparaffins.

The validity of this representation will now be confirmed by a calculation of the interactions between the component three-centre  $\pi$ -bonds; this will be found to be small, confirming the correctness of the localised  $\pi$ -bond approximation.

The molecular orbitals of the two allylic systems are given by:

$$\begin{aligned}\psi_i &= a_{1i}\phi_1 + a_{2i}\phi_2 + a_{3i}\phi_3; \text{ Energy} = E_i \\ \chi_j &= b_{4j}\phi_4 + b_{5j}\phi_5 + b_{6j}\phi_6; \text{ Energy} = F_j\end{aligned}$$

where the orbitals are numbered as in Fig. 4.

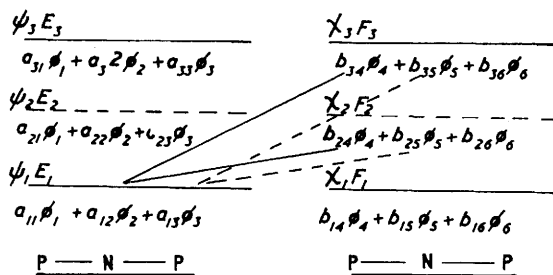


FIG. 4. Interaction between the allylic systems.

If the Coulomb integral of the phosphorus atom be  $\alpha_A$  and that of the nitrogen atom be  $\alpha_B$ , then:

$$\alpha_B = \alpha_A + \rho\beta$$

where  $\beta$  is the resonance integral between the phosphorus  $d_\pi$ -orbital and the nitrogen  $p_\pi$ -orbital within a given allylic system:

$$\beta = \int \phi_{d\pi}^a H \phi_{p\pi}^a d\tau$$

and  $\rho$  is a parameter measuring the electronegativity difference between the phosphorus and the nitrogen orbitals. The energy levels and the coefficients of the unperturbed allylic system may then be calculated by using the secular determinant:

$$\begin{vmatrix} \alpha_A - E & \beta & 0 \\ \beta & \alpha_B - E & \beta \\ 0 & \beta & \alpha_A - E \end{vmatrix} = 0$$

whence

$$\begin{aligned} F_3 = E_3 &= \text{antibonding} = \frac{1}{2}(2\alpha_A + \rho\beta - \sqrt{\rho^2\beta^2 + 8\beta^2}) \\ F_2 = E_2 &= \text{non-bonding} = \alpha_A \\ F_1 = E_1 &= \text{bonding} = \frac{1}{2}(2\alpha_A + \rho\beta + \sqrt{\rho^2\beta^2 + 8\beta^2}) \end{aligned}$$

The corresponding coefficients are shown in Table 2, in which  $(\alpha_A - E_i)/\beta = W_i$ . While

TABLE 2.

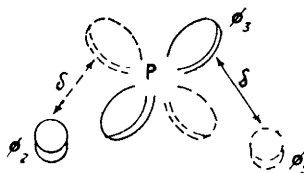
$$\begin{array}{lll} a_{11} = b_{14} = -1/\sqrt{W_1^2 + 2} & a_{12} = b_{15} = W_1/\sqrt{W_1^2 + 2} & a_{13} = b_{16} = -1/\sqrt{W_1^2 + 2} \\ a_{21} = b_{24} = 1/\sqrt{2} & a_{22} = b_{25} = 0 & a_{23} = b_{26} = -1/\sqrt{2} \\ a_{31} = b_{34} = -1/\sqrt{W_3^2 + 2} & a_{32} = b_{35} = W_3/\sqrt{W_3^2 + 2} & a_{33} = b_{36} = -1/\sqrt{W_3^2 + 2} \end{array}$$

the bonding and antibonding coefficients are symmetric the non-bonding are anti-symmetric.

*Perturbation Treatment.*—The formation of a polymer from the independent allylic systems is shown in Fig. 4 and the orbital interactions are indicated.

The interactions between the allylic systems can be calculated by using perturbation theory. Although the unperturbed system is degenerate, there is no need to use first-order perturbation theory. We need only the *total* perturbation for the whole system. Since the component parts have closed-shell configurations the total first-order perturbation vanishes.<sup>10</sup> It can be shown<sup>10</sup> that the total second-order perturbation can be calculated by using the unperturbed orbitals as a basis and simply neglecting terms with vanishing denominators.

FIG. 5. Perturbation at the phosphorus atom between the two allylic systems formed by  $d_{\pi^a}$ - and  $d_{\pi^b}$ -orbitals (cf. Fig. 2a).



The perturbation (Fig. 5) is of the form

$$P_2 = \sum_r \sum_s \frac{(a_{mr}b_{ns}\gamma_{rs})^2}{E_m - F_n}$$

where  $\gamma_{rs}$  is the resonance integral between atoms  $r$  and  $s$ . In the above allylic systems two such interactions occur, and since only two orbitals are involved, the preceding expression becomes

$$P_2 = \frac{(a_{12}b_{24} + a_{13}b_{25})^2\gamma^2}{E_1 - F_2} + \frac{(a_{12}b_{34} + a_{13}b_{35})^2\gamma^2}{E_1 - F_3}$$

where  $\gamma$  is the resonance integral between the  $d_{\pi^a}$ - and the  $p_z^b$ -orbitals (Fig. 2a). The relation between the integrals  $\gamma$  and  $\beta$  is illustrated in Fig. 2c; thus for the trimer we have:

$$\gamma = \beta \cos 75^\circ / \cos 15^\circ = k\beta$$

Hence

$$\begin{aligned} P_2 &= \frac{\frac{1}{4}(\rho + \sqrt{\rho^2 + 8})^2 k^2\beta}{[\frac{1}{4}(\rho + \sqrt{\rho^2 + 8})^2 + 2][\rho + \sqrt{\rho^2 + 8}]} \\ &+ \frac{\rho^2 k^2\beta}{\sqrt{\rho^2 + 8} \cdot [\frac{1}{4}(\rho + \sqrt{\rho^2 + 8})^2 + 2][\frac{1}{4}(-\rho + \sqrt{\rho^2 + 8})^2 + 2]} \end{aligned}$$

giving for  $P_2$  with various values of  $\rho$ :

$$\begin{array}{lll} \rho = 0 & 1 & 2 \\ P_2 = 0.0013\beta & 0.0013\beta & 0.0016\beta \end{array}$$

<sup>10</sup> Dewar, *J. Amer. Chem. Soc.*, 1952, 3341.

It will be seen that  $P_2$  is indeed small, confirming the view that the molecule can be represented to a good approximation in terms of localised three-centre bonds.

*Resonance Energy and Structure of the Phosphonitrilic Chlorides.*—In a "classical" structure for a phosphonitrilic chloride, each nitrogen atom is attached to one adjacent phosphorus atom by a single bond, and to the other by a double bond. In the picture we have reached, each nitrogen is attached by equally strong  $\pi$ -bonds to both phosphorus atoms, since the three atoms are all linked by a three-centre  $\pi$ -bond. All phosphorus-nitrogen bonds in all phosphonitrilic chlorides should therefore have the same length, intermediate between the lengths of pure single and pure double P-N bonds. At the same time the molecules are *not* aromatic, there being no unbroken path of conjugation round the ring. The conjugation is broken at each phosphorus atom; there is therefore no need for coplanarity—the phosphorus atoms can act as hinges, permitting buckling of the molecule with little loss of resonance energy. It is always possible to select two hybrid orbitals  $d_{\pi^a}$ ,  $d_{\pi^b}$ , whose orientation matches that of the adjacent nitrogen  $p$ -orbitals, for puckering of the ring permits mixing the  $d_{xy}$ -orbital with the  $d_{xz}$ - and  $d_{yz}$ -orbitals.

The calculated resonance energy is large. Each set of three-centre  $\pi$ -orbitals must accommodate two electrons; these can occupy the low-energy bonding orbital of the set. The total  $\pi$ -energy  $E_{\pi}$  for the  $n$ -mer  $(\text{PNCl}_2)_n$  is then given (cf. above) by:

$$E_{\pi} = n(2\alpha_A + \rho\beta + \sqrt{\rho^2\beta^2 + 8\beta^2})$$

In the classical structure, each pair of  $\pi$ -electrons occupies a bonding phosphorus-nitrogen  $\pi$ -molecular orbital; the energy ( $e$ ) of this can be shown to be:

$$e = \frac{1}{2}(2\alpha_A + \rho\beta + \sqrt{\rho^2\beta^2 + 4\beta^2})$$

The total classical  $\pi$ -energy for the  $n$ -mer is given by  $2ne$ . If  $\rho$  is small (so that  $0.1\rho^2$  is negligible compared with unity), the computed resonance energy (RE) is then given by:

$$\text{RE} = E_{\pi} - 2ne = n[\sqrt{\rho^2\beta^2 + 8\beta^2} - \sqrt{\rho^2\beta^2 + 4\beta^2}] \approx 0.83n\beta$$

This is a large quantity. For the trimer the calculated resonance energy is  $2.5\beta$ , compared with  $2.0\beta$  for a benzenoid six-ring. The predicted stabilisation of the phosphonitrilic chlorides is therefore of aromatic proportions.

It is also noteworthy that the second-order perturbation *per*  $\text{PNCl}_2$  unit is only about a five-hundredth of the allylic resonance energy; this again indicates that the polyallylic representation is close to the truth.

The ultraviolet spectra of the cyclic polymers<sup>11,12</sup> show little resemblance to those of organic aromatic systems which have considerable absorption in the near-ultraviolet region. Moreover, the spectra of all the cyclic polymers are almost the same, consisting of a broad-based peak with a maximum of 200  $m\mu$  [ $(\text{PNCl}_2)_3 = 199 m\mu$ ;  $(\text{PNCl}_2)_4 = 203 m\mu$  in cyclohexane] and an extinction coefficient increasing with increasing molecular weight. This would be expected if the size of the basic conjugated unit remained unchanged throughout the series, but not if its size increased by conjugation through the phosphorus atom. Likewise, the linear polymers should show absorption due to the same basic conjugated unit, whereas if conjugation occurred across the phosphorus atom, they would resemble the carotenes and show absorption in the visible region.

The present evidence from infrared spectra is not fully elucidated. It does show that all the P-N bonds are of equal length, in agreement with the X-ray results. The chemical properties of the polymers are compatible with both aromatic and allylic systems.

Recent nuclear quadrupole resonance measurements on the  $(\text{PNCl}_2)_n$  compounds, substituted polymers, and other phosphorus compounds have led to a surprising similarity in frequency between the individual polymers and phosphorus oxychloride and compounds

<sup>11</sup> Shaw, *Chem. and Ind.*, 1959, 52, 53, 54, 412, and references therein.

<sup>12</sup> Paddock and Searle, *Adv. Inorganic and Radio Chem.*, 1959, **1**, 347, and reference therein.

$R\cdot POCl_2$  and  $R_2POCl$ , which suggests that there is no fundamental difference between the various types of compounds. Further results are being collected to fill in the picture.

In conclusion it is emphasised that the arguments developed in this paper could equally be applied to other examples of  $d_{\pi}-p_{\pi}$   $\pi$ -bonding; they suggest that no significant through-conjugation should be observed in such cases between groups attached to the central atom with  $d$ -orbitals, a view which seems to be supported by the chemistry of both phosphorus and sulphur.

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