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## HMO theory and cyclophosphazenes

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Hückel molecular orbital (HMO) theory is applied to (1) the bond lengths in phosphazenes arising from inhomogeneous substitution or complex formation, (2) conjugation between exocyclic groups and the ring and its consequences, and (3) chemical reactivity, carbanion stabilization and molecular rearrangements. Such bond characteristics as order, polarizability and electron localizability depend differently on relative orbital electronegativity. Ring size effects distinguish interactions of different symmetry types. Necessary theoretical improvements are briefly considered.

### 1. Introduction

The multiple bonds formed by the elements silicon, phosphorus, and sulphur are more varied than those which involve only carbon and nitrogen. The overlap of  $3p\pi$ -orbitals is comparatively weak, so that the formation of two  $\sigma$ -bonds is usually more energetically favourable than a  $(\sigma + \pi)$  combination; the preparation of stable disilenes  $R_2Si=SiR_2$  (West *et al.* 1981) and diphosphenes  $RP=PR$  (Yoshifuji *et al.* 1981) depends on the use of bulky substituents which prevent polymerization.  $3p\pi-2p\pi$  bonding is expected to be stronger, and phospho-alkenes and phospho-alkynes have an elaborate chemistry (Appel *et al.* 1981), which is related to, but not identical with, that of their carbon analogues, and which extends to the aromaticity of phosphabenzene (Märkl 1966, Ashe 1971).  $\lambda^3$ -phosphazanes usually have singly-bonded cyclic structures, but  $t\text{-BuP}=\text{N}\cdot t\text{-Bu}$  is monomeric and highly reactive (Niecke *et al.* 1981).

Many of the multiple bonds of phosphorus and sulphur, especially, formally require  $d\pi$ -orbitals (Mitchell 1969), and some compounds, typically the  $\lambda^3$ -phosphazanes, may use them even when the normal valencies are otherwise satisfied. The nature of such  $p\pi-d\pi$  bonds, which may be either localized or delocalized, can be conveniently investigated in the series of cyclic phosphazenes  $(-\dot{\text{N}}=\text{PX}_2-)_n$ , because the range of ring sizes and substituents is large. The series is well adapted to the systematic correlation of electronic structure and chemical properties, through the use of simple theoretical models, and the reasons for the differences from  $p\pi-p\pi$  bonding become apparent.

### 2. Basic concepts

The conditions for d-orbital bonding have been known for many years (Craig *et al.* 1954). In a  $p\pi-d\pi$  bond, the shape of the d-orbital ensures that the principal overlap occurs in the region of the  $p\pi$ -orbital, so reinforcing, in a phosphazene, the natural polarity of the P-N bond. Also, the d-orbitals are contracted and made more electronegative by electronegative ligands, and thereby bind more strongly (Craig and Magnusson 1956). The relative orbital electronegativity  $\rho = (\alpha_N - \alpha_P)/\beta$ , an important and substituent-dependent variable, is used extensively below. Two other differences from  $p\pi$ -bonding depend upon the availability of all five d-orbitals; in  $\text{Cl}_3\text{PO}$ , for

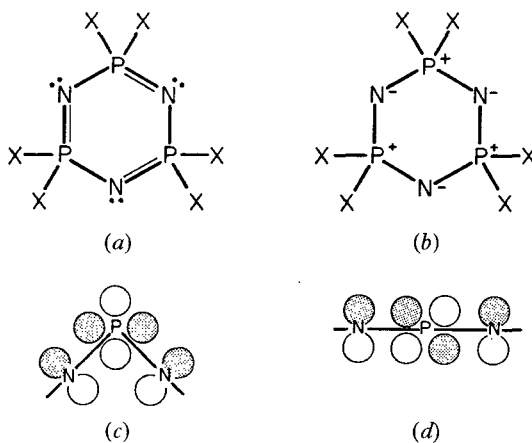


Figure 1.  $(NPX_2)_3$ , (a) conventionally, (b) with potential  $\pi$ -electrons localized on N. Lower, overlap schemes for strongly interacting d-orbitals; (c) in-plane,  $d_{x^2-y^2}$ , (d) out-of-plane,  $d_{xz}$ .

instance, the  $\pi$ -orbitals are doubly degenerate, (so forming a partial triple rather than a true double bond), and, finally, conjugation through phosphorus does not require planarity. This point of view was adopted in an earlier, more extensive review (Craig and Paddock 1971); some more recent illustrative examples are included here.

The usual formulation of a trimeric phosphazene is as shown in figure 1 (a). Since the formally unshared electrons contribute to the bonding, it is equally satisfactory to write the basic  $\sigma$ -skeleton as in figure 1 (b), the  $\pi$ -bonds then being formed by the delocalization of the two lone pairs on nitrogen. The site group at phosphorus is  $C_{2v}$ , so that the  $\pi$ -components are no longer degenerate, The d-orbitals fall into two symmetry classes, interacting, respectively, symmetrically and antisymmetrically with adjacent  $p\pi$ -orbitals, a distinction first recognized by Craig (1959), and applicable to both in-plane and out-of-plane components (figures 1 (c) and (d)). They so form homomorphic (Hückel) and heteromorphic cyclically delocalized molecular orbitals, which differ in the way in which the  $\pi$ -electron energy (per electron) varies with ring size (figure 2 (a)). The decreasingly exothermic polymerization of the chlorophosphazenes  $(NPCl_2)_{3-7}$  (Jacques *et al.* 1965) and the formation of much larger rings in the ammonolysis of phosphorus pentachloride, suggest that the heteromorphic system, in which stability increases steadily with ring size, makes the larger contribution to skeletal bonding. By contrast, the  $\pi$ -system in borazines is exclusively homomorphic, and, in agreement, the six-membered ring is the only product of the ammonolysis of boron trichloride. On the other hand, the first ionization energies of the fluorophosphazenes  $NPF_2)_{3-8}$  (Branton *et al.* 1970) oscillate with ring size, in the way expected of a homomorphic  $\pi$ -system. This system plays an important role in the chemistry of the phosphazenes. We consider first the molecular and electronic structure of the ring, then the significance of exocyclic  $\pi$ -bonding, and finally describe some chemical applications.

### 3. Ring structure

In almost all homogeneously substituted cyclic phosphazenes, the lengths of the P-N bonds are equal and short, and decrease with increasing ligand electronegativity. Significant inequalities result from inhomogeneous substitution or from complex

formation, and are conveniently considered in terms of the atom-bond polarizability  $\pi_{rs,t} = \partial p_{rs} / \partial \alpha_t$ . This quantity was introduced and expressed in terms of orbital coefficients by Coulson and Longuet-Higgins (1947), but found little application at the time because the available experimental results related mainly to alternant hydrocarbons, for which  $\pi_{rs,t}$  is identically zero.

For phosphazenes this is not so. If  $\phi_P, \phi_N$  are symmetry-adapted combinations, a bonding orbital  $\Phi = a\phi_P + b\phi_N$  is mixed by a perturbation with (among others) the paired antibonding orbital  $\Phi^* = b\phi_P - a\phi_N$ , in which the charges on P, N are reversed. For alternant hydrocarbons,  $a$  and  $b$  are equal, the non-zero contributions to  $\pi_{rs,t}$  in other molecules arising from the loss of charge symmetry (figure 2 (b) (i)). As  $\rho$  increases, so does  $\pi_{rs,t}$ , so that, although an increase in  $\rho$  weakens the  $\pi$ -bonds (figure 2 (c) (i)), it initially increases their sensitivity to a perturbation. The situation is a little different for eight-membered rings, because the perturbation mixes in a non-bonding orbital of a different symmetry species from the corresponding occupied level, so that  $\pi_{rs,t} \neq 0$  at  $\rho = 0$ , but still increases to a maximum. Further increase of  $\rho$  then concentrates the electrons on the more electronegative atom (figure 2 (c) (v)), so that eventually both  $p_{rs}$  and  $\pi_{rs,t}$  are zero for all ring sizes. For intermediate values of  $\rho$ , the magnitude of  $\pi_{12,1}$  is great enough to cause significant inequalities in the lengths of the ring bonds, so that structural analysis becomes a major tool in the investigation of the electronic structure of phosphazenes. There have been many examples since the first application to the ring bond inequalities in *gem*- $N_4P_4F_6Me_2$  (Ranganathan *et al.* 1973); table 1 shows the agreement to be expected. The concepts are applicable to the localization of a pair of bonding electrons in the formation of complexes (figure 2 (c) (ii)), and can be used to describe qualitatively the irregular pattern of bond lengths resulting from a combined positive and negative perturbation in  $N_4P_4(NMe_2)_8 \cdot Mo(CO)_4$  (Calhoun *et al.* 1973). Figure 2 (c) illustrates another important point; the localization of electrons resulting from an increase in  $\rho$  affects different  $\pi$ -properties unequally, diamagnetic susceptibility being especially strongly attenuated. Ring-current effects have indeed been detected (Craig *et al.* 1961) but are difficult to assess quantitatively; magnetic measurements are likely to be less informative than molecular structure determinations.

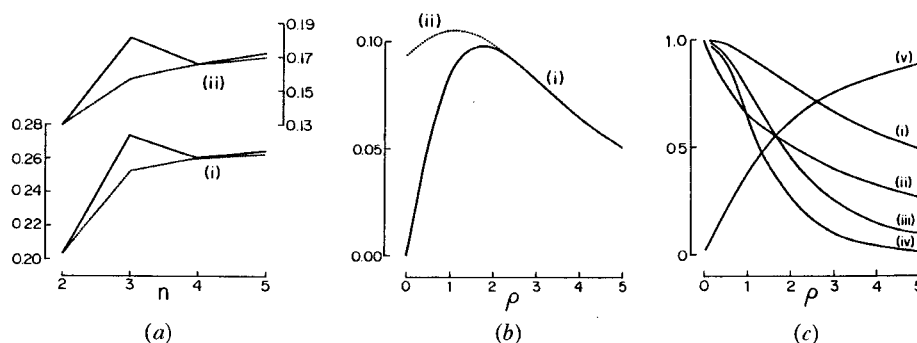


Figure 2. (a) (i) Delocalization energy, per electron, as a function of ring size, for homomorphic (full line) and heteromorphic  $\pi$ -systems, units of  $\beta$ . (ii) Self-polarizability  $\partial q_1 / \partial \alpha_1$ , units of  $-1/\beta$ . For (i), (ii),  $\rho = 2$ . (b) Atom-bond polarizability  $\pi_{12,1}$  as a function of  $\rho$  for (i) homomorphic six-membered ring, (ii) eight-membered ring. (c) For six-membered homomorphic ring, (i) bond order, (ii) two-electron localization energy, (iii) self-polarizability  $\pi_{1,1}$ , (iv) diamagnetic susceptibility, all relative to their values at  $\rho = 0$ , (v)  $\pi$ -charge on N in excess of that for  $\rho = 0$ .

Table 1. Comparison of measured and calculated bond length variations in  $N_4P_4F_6Me_2$ .†

Bond‡	12	23	34	45
Deviation from mean (Å)	0.066	-0.048	0.014	-0.031
Calculated§	(0.066)	-0.036	0.010	-0.013

† Marsh and Trotter (1971).

‡ Bonds numbered from  $PMe_2$  group.

§  $\pi_{rs,1}$  calculated with  $\rho = 1$ , and scaled to first deviation.

Finally, the conformations of cyclic phosphazenes appear to depend on steric interactions. The lack of preference for any particular torsion angle about the P-N bonds suggests that the inequality between the two  $\pi$ -components is too small to exert any effective steric control. Whether the heteromorphic and homomorphic  $\pi$ -components correspond to out-of-plane and in-plane interactions, respectively, as expected from overlap calculations, is not yet known.

#### 4. Conjugative interactions

Suitable exocyclic groups can also form  $\pi$ -bonds to phosphorus, and the whole molecular  $\pi$ -system can then be regarded as formed by the joining of tetrahedral units, in each of which the four groups donate electrons to phosphorus, an interaction which is inductively competitive and conjugatively cooperative. This view of the double  $\pi$ -system has been developed by Cruickshank (1961). With small modifications, it could give an account of bond length inequalities similar to that outlined above. From either standpoint, exocyclic conjugation requires electron release to the ring, as found by  $^{19}F$  N.M.R. spectroscopy for the inductive and conjugative interaction of fluoroaryl groups with fluorophosphazanyl rings (Chivers and Paddock 1972), and by ultraviolet spectroscopy for the 2-pyrrolyl-fluorophosphazenes (Sharma *et al.* 1982). Conjugative interactions with a phosphazene ring increase in the order phenyl < 1-methylpyrrolyl < dimethylamido. For this last group, electron transfer is great enough to make a ring nitrogen atom the basic centre; the exocyclic bond is short, and the  $PNC_2$  group nearly planar (figures 3(a) and (b)). Figures 3(c) and (d) show the structural changes induced by protonation of a conjugated molecule. The localization of a pair of bonding electrons increases the mean ring length by 0.021 Å. The withdrawal of bonding electrons makes P(1), P(2) more electrophilic, shortens their exocyclic  $\pi$ -bonds, and increases both the exocyclic NPN angle and the mean sum of angles at nitrogen (from 353° to 356°). The bond lengths are adequately described by the HMO calculations; the environment of P(3) is only slightly affected by the perturbation at the remote nitrogen atom. The dimeric phosphazene  $N_2P_2[N(iPr)_2]_4$ , the first example of its kind (Baceiredo *et al.* 1984) probably owes its stability, as do some dimeric borazines, to exocyclic conjugation; the exo-bonds are short (1.645 Å) and the angular sum at the nitrogen atoms is large (mean 358.8°). The strength of the delocalized bonding within the ring is indicated by the short (1.650 Å) and equal bond lengths, and it may be significant that, although the delocalization energy per electron is zero for cyclobutadiene (in the simplest approximation), it is positive for  $\rho > 0$  (figure 2(a)(i)), and rises to a maximum near  $\rho = 2$ .

### 5. Chemical applications

A few examples will show how some chemical properties depend on  $p\pi-d\pi$  bonding. Most substitution reactions of phosphazenes involve nucleophilic attack at phosphorus, and, in a reaction in which there is no net change in electron density, the activation energy is correlated with the calculated  $\pi$ -charge (table 2). Amination of the halogenophosphazenes has been extensively studied (Goldschmidt *et al.* 1981), but, although the reaction rate increases from six to eight-membered rings, (Moeller and Kokalis 1963, Capon *et al.* 1965), the reaction is multistage, and there is no clear indication of  $\pi$ -electron effects on rate or substitution patterns.

In another reaction, the introduction of a fluorine atom into a chlorophosphazene adds inductive interactions which may be decisive; reactivity (to  $F^-$ ) increases with the degree of substitution, for all ring sizes, and a second fluorine atom enters geminally. The effect of the  $\pi$ -interactions shows in the self-polarizabilities  $\pi_{1,1}$  (figure 2 (a) (ii)); an electronegative substituent induces a smaller  $\pi$ -density in an eight-membered than in either a (homomorphic) six-membered or ten-membered ring, and the rate of a second substitution is correspondingly greater (Paddock and Serreqi 1974). The predominantly geminal substitution found in the reaction of octafluorocyclotetraphosphazene

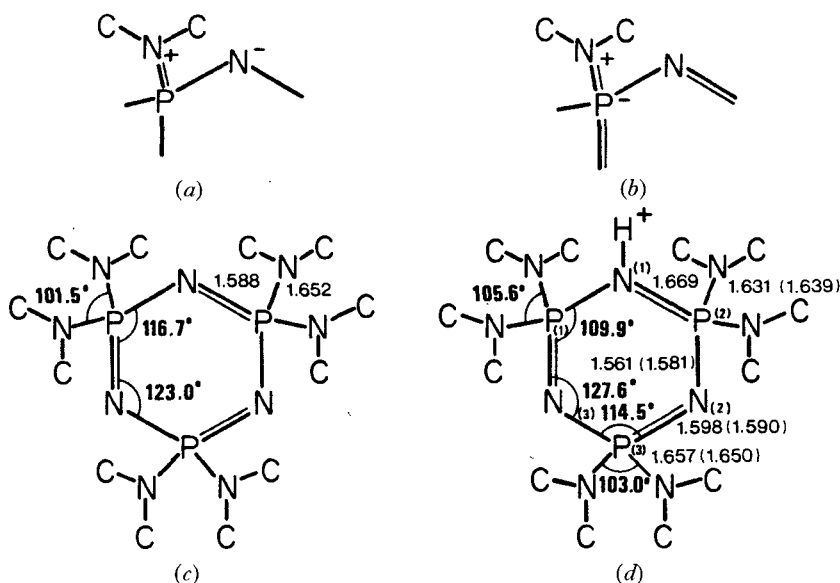


Figure 3. Normal (a) and valence-expanded (b) schemes for conjugation of exo-NMe<sub>2</sub> group. (c) Geometry of N<sub>3</sub>P<sub>3</sub>(NMe<sub>2</sub>)<sub>6</sub> (Rettig and Trotter, 1973) and (d) of its conjugate acid (Allcock *et al.* 1973). Equivalent lengths and angles averaged. Calculated ( $\rho=2$ ) lengths in brackets, scaled to N(1)P(2).

Table 2. Comparison of activation energies and  $\pi$ -electron density.†

$n$ in (NPCL <sub>2</sub> ) <sub>n</sub>	3	4	5	6
$E_{act}$ (kcal mole <sup>-1</sup> )	18.3	16.3	17.0	16.3
$\pi$ -electron density at P‡	0.621	0.523	0.582	0.551

† For reaction with Cl<sup>-</sup> in acetonitrile (Sowerby 1965).

‡  $\rho=1$ .

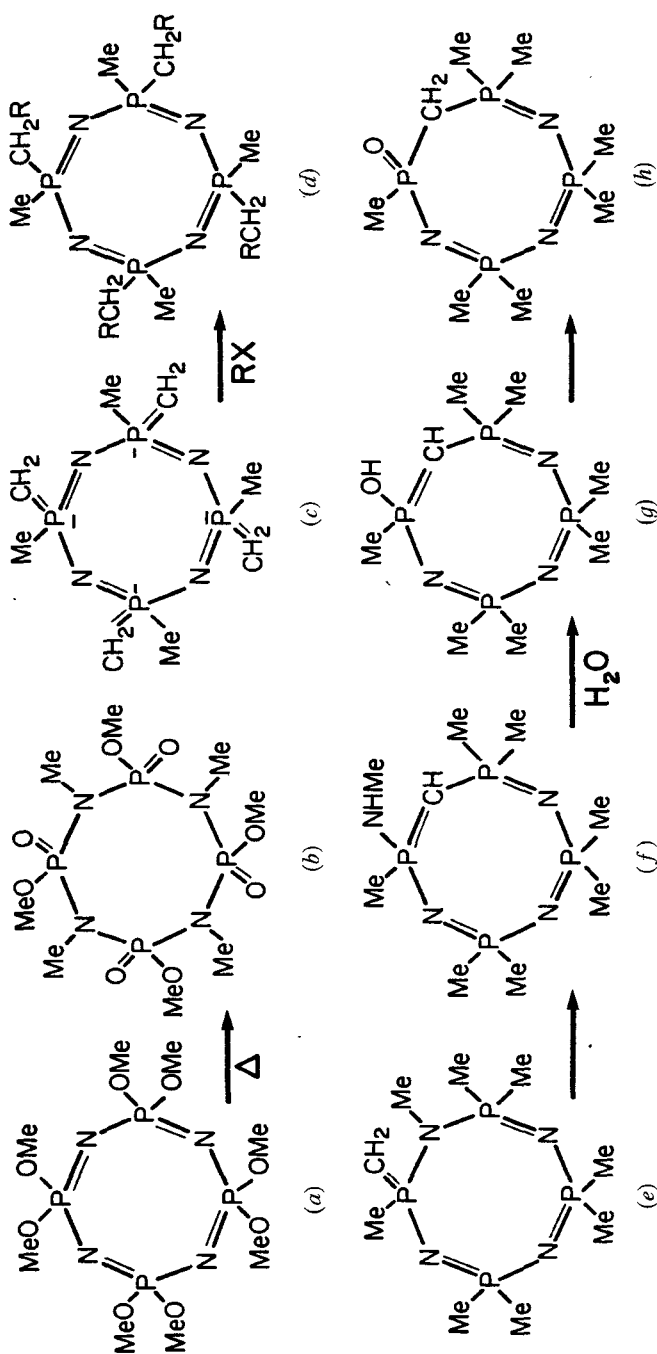


Figure 4. (a), (b); The phosphazene-oxophosphazene rearrangement. (c), (d); The formation of C-derivatives from a phosphazene carbanion (one canonical form). (e), (f); Rearrangement of an exo-ylide to an azaphosphorin, and (g), (h) of its hydrolysis product to an exo-oxide.

with methyllithium is surprising, but the  $\pi$ -density changes arising from dimethylation show themselves in the ( $\rho$ -dependent) orientation pattern, succeeding methyl groups occupying the trans-antipodal position (Ranganathan *et al.* 1973).

The importance of relative electronegativity to  $p\pi$ - $d\pi$  bonding is shown by the thermal isomerization of methoxyphosphazenes to oxophosphazanes (figures 4(a) and (b)) (Fitzsimmons *et al.* 1964) in which strong localized exocyclic  $\pi$ -bonds are formed, partly at the expense of the delocalized ring bonds with which they are conjugated (Bullen *et al.* 1981). Phosphazene carbanions (figure 4(c)) owe their existence to the strong conjugative interactions of a negatively charged group carrying a formally unshared pair; their orientational properties can be understood in terms of HMO theory (Gallicano *et al.* 1981). As a final example, the nonamethylcyclotetraphosphazanium ion can be deprotonated, but the ylide (figure 4(e)) which is presumably first formed rearranges to an azaphosphorin, cyclic delocalization now being made possible by a proton migration to the exocyclic nitrogen atom (figure 4(f)). The reverse migration takes place on hydrolysis of this methylamino-derivative (figures 4(g) and (h)), the strength of the exocyclic  $\pi$ -bond now being dominant. Again, these changes depend on relative electronegativity, and can similarly be described by HMO theory (Oakley and Paddock 1976).

## 6. Conclusion

In this account of bonding in the cyclophosphazenes, we have stressed the ability of the HMO method to describe structures and the changes in them induced by a perturbation, to interrelate the effects of exocyclic conjugation and protonation, and, through the concept of relative orbital electronegativity, to explain some aspects of reactivity, and the energetics of some molecular rearrangements.

The breadth of the application depends on the simplicity of the model, and, in particular cases, theoretical methods at the next degree of complexity have proved useful. For example, the polar, cyclically conjugated structure of  $\lambda^5$ -phosphorins has been established by CNDO methods (Schäfer *et al.* 1976), and MNDO calculations have been used to discuss the chemistry of an iminophosphane (Niecke *et al.* 1981); its easy dimerization to an azadiphosphiridine may perhaps be driven by the formation of an *exo*- $\pi$  bond of the type discussed above.

The value of the HMO method is of course limited chiefly by its neglect of charge correlation, and, for realistic estimates of ionization energies, better methods, such as  $X_\alpha$ -SW are required (Mitchell *et al.* 1977). A good *ab initio* calculation would allow a critical examination of the overlap criterion, show whether or not the d-orbitals are contracted differently, and in general provide  $p\pi$ - $d\pi$  bonding with a firm numerical foundation.

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