

Conjugation in Phosphazenes: Pyrrolylphosphazenes and Phosphazenyl Carbanions

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The bonding system in phosphazenes is closely analogous to that in phosphoryl compounds, in which conjugative P-C interactions require electron release from the substituent. Although there is only weak conjugation between phenyl and phosphoryl groups (1), the electronic spectra of tris(pyrrolyl)phosphine oxides show a strong low frequency band attributable to $\pi\pi$ - $d\pi$ bonding between the pyrrolyl and phosphoryl groups (2); its nature, for acylpyrroles, has been confirmed theoretically (3).

In the expectation that phosphazenyl and phosphoryl groups would behave similarly, we have prepared the 1-methyl-2-(fluorophosphazenyl)pyrroles $N_nP_nF_{2n-1}.C_4H_3NMe$ ($n = 3-6$; 2,a-d) and have measured their electronic spectra. Figure 1 illustrates possible modes of conjugation to phosphoryl and N_3P_3 rings. Like the pyrrolylphosphine oxides, the fluorophosphazenylpyrroles show a band characteristic of $\pi\pi$ - $d\pi$ conjugative charge transfer, and an interaction of this type is equally well established for the two series. The numerical results are shown in Table I.

Table I: Electronic spectra of fluorophosphazenylpyrroles.^a

Cpd.	$\lambda(\epsilon)$	$\lambda(\epsilon)$	Cpd.	$\lambda(\epsilon)$	$\lambda(\epsilon)$
1 ^b	213(6.7)	-	2c(n=5)	235(11.5)	220(9.9)
2a(n=3)	237(10.9)	220(10.1)	2d(n=6)	240(11.8)	220(10.1)
2b(n=4)	240(12.4)	220(10.4)	3 ^c	243(12.9)	218(8.4)

^a $\lambda(\text{nm})$ and $\epsilon(\times 10^{-3})$ at maxima. ^b1-methylpyrrole. ^ctris(1-methylpyrrol-2-yl)phosphine oxide (2).

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The wavelength of the charge transfer band increases in the series phosphazenyl < phosphoryl < formyl (289.5 nm)(3), so that the degree of conjugation increases in that order, the first two being comparable. The slight alternation in the phosphazenyl series, if real, is consistent with the transfer of charge to an antibonding π -level of the phosphazene ring. Ground state stabilisation of 2b is demonstrated by its molecular structure (4) (Figure 2), the P-C bond being 0.06 Å shorter than in phenylphosphazenes (5).

Conjugative interactions have important preparative consequences (6). Primarily, deprotonation of an alkylphosphazene is promoted by conjugation in the carbanion so formed, and a number of new phosphazene derivatives have been made by the reaction of the lithio-derivatives with electrophiles; some are illustrated in Figure 3. The reactions of the monocarbanion formed from gem-N₃P₃Ph₄Me₂ are the simplest, and compounds of Type 4 have been obtained in high yield. Rings can be joined, either by the use of a difunctional halide, or through a coupling reaction, involving CuCl₂/O₂(7), to give 5. The tricarbanion formed from N₃P₃Me₆ gives the expected derivatives N₃P₃Me₃(CH₂R)₃; both cis-cis-cis and cis-trans-trans stereo-isomers of the tribromo-derivative have been isolated.

Tetrasubstituted derivatives 6 are easily obtained from N₄P₄Me₈, and π -electron calculations show that antipodal di-substitution is to be expected for electropositive substituents, as found for R = Me₃Si, Me (7). Monocarbanions are not obtained, principally because the intra-ring exothermic electrostatic interactions are reduced less by charge transfer from the second ylidic group than the first; if the added base is strong enough to remove the first proton, it will also remove the second.

Normally electronegative substituents facilitate full substitution, but if the withdrawal is strong enough, charge transfer may remove all charge from the ylidic groups of, e.g., N₄P₄Me₄(CH₂R)₂(CH₂⁻)₂, so that it is no longer a nucleophile. This evidently occurs in the reaction of N₄P₄Me₄(CH₂Li)₄ with ethyl benzoate, which gives a high yield of the vicinal di-derivative (Figure 3, 8); the reaction cannot be made to go further. The effect of the substituent can be modelled as a perturbation of the local Coulomb parameter α_p , and Figure 4 shows that, as this phosphorus atom is made more electronegative, the favoured mode of substitution changes from antipodal to vicinal, and the ylidic charge decreases, becoming zero near the point where the vicinal isomer is the more stable. The dicarbanion is then no longer a nucleophile, and the reaction stops. This is evidently what happens in the reaction of N₄P₄Me₄(CH₂⁻)₄ with ethyl benzoate.

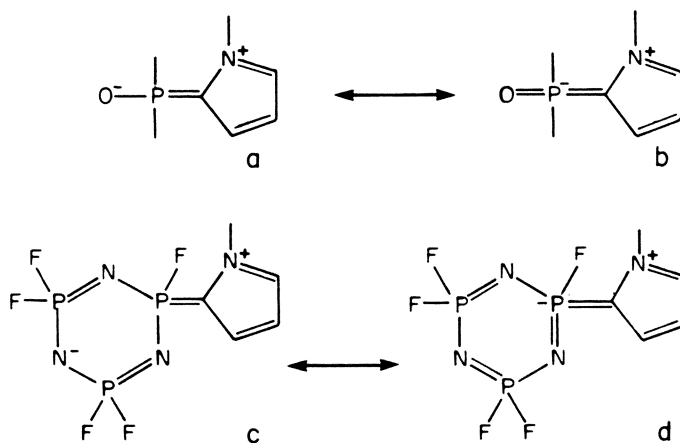
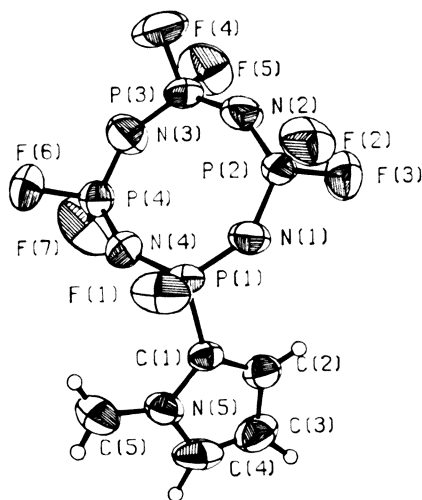
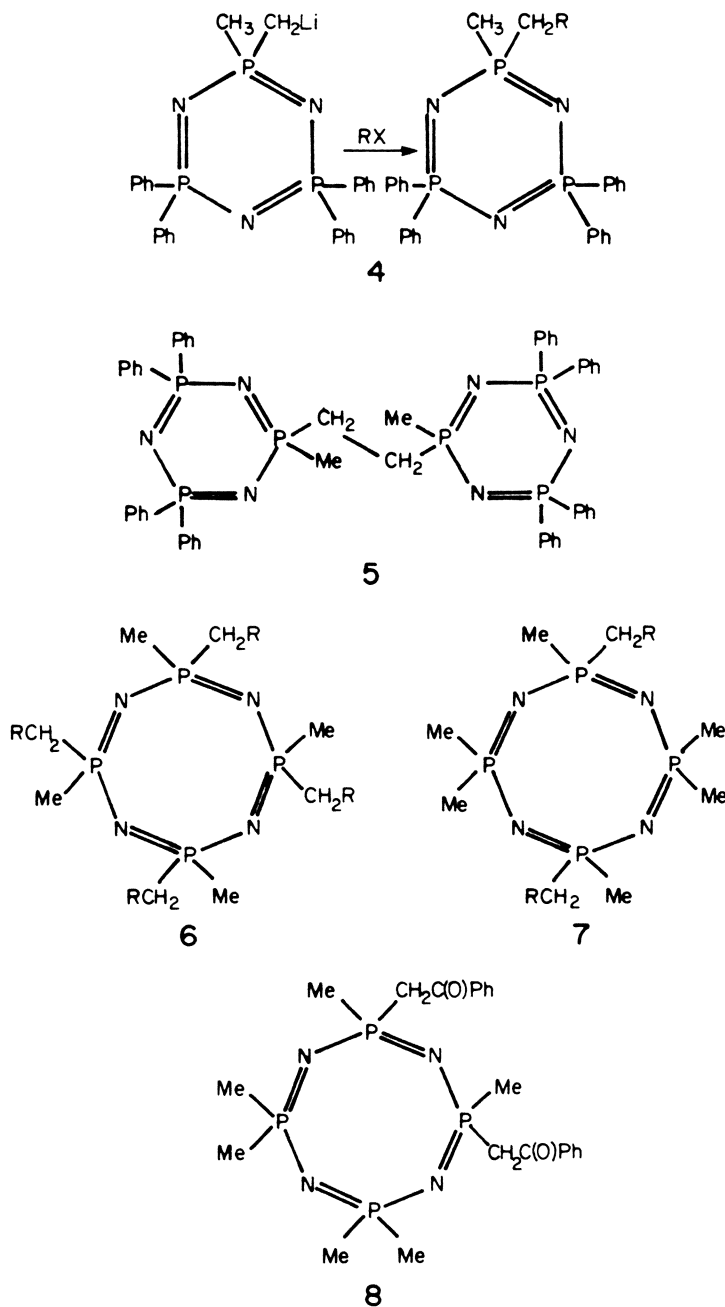


Figure 1. Some canonical forms involving conjugation in 1-methylpyrrol-2-yl derivatives. Valence shell expansion is implied in b and d.



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Figure 2. The molecular structure of 2b (4). $P(1)C(1) = 1.765(5) \text{ \AA}$, $P(1)F(1) = 1.561(4) \text{ \AA}$; mean length of other $P-F$ bonds = 1.536 \AA . Bonds from $P(1)$ to $N(1)$, $N(4)$, lengthened by $0.027(12) \text{ \AA}$.



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Figure 3. Products of carbanion reactions (6): 4, $R = \text{Me}_3\text{Sn}, \text{Br}, \text{PhC}(0), \text{COOH}$; 6, $R = \text{Me}, \text{Me}_3\text{Si}, \text{Me}_3\text{Ge}, \text{Me}_3\text{Sn}, \text{Br}, \text{I}, \text{Me}_2\text{As}$; and 7, $R = \text{Me}_3\text{Si}, \text{Me}_3\text{Ge}, \text{Me}_3\text{Sn}, \text{Me}$.

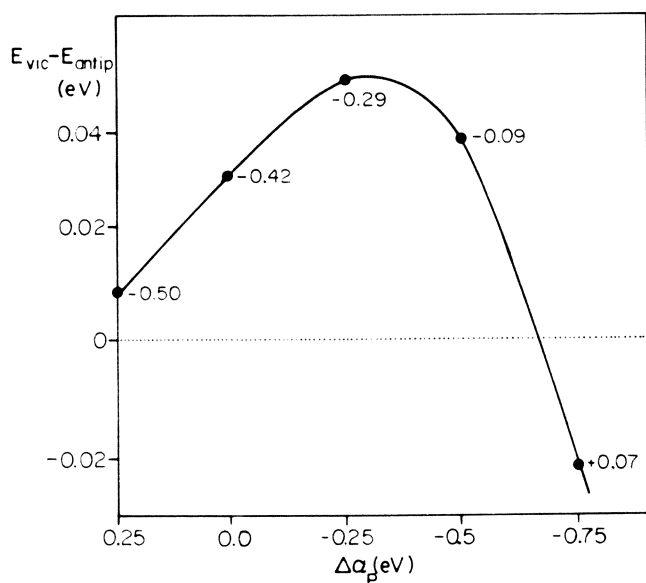


Figure 4. π -Electron energy of vicinal relative to antipodal $N_4P_4Me_4(CH_2R)_2(CH_2^-)_2$, as a function of the perturbation $\Delta\alpha_p$ induced by R(6). The residual π -charge on the ylidic carbon atoms is marked on the curve.

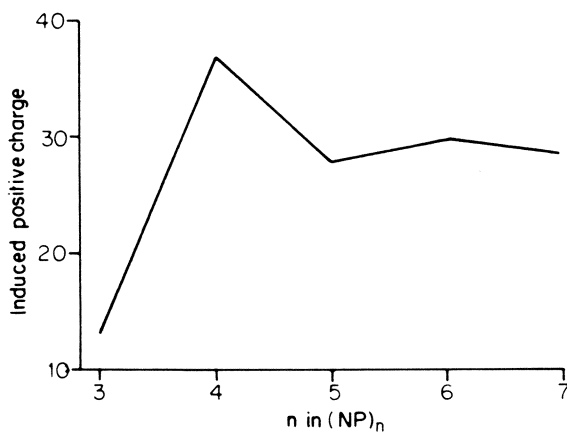


Figure 5. Positive charge ($\times 10^4$) induced at P(2) by a perturbation of -0.5 eV at P(1) (8).

As an interesting contrast, the benzylation of $N_3P_3Me_6$ goes to completion, a fact which has a related explanation. The effect of an electronegative perturbation at phosphorus is to concentrate electron density locally, at the expense of the next nearest atoms. In a homomorphic system, the induced electron density is an oscillating function of ring size (Figure 5)(8). The positive charge induced at P(2) by an electronegative substitution at P(1) is greatest for the 8-membered and least for the 6-membered ring, and the secondary withdrawal from the exo-carbon atoms must be greater for the tetramer. If the same parameters are used as for the tetramer, the exo-charge on a di-substituted trimer is -0.2 when it is 0.0 in the tetramer. This is much reduced from the value of -0.54 found for the unperturbed molecule, but it still corresponds to pronounced nucleophilic character, and demonstrates one of the differences between $N_3P_3Me_6$ and $N_4P_4Me_8$ arising from π -interactions.

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