503. *Structure and Basicity. Part III.*[1] *The Basicity of Homogeneously Substituted Cyclotriphosphazatrienes and Cyclotetraphosphazatetraenes*

By D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw

The basicities of a series of homogeneously substituted cyclotriphosphazatrienes, $N_3P_3Y_6$ (Y = OMe, OEt, OPr^i, OBu^n, OCH_2Ph, OCH_2CF_3, OPh, OC_6H_4-*p*-OMe, β-$OC_{10}H_7$, SEt, SPr^n, SC_6H_{11}, SCH_2Ph, SPh, Et, CF_3, Ph, C_6H_4-*p*-Cl, Cl), and cyclotetraphosphazatetraenes, $N_4P_4Y_8$ (Y = OMe, OEt, OPr^i, OBu^n, OCH_2Ph, OCH_2CF_3, OPh, OC_6H_4-*p*-OMe, β-$OC_{10}H_7$, Et, Ph, Cl) have been measured in nitrobenzene, and the ethylphosphazenes in water as well. The basicities are discussed in terms of the structure of, and the bonding in, these compounds. The basicities of homologues in the two series are compared. The substituent effects in cyclophosphazenes and pyridines are discussed.

Although the parent chlorides have basicities which are too weak to be measured by the methods so far described in this Series,[2] we have shown [1] that the fully aminolysed derivatives of hexachlorocyclotriphosphazatriene (I) and octachlorocyclotetraphosphazatetraene (II) are comparable with the parent amines in basic strength. Since the cyclic rather than the exocyclic nitrogen atoms prove to be the basic centres, these high basicities derive from the electron-releasing powers of the amino-groups. We therefore expected that the replacement of the chlorine atoms by other relatively electron-releasing substituents would

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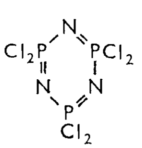
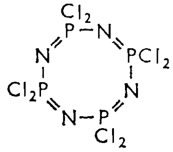
[1] Part II, D. Feakins, W. A. Last, and R. A. Shaw, *J.*, 1964, 4464.

[2] D. Feakins, W. A. Last, and R. A. Shaw, *J.*, 1964, 2387.

also lead to compounds having basicities readily accessible to measurement by our technique. We now record measurements of the basicities of compounds in which groups including alkyl, aryl, alkoxy, and thioalkoxy have been substituted for the chlorine atoms.


(I)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All compounds are fully and homogeneously substituted, *i.e.*, have the general formulæ $N_3P_3Y_6$ and $N_4P_4Y_8$. A preliminary account of some of this work has appeared.[3]

Values of $pK_{a,1}'$ and $pK_{a,2}'$, pertaining to solutions in nitrobenzene, and of $pK_{a,1}$ and $pK_{a,2}$ for the few water-soluble compounds are in Table 1, with values for selected aminophosphazenes for comparison. In only a few cases are the $pK_{a,2}$ or $pK_{a,2}'$ values accessible by our technique.

pK_a and pK_a' Values were measured as before.[2] For the preparation of the phosphazenes, see ref. 4.

TABLE 1

Phosphazenes

Basicities in nitrobenzene

Y	$N_3P_3Y_6$ $pK_{a,1}'$	$N_4P_4Y_8$ $pK_{a,1}'$
OMe	−1·9	−1·0
OEt	−0·2	0·6
OPr^i	1·4	2·1
OBu^n	0·1	0·7
OCH_2Ph	−2·1	−1·6
OCH_2CF_3	< −6·0	< −6·0
OPh	−5·8	−6·0
OC_6H_4-*p*-OMe	−5·4	−5·2
β-$OC_{10}H_7$	< −6·0	< −6·0
SEt	−2·8	
SPr^n	−2·6	
SC_6H_{11}	−2·2	
SCH_2Ph	−4·2	
SPh	−4·8	

Basicities in nitrobenzene

Y	$N_3P_3Y_6$ $pK_{a,1}'$	$N_4P_4Y_8$ $pK_{a,1}'$
Cl	< −6·0	< −6·0
Et	6·4	7·6 ($pK_{a,2}'$ = 0·2)
CF_3	< −6·0	—
Ph	1·5	2·2 ($pK_{a,2}'$ = −5·8)
C_6H_4-*p*-Cl	−1·4	—
NHEt	8·2 ($pK_{a,2}'$ = −1·3)	8·1 ($pK_{a,2}'$ = 3·8)
NEt_2	8·5 ($pK_{a,2}'$ = −3·2)	8·3 ($pK_{a,2}'$ = −0·9)

Basicities in water

	$pK_{a,1}$	$pK_{a,1}$
Et	5·85	6·45
NHEt	8·67	8·70 ($pK_{a,2}$ = 6·08)

DISCUSSION

It will be assumed, as a first approximation, that all the cyclic species concerned, when in solution, are planar, or are of sufficiently high symmetry, to ensure that all atoms or bonds of a given type are equivalent.

It seems likely that in all these compounds, protonation is on the cyclic nitrogen atoms rather than on the exocyclic groups.

Craig and Paddock's analysis [5] of the electronic structure of these compounds, summarised in Part II,[1] forms the basis of our discussion.

Differences in Basicity between the Cyclotriphosphazatriene and Cyclotetraphosphazatetraene

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[3] D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Shaw, *Chem. and Ind.*, **1963**, 164.

[4] B. W. Fitzsimmons and R. A. Shaw, *J.*, **1964**, 1735; K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J.*, **1964**, 121; A. P. Carroll and R. A. Shaw, *Chem. and Ind.*, **1962**, 1908.

[5] D. P. Craig and N. L. Paddock, *J.*, **1962**, 4118.

Rings.—Some of the factors that might lead to differences in basicity between a cyclotriphosphazatriene and a cyclotetraphosphazatetraene fully substituted with the same groups, *e.g.*, $N_3P_3Et_6$ and $N_4P_4Et_8$, are:

1. *Changes in π-electron energy on protonation.* These will be examined by the LCAO–MO method. For simplicity we shall at this point (i) ignore any multiple bonding between the substituents and the ring; (ii) ignore the π′-bonding; and (iii) discuss the π-bonding from two extreme standpoints, (*a*) that of complete cyclic delocalisation, as in Craig and Paddock's original theory,[6] and (*b*) that in which the delocalisation is restricted to P–N–P "islands."[7]

For a nitrogen atom, r, bonded to phosphorus atoms s, it may be shown[8] that

$$\Delta E = q_r \Delta\alpha_r + 2\Sigma p_{rs} \Delta\beta. \qquad (1)$$

ΔE is the change in the π-electron energy occurring, say, on protonation, $\Delta\alpha_r$ and $\Delta\beta$ are, respectively, the changes in the coulomb integral, α_r, of atom r, and in the resonance integral, β, between r and s. q_r Is the π-electron charge-density at r, and p_{rs} the π-electron bond order between r and s. Considering case (*a*) and assuming a difference in electronegativity between nitrogen and phosphorus such that

$$\alpha_N = \alpha_P + \beta, \qquad (2)$$

where α_N and α_P are the coulomb integrals of nitrogen and phosphorus, respectively,[6] we find that for the triene ring $q_r = 1{\cdot}521$, $p_{rs} = 0{\cdot}554$, and for the tetraene ring $q_r = 1{\cdot}477$ $p_{rs} = 0{\cdot}576$. Thus, if $\Delta\alpha_r \sim 24$ kcal./mole, as suggested by Longuet-Higgins[9] for heterocyclic –N= in organic systems, and $\Delta\beta = 0$, the corresponding difference in basicity would be about one p*K* or p*K*′ unit in favour of the triene. The estimated upper limit of the excess strength of the bonds in hexachlorocyclotriphosphazatriene over that of single phosphorus–nitrogen bonds is 6—10 kcal./mole,[5] making β = 5—8 kcal./mole. Δβ itself is unlikely to be greater than this, and if it is of this order, with $\Delta\alpha_r = 0$, a difference of one p*K* or p*K*′ unit would again arise, now in favour of the eight-membered ring.

This procedure though barely even semi-quantitative, shows that the expected differences in basicity between the different sizes of ring are small compared with the observed variation in pK_a' values (<-6 to $+9$) as the substituents are varied.

In case (*b*), each nitrogen atom is part of a three-centred allylic system having identical properties in rings of both sizes. The changes in π-electron energy on protonation, and therefore the basicities, would be expected to be the same in rings of either size.

2. *Hybridisation of the cyclic nitrogen atoms.* Ingold[10] has proposed that the difference in basicity between pyridine ($pK_a = 5{\cdot}17$) and a typical aliphatic tertiary amine (*e.g.*, trimethylamine, $pK_a = 9{\cdot}80$) stems largely from the difference in hybridisation, sp^2 and sp^3, respectively, of the lone-pair orbital, in the two cases. The higher the *s*-character of this orbital, the greater is the concentration of its electrons near the nucleus, and the lower therefore is its tendency to accept protons.

In compounds of known structure, the cyclic P–N–P angles in the derivatives of the cyclic trimer are approximately 120°, while in cyclic tetramer derivatives (except the fluoride where they are 147°) they are approximately 132°.[11] Assuming that one pure *p*-orbital participates in the π-bonding of the ring, and ignoring for the moment the π′-bonding, the lone-pair electrons will occupy a pure sp^2-orbital in the triene rings. In the tetraenes, the larger bond angle will confer much more *p*-character on the lone-pair orbital,

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[6] D. P. Craig and N. L. Paddock, *Nature*, 1958, **181**, 1052; D. P. Craig, *J.*, 1959, 997.

[7] M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J.*, 1960, 2423.

[8] H. C. Longuet-Higgins and C. A. Coulson, *J.*, 1949, 971.

[9] H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265, 275, 283.

[10] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, 1953, p. 174.

[11] N. L. Paddock, *Quart. Rev.*, 1964, **18**, 168.

which, with a bond angle of 132°, is practically a pure sp^3 hybrid. On this basis, the difference in $\mathrm{p}K_\mathrm{a}$ or $\mathrm{p}K_\mathrm{a}'$ between corresponding trienes and tetraenes should be of the order of that between pyridine and trimethylamine, *i.e.*, 4·6 units in favour of the tetramer. The differences observed here, although usually in this sense, are never larger than 1·2 $\mathrm{p}K_\mathrm{a}'$ units.

Two explanations of the discrepancy are possible. The lower basicity of pyridine compared with trimethylamine may spring wholly or largely from the loss of resonance energy which occurs on protonation of pyridine,[12] and not from the different states of hybridisation of the lone-pair orbital. Alternatively, Craig and Paddock,[5] have discussed another consequence of the difference in hybridisation of the lone-pair orbital in the two cases. The donation of the lone-pair electrons into suitable *d*-orbitals of phosphorus gives rise to the π'-bonding. The greater the *p*-character of the lone-pair orbital, the greater should be the loss of electrons from it. This effect, opposite in direction to the one already discussed, led Craig and Paddock [5] to predict that cyclic tetramer derivatives would in general be weaker bases than cyclic trimer derivatives, a prediction not supported by the present basicity values. We suggest that the balance between these two opposing effects causes differences in basicity between corresponding compounds of different ring-size to be small.

In support of the theory of Craig and Paddock, Paddock [11] quotes our preliminary results,[3,13] for two pairs of amino-compounds. The basicities of these amino-compounds are generally rather anomalous,[2] and the tendency in the present measurements is for the trimeric compounds to be weaker bases than their tetrameric homologues. The reverse may be true for the chlorides.[11] A slight trend towards equality of basicity between the homologues can be observed with decreasing $\mathrm{p}K_{\mathrm{a},1}'$ values. The experimental error in this low $\mathrm{p}K_\mathrm{a}'$ range does not however permit firm conclusions to be drawn.

Effects of Substituents.—We begin by comparing the effects of substituents in the chemistry of carbon and phosphorus. The paucity of basicity data for the 1,3,5-triazines, the best carbon analogues of cyclic phosphazenes forces instead a comparison with the substituted pyridines. Their basicities (Table 2) will first be briefly discussed using an analysis of substituent effects similar to Dewar's.[14]

For those substituents, *e.g.*, $-\mathrm{NH_2}$ and $-\mathrm{OMe}$, capable of a mesomeric base-strengthening release of electrons into the ring, the biggest increases in electron density at the cyclic nitrogen atom are expected when the substituents are in the 2- or 4-positions. Here a direct resonance interaction of the exocyclic group with the ring nitrogen atom is possible, indicated by participation of the structures (III) and (IV). A structure such as (V) [15] is

TABLE 2

Monosubstituted pyridines * Basicities in water, $\mathrm{p}K_{\mathrm{a},1}$				Cyclophosphazenes Basicities in nitrobenzene, $\mathrm{p}K_{\mathrm{a},1}'$		
R	2–R–py	3–R–py	4–R–py	R	$\mathrm{N_3P_3R_6}$	$\mathrm{N_4P_4R_8}$
H	5·17	5·17	5·17	H	—	—
OMe	3·28	4·88	6·62	OMe	−1·9	−1·0
SMe	3·62	4·45	5·97	SEt	−2·8	—
Et	5·97	5·70	6·02	Et	6·4	7·6
Ph	4·48	4·80	5·55	Ph	1·5	2·2
Cl	0·72	2·84	—	Cl	$<-6·0$	$<-6·0$
$\mathrm{NH_2}$	6·86	5·98	9·17	NHEt	8·2	8·1

* Values from a collection by A. Albert, in " Physical Methods in Heterocyclic Chemistry," vol. I, ed. A. R. Katritzky, Academic Press, New York, 1963, p. 67.

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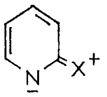
[12] M. J. S. Dewar, " Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949, p. 186.

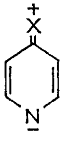
[13] D. Feakins, W. A. Last, and R. A. Shaw, *Chem. and Ind.*, 1962, 510.

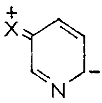
[14] M. J. S. Dewar, " Hyperconjugation," The Ronald Press, New York, 1962, p. 153.

[15] D. A. Brown and M. J. S. Dewar, *J.*, 1953, 2406; 1954, 2151.

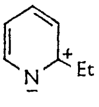
less important than (III) or (IV); while all the amino-pyridines are stronger bases than pyridine, 3-amino-pyridine is the weakest. The *p*-quinonoid structure (IV) may be more important than the *o*-quinonoid structure (III).[16]

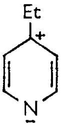

(III)

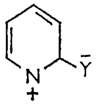

(IV)

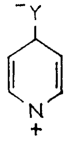

(V)

There are at least three ways in which the inductive effect of a group may be transmitted across a conjugated system.[14] First, the π-electrons may be polarised by the substituent. Thus in the ethylpyridines the 2- and 4-isomers could well be stronger bases than 3-ethylpyridine because of contributions from structures (VI) and (VII). (An alternative explanation is in terms of hyperconjugation.[16]) This mode of transmission will if anything tend to enhance the effect of the group in the 4- as compared with the 2-position. The other two modes, relay by σ-bond polarisation, and the direct field effect will have the opposite effect. The observed equality of basic strengths of the 2- and 4-ethylpyridines arises from a balance between these opposing effects.


(VI)


(VII)


(VIII)


(IX)

By contrast, a substituent whose inductive effect is base-weakening will stabilise structures (VIII) and (IX) of high energy, and the other two modes of transmission will therefore be of overriding significance.

The pK_a values for substituents such as $-NH_2$, $-OMe$, and $-Cl$ may be understood in terms of competition between such a base-weakening inductive effect diminishing steadily from the 2- to the 4-position, and a base-strengthening electron-releasing effect much greater in the 2- and the 4- than in the 3-position, and possibly greater in the 4- than in the 2-position.

Considering now the phosphazene rings, Craig and Paddock's more recent treatment [5] admits of partial cyclic delocalisation, and therefore of transmission of substituent effects *via* the π- and π'-bonding, to any atom in the ring, though some of the *d*-orbitals on a given phosphorus atom may participate only in the 3-centre orbitals covering P–N–P "islands." [7]

Through its σ-bond to the ring, the substituent may exert an inductive effect, which may be relayed to the cyclic nitrogen atoms, as in the pyridines, *via* the σ-bonding, or by the direct field effect. Its effect may also be relayed by polarisation of the π- or π'-electrons as far as the delocalised π- or π'-molecular orbitals extend from the phosphorus atom to which it is bonded. Its position with respect to the nitrogen atoms being analogous to the 2- or 4-positions in pyridine, its resonance interaction with them will be at least qualitatively similar.

The substituent may also be multiply bonded to the ring. This bonding may involve a *d*-orbital of phosphorus which does not itself form part of the π- or π'-systems. The π- and π'-systems may none the less be strongly polarised as far as the delocalised π- or π'-molecular orbitals from the phosphorus atom in question extend. This effect may probably not be distinguished qualitatively by the present type of measurement from that

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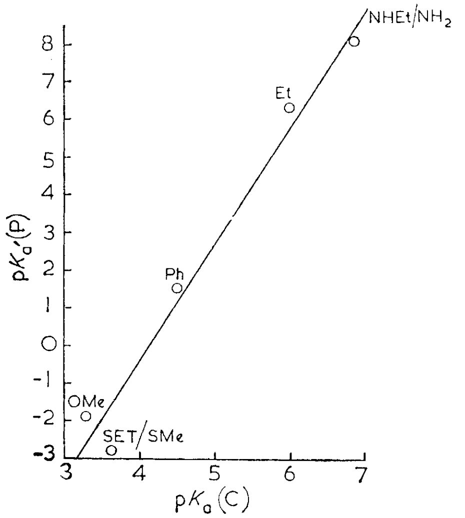
[16] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723.

in which the multiple bonding of the substituent involves a *d*-orbital of phosphorus which is part of the π- or π′-systems.

Broadly then, the effects of a substituent upon the electron density at a nitrogen atom in a phosphazene ring may be divided into two classes; first, those due to the σ-bonding of the substituent, or " inductive " effects, and secondly, those due to the multiple bonding of the substituent, or " multiple-bonding " effects. Possible differences between carbon and phosphorus compounds lie in the degree of transmission of the effects to nitrogen atoms further away than those to which the group is in the α-position, and in the absolute and relative magnitudes of the effects.



Graph of pK_a'(P) against pK_a(C)

In the figure pK_a' values for five trimeric phosphazenes [pK_a'(P)] are plotted against pK_a values for the 2-pyridines [pK_a(C)] substituted either with the same groups, or with closely similar ones. A fair correlation is seen to exist, the data fitting the equation:

$$\mathrm{p}K_a'(\mathrm{P}) = 3{\cdot}2\,\mathrm{p}K_a(\mathrm{C}) - 13{\cdot}0 \qquad (3)$$

Table 2 shows that no correlation exists between the p$K_{a,1}'$ values of the phosphazenes and the pK_a values of the 3- or 4-substituted pyridines.

The electron density on a particular nitrogen atom in the trimeric phosphazene rings is influenced by four substituents in the positions α to it and two substituents in the position γ to it. It does not, however, follow from equation (3) that the groups in the γ-position of the phosphazene have no influence on the electron density at this nitrogen atom.

The " multiple-bonding " affects the distribution of the mobile π- or π′-electrons. In the phosphazenes, the effect of six groups is spread over three nitrogen atoms, or, on average, each nitrogen atom is influenced by two groups. In the pyridines the effect of one group is confined to one nitrogen atom.

In both rings there is some small " wastage " of the effect over the phosphorus or carbon atoms, respectively, this being presumably greater in the pyridines with the lower ratio of nitrogen atoms to other cyclic atoms. Thus, if all other things were equal, changing the substituents in the two types of ring would have rather more than twice the effect on the basicity of the phosphazene ring as on the basicity of the pyridine ring.

The exocyclic groups in the phosphazenes are not coplanar with the ring. This is relatively unimportant in assessing the multiple-bonding effect, in view of the geometrical characteristics of the *d*-orbitals of phosphorus, but it must be considered in relation to the inductive effect. The bonds joining cyclic phosphorus atoms to exocyclic groups make angles of about 50—52° with the plane, or local plane of the ring. Their inductive effects will be reduced by a factor of cos 51°, compared with a group coplanar with the ring, as in the pyridines.

That part of the inductive effect arising from polarisation of the mobile electrons may be conveniently treated in the same way as the multiple-bonding effect. The other part may not be averaged in the same way. A substituent in the 2-position of pyridine will, by polarisation of the σ-bonds, and by the direct field effect, affect not only the neighbouring nitrogen atom but also the neighbouring carbon atom. In the phosphazenes, a given phosphorus atom is flanked on both sides by nitrogen atoms, both of which are influenced inductively by the groups on the phosphorus atom. Thus each nitrogen atom in the phosphazene is affected by four non-coplanar substituents in α-positions, an effect roughly 4 cos 51° or 2·5 times that of a group in the 2-position of a pyridine. The additional *inductive* effect of the groups in the γ-positions is expected to be of a smaller order of magnitude.

Thus the groups in a phosphazene exert rather more than twice the effect, both inductively and by the multiple-bonding effect, upon the electron density at a cyclic nitrogen atom than a single group in the 2-position of a pyridine.

In equation (3), the constant of proportionality is 3·2, but this relates a pK_a' (nitrobenzene) value for the phosphazene to a pK_a (aqueous) value for a pyridine. Last [17] has shown that if the pK_a values of compounds in a closely related series are plotted against their pK_a' values then approximately

$$pK_a' = a + bpK_a \tag{4}$$

with b varying from 1·3—1·8 depending on the type of compound. This would make the constant of proportionality between the basicities of the two types of ring if measured in the same solvent 1·8—2·5 in line with the arguments outlined above.

This correlation suggests that the effects of substituents upon the basic strength of cyclic nitrogen, –N=, are substantially the same in phosphorus-containing as in carbon-containing systems. Attention is drawn particularly to the importance of the multiple-bonding effect. There is also ample and independent evidence for this effect in the aminophosphazenes.[2] The protonation of a pyridine or phosphazene does not however involve the making or breaking of multiple bonds. The multiple-bonding effects of substituents certainly vary from carbon to phosphorus under these circumstances.[18]

It has been suggested [19] that the hyperconjugation of alkyl groups is more important with phosphorus than with carbon. There is no evidence that this is the case for the ethylphosphazenes, since the figures for the trimeric compound fit equation (3). Hyperconjugation, if present at all, is of no greater importance in the phosphazenes than in the pyridines in determining basic strength.

A similar correlation exists also for cyclotetraphosphazatetraenes and 2-substituted pyridines, and can be similarly interpreted. Some particular features of interest in the results may be remarked.

The relative basicities of the compounds substituted with alkoxy groups appear to be straightforwardly determined by inductive effects. In both series, $N_3P_3R_6$ and $N_4P_4R_8$, the basicities increase in the order $R = OCH_2CF_3 < OCH_2Ph < OMe < OEt \sim OBu^n < OPr^i$. A similar effect appears to operate in the thioalkoxy series, $R = SCH_2Ph < SEt \sim SPr^n < SC_6H_{11}$, but fewer examples are available. This effect is not found, either in the $pK_{a,1}'$ or in the $pK_{a,2}'$ values of the aminophosphazenes,[1] but the difference is readily explained.

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[17] W. A. Last, Ph.D. Thesis, University of London, 1962.

[18] R. F. Hudson and L. Keay, *J.*, 1960, 1859.

[19] N. L. Paddock, " Structure and Reactions in Phosphorus Chemistry," The Royal Institute of Chemistry, Lecture Series, 1962, No. 2, p. 36.

Firstly, alkoxy and thioalkoxy groups are less powerful electron supplying substituents than amino groups, hence the "saturation effect,"[1] which controls the $pK_{a,1}'$ values of the aminophosphazenes will be of no importance. Secondly, steric effects, which control the $pK_{a,2}'$ values of the aminophosphazenes, will be much reduced. Oxygen and sulphur, in contrast to nitrogen, carry only one substituent. Furthermore, both have two lone-pairs of electrons available for multiple π-bonding to phosphorus, and hence the possibility that the group will be forced into a situation unfavourable to conjugation is much reduced compared with a group containing nitrogen, which has only one lone-pair orbital.

That alkoxy groups, including benzyloxy, confer greater basicity than their thio analogues on the phosphazenes, probably arises from the greater ability of oxygen compared with sulphur to form multiple bonds with the phosphorus atom. The reversal of basicities with the groups $R = SPh > OPh$ is probably due to the relative competition of the aromatic ring for the lone-pairs of electrons of the oxygen and sulphur atoms, respectively. Whereas this is strong with oxygen, leading to a very low basicity, the effect is only of minor importance with sulphur. This is clearly demonstrated by the relative effects of the phenyl group in phenoxy- and benzyloxy-phosphazenes and their thio-analogues. The close similarity in the basicity of the latter two which may be compared with the large difference in basicity of the former two, shows that the multiple bonding of sulphur to the aromatic ring is of little significance compared with that of oxygen.

However, even in the aryloxyphosphazenes, the phosphorus atom is to some extent successful in competing with the phenyl group for the lone-pair electrons, as can be shown from their ultraviolet absorption spectra.[20]

The electron availability on the cyclic nitrogen atoms of suitable phosphazenes is further exemplified by their ability to form adducts with protonic or Lewis acids. Solid adducts have been isolated for amino-[21] and phenyl-phosphazenes,[22] and there is indirect evidence of addition compounds acting as reaction intermediates in the alkoxyphosphazene–oxophosphazane rearrangement.[23]

The low basicity of the trifluoromethylphosphazene agrees with general observations which give this group an electronegativity close to those of chlorine and fluorine.

Since the basicities of the ring nitrogen atoms reflect to some extent their nucleophilic reactivities, it is perhaps not surprising that whereas the ethoxyphosphazenes undergo alkoxyphosphazene–oxophosphazane rearrangements,[23] the corresponding trifluoroethoxy-derivatives are completely stable under similar or more drastic conditions, although other effects undoubtedly contribute to this stability as well.[23]

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