

Structure and Basicity. Part VIII.¹ Oligomeric Dimethylaminocyclophosphazenes

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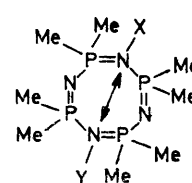
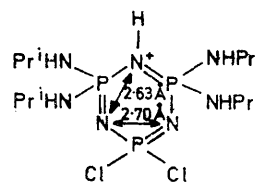
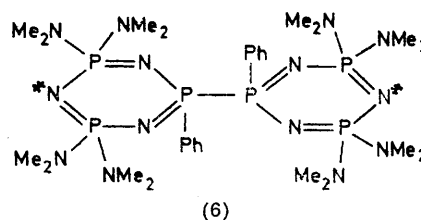
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The basicities of the homologous dimethylaminocyclophosphazenes $[\text{NP}(\text{NMe}_2)_2]_n$ ($n = 3-7$) and of the two ring assembly $[\text{N}_3\text{P}_3\text{Ph}(\text{NMe}_2)_4]_2$ have been measured in nitrobenzene. The results are discussed in terms of their structures and of possible contributions from 'direct field' and 'through-bonds effects'.

In Part II² of this series we reported the basicities of a number of fully aminolysed cyclotriphosphazatrienes and cyclotetraphosphazetriaenes. In the case of the fully dimethylaminated derivatives $[\text{NP}(\text{NMe}_2)_2]_n$ we have been able to extend these measurements to larger ring systems. The Table shows values of $\text{p}K'_{a,1}$ and $\text{p}K'_{a,2}$, measured in nitrobenzene,³ for the complete series from $n = 3-7$ (compounds 1-5),^{4,5} i.e., from the trimer to the heptamer. Values for the dimethylamino-derivative of the two-ring assembly $[\text{N}_3\text{P}_3\text{Ph}(\text{NMe}_2)_4]_2$ (6)⁶ are included for comparison.

For a wide range of amino-compounds in the trimeric and tetrameric series, detailed analyses of the basicity data showed that both the first and second protonations

take place at ring nitrogen atoms rather than at the exocyclic nitrogen atoms;^{1,2} the relatively low basicity



Approx. $r_{\text{N-N}}$
(marked) Å

¹ Part VII, D. Feakins, S. N. Nabi, R. A. Shaw, and P. Watson, *J. Chem. Soc. (A)*, 1969, 2468.

² D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 1964, 4464.

³ D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 1964, 2387.

⁴ R. A. Shaw, B. C. Smith, and C. P. Thakur, unpublished results.

⁵ G. Allen, D. J. Oldfield, N. L. Paddock, F. Rallow, J. Serregi, and S. M. Todd, *Chem. and Ind.*, 1965, 1032.

⁶ M. Biddlestone and R. A. Shaw, *J. Chem. Soc. (A)*, 1971, 2715.

	X	Y	
8a	nothing	nothing	3.6
8b	H ⁺	nothing	3.6
8c	H ⁺	CuCl ₃ ⁺	3.7

* Most probable sites for first and second protonations.

of the exocyclic nitrogen atoms is no doubt due to the release of electrons into the ring. It is unlikely that mere increase in ring-size would markedly affect the basicities of the two types of basic centre relative to each other and it may reasonably be assumed that protonation of the higher homologues is also exclusively on the ring nitrogen atoms. In comparing the pK'_a values a correction must first be made for statistical effects.¹³ The increase in the corrected $pK'_{a,1}$ from the trimer to the tetramer is fairly general for a number of fully substituted compounds,¹⁴ when the 'saturation effect'^{1,2}

substituents R (*cf.* ref. 16); additionally, the effect of positive charges in the protonated species is likely to cause further distortions. Nevertheless in those compounds studied by X-ray crystallography, *e.g.*, 7, 8a, b, and c) the longest nitrogen–nitrogen distances remain remarkably constant (± 0.1 Å).¹⁷ Whilst in solution the conformation might well be different from those in the solid state, large changes in r_{N-N} are unlikely. The decrease in $\Delta pK'_a$ on passing from one oligomer to the next higher one is much greater when this is accompanied by an increase in the number of bonds between

Basicities in nitrobenzene

No.	Compound	$pK'_{a,1}$			$pK'_{a,2}$			$\Delta pK'_a = pK'_{a,1} - pK'_{a,2}$		Largest $N_{ring}-N_{ring}$ distances ^c in Å	Ref.
		Statistical			Statistical						
		Observed	correction	Corrected	Observed	correction	Corrected	Observed	Corrected		
(1)	$N_3P_3(NMe_2)_6$	7.5	0.5	7.0	−3.1	0.3	−3.4	10.6	10.4	2.7	7, 8
(2)	$N_4P_4(NMe_2)_8$	8.2	0.6	7.6	0.2		0.2	8.0	7.4	3.6	9
(3)	$N_5P_5(NMe_2)_{10}$	8.5	0.7	7.8	1.5	0.3	1.2	7.0	6.6	4.9 ^b	10
(4)	$N_6P_6(NMe_2)_{12}$	8.8	0.8	8.0	3.9		3.9	4.9	4.1	5.3	11
(5)	$N_7P_7(NMe_2)_{14}$	8.3	0.9	7.4	3.9	0.3	3.6	4.4	3.8		
(6)	$[N_3P_3Ph(NMe_2)_4]_2$	6.9	0.3	6.6	3.8 ^a		3.8	3.1	2.8	7.8 ^b	12

^a An inflection at −4.6 might be associated with $pK'_{a,3}$. ^b From chloro-analogue. ^c From X-ray crystallographic data.

is not operative; a further rise as far as the hexamer is followed by a fall to the heptamer. There is no obvious theoretical basis for these rather small differences and they probably derive from such factors as the effect of changes in ring geometry or hybridisation. The fact that there are four γ -substituents (for $n \geq 4$) might also contribute to an increase in basicity in the homologues beyond the trimer.

The changes in (the corrected) values of $pK'_{a,2}$ and $\Delta pK'_a (= pK'_{a,1} - pK'_{a,2})$ are very much more pronounced, varying from compound (1) to compound (5) from −3.4 to +3.6 (for $pK'_{a,2}$) and from 10.4 to 3.8 (for $\Delta pK'_a$) respectively. The likely causes have been discussed earlier.² The 'direct-field' effect [and any additional effect arising from a lowering of the basicity of the second basic centre after protonation of the first by transmission through the bonds ('through-bonds' effect)] would be expected to cause the two protons to add at ring nitrogen atoms as far apart as possible. The appropriate crystallographic distances are given (where known) in the Table, and $\Delta pK'_a$ does indeed decrease with r_{N-N} .

The nitrogen–nitrogen distances in compounds (1) and (6) (based on six-membered ring systems) are probably little affected by substituents and/or protonation (*cf.* refs. 12 and 15). In larger ring systems, *e.g.*, $N_4P_4R_8$, the ring shape is dependent on the nature and position of the

the protonated sites, the corrected values being 3.0, 0.8, 2.5, and 0.3 pK'_a units respectively. This might well reflect a contribution from a 'through-bonds' effect.

The $pK'_{a,1}$ value of the two-ring assembly (6) reveals an interesting point. If we calculate (using the usual substituent constants, $\gamma_{NMe_2} = 2.8$, $\gamma_{Ph} = 2.3$) the $pK'_{a,1}$ value of the hypothetical compound, $[N_3P_3(NMe_2)_5 \cdot N_3P_3Ph(NMe_2)_4]$, we obtain for the nitrogen atom [in the $N_3P_3(NMe_2)_5$ moiety] *para* to the phosphorus–phosphorus bond a corrected value of 7.1, indicating that the substituent effect of $\gamma_{N_3P_3Ph(NMe_2)_4}$ is approximately the same as that of γ_{NMe_2} . The $\Delta pK'_a$ value is the smallest so far reported for a cyclophosphazene.

EXPERIMENTAL

The technique of measuring basicities in nitrobenzene,³ and the preparation of the compounds^{4–6} are described elsewhere.

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