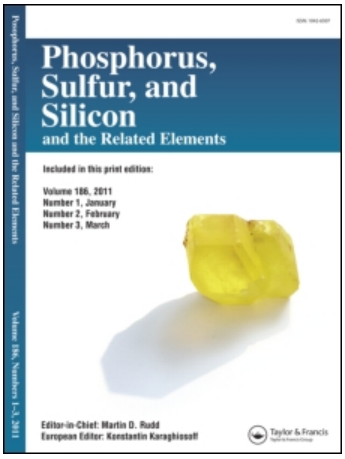

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Bicyclic Phosphazenes Derived from (Amino)Cyclotetraphosphazenes

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To cite this Article Krishnamurthy, S. S.(1989) 'Bicyclic Phosphazenes Derived from (Amino)Cyclotetraphosphazenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 375 — 391
To link to this Article: DOI: 10.1080/10426508908039728
URL: http://dx.doi.org/10.1080/10426508908039728

Phosphorus, Sulfur and Silica, Vol. 41, pp. 375-391
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BICYCLIC PHOSPHAZENES DERIVED FROM (AMINO)CYCLOTETRAPHOSPHAZENES

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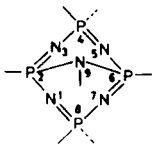
Abstract Amination reactions of 2,6-bis(primary amino)cyclotetraphosphazenes yield not only the expected (amino)cyclotetraphosphazenes but also novel trans-annular bridged bicyclic phosphazenes by an intramolecular substitution pathway. In addition, resins are formed in some reactions by an intermolecular condensation. The effect of substituents attached to the phosphazene ring, the attacking nucleophile and solvent on the formation of the trans-annular P-N-P bridge is considered in detail in relation to plausible reaction mechanisms. Analytical separation of bicyclic phosphazenes by high performance liquid chromatography (HPLC) on a reverse phase silica column is demonstrated. Structural features of bicyclic phosphazenes and salient aspects of their NMR spectroscopic data are discussed.

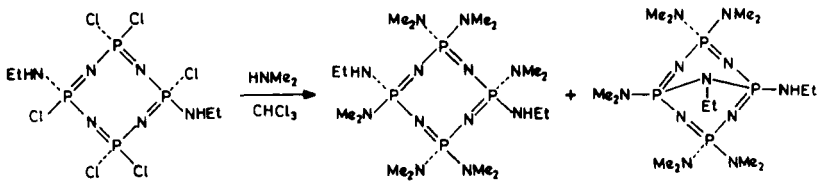
INTRODUCTION

The discovery of the P_4N_5 ring system(I) derived from cyclotetraphosphazenes in our laboratory by Sau[1] was marked by serendipity.



I

The bis(ethylamino)cyclotetraphosphazene(II) was subjected to exhaustive dimethylamination in chloroform with a view to preparing its dimethylamino derivative(III). The choice of solvent was unintentional and the major product isolated from the reaction was the bicyclic derivative, $N_4P_4(NMe_2)_5(NHEt)(NEt)$(IV). Subsequently, when the same reaction was carried out in diethyl ether, only the (amino)cyclotetraphosphazene(III) was obtained[2]. Further studies have revealed

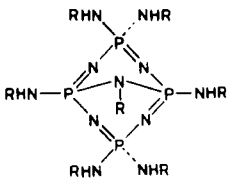


II III IV

that the amination reactions of octachlorocyclotetraphosphazene ($N_4P_4Cl_8$) or its 2,6-bis(primary amino)derivatives can proceed in three ways : (i) stepwise replacement of chlorine atoms to give chloro(amino) and octakis(amino)cyclotetraphosphazenes (ii) intramolecular nucleophilic attack that yields novel trans-annular bridged bicyclic phosphazenes and (iii) intermolecular condensation resulting in crosslinked resins. The competition among these three processes depends on the substituents attached to the phosphazene ring, the reacting nucleophile and (to a very significant extent) on the nature of the reaction medium[3-10]. In this paper, we shall be concerned with the synthesis of bicyclic phosphazenes, their structural and NMR spectroscopic features and mechanism of their formation with particular emphasis on recent studies which have led to a directed synthetic strategy for this class of compounds[8].

SYNTHESIS OF BICYCLIC PHOSPHAZENES : SUBSTITUENT AND SOLVENT EFFECTS

Symmetrically substituted bicyclic phosphazenes of type, $N_4P_4(NHR)_6(NR)$(V), are formed when $N_4P_4Cl_8$ reacts with an excess of primary amine in chloroform[3,4,7]. The yield of bicyclic phosphazene increases in the order R = Me < Et < $Pr^n \gg Bu^n$. The formation of the P-N-P bridge is inhibited considerably if the R group is branched at the α-carbon atom. Thus t-butylamine does not afford a bicyclic phosphazene; the yield of bicyclic phosphazene with isopropylamine is low (<10%). Cyclopropylamine is an exception



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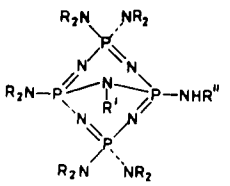


VI

in that a significant amount (38%) of the bicyclic derivative $N_4P_4(NHC_3H_5)_6(NC_3H_5)$ is isolated[10]. Apparently, the relatively small size of the C_3H_5 group and the low propensity for back donation to phosphorus from the NHC_3H_5 group are the contributing factors for accommodating the cyclopropyl group at the bridging nitrogen atom. However, when $N_4P_4(NHEt)_2Cl_6$ (II) is treated with cyclopropylamine in chloroform, the resulting bicyclic phosphazene (yield > 50%) has an ethyl group and not a cyclopropyl group at the bridging nitrogen atom[10].

Unsymmetrically substituted bicyclic phosphazenes of type $N_4P_4(NR_2)_5(NHR'')(NR')$(VI) are obtained from the reactions of $N_4P_4Cl_6(NHR')(NHR'')$ with an excess of a secondary amine[3,5,10,13]. When dimethylamine is the reacting nucleophile, the relative yields of bicyclic phosphazenes increases in the order - R' = R'' = CH_2Bu^t < Bu^n < Me < CH_2Ph < Et ≤ Pr^n. Bicyclic phosphazenes are not formed when the R' and R'' groups are both α-branched (e.g. Pr^i, Bu^t or Ph)[5].

We have recently shown that the formation of bicyclic phosphazenes from $N_4P_4Cl_8$ occurs only after the tetrakis stage of chlorine replacement[8]. The tetrakis(amino) derivatives, $N_4P_4Cl_4R_2(NHEt)_2$ (VII, R = NMe_2 or NMePh) have been isolated and their utility for the preparation of bicyclic phosphazenes containing different amino substituents has been established. Treatment of VII (R = NMe_2 or NMePh) with one molar equivalent of dimethylamine or ethylamine in $CHCl_3/Et_3N$ yields the (chloro)bicyclic derivatives, $N_4P_4Cl_2R_2$ NR'R''(NHEt)(NEt)(VIII)[8,11,12]. Similarly

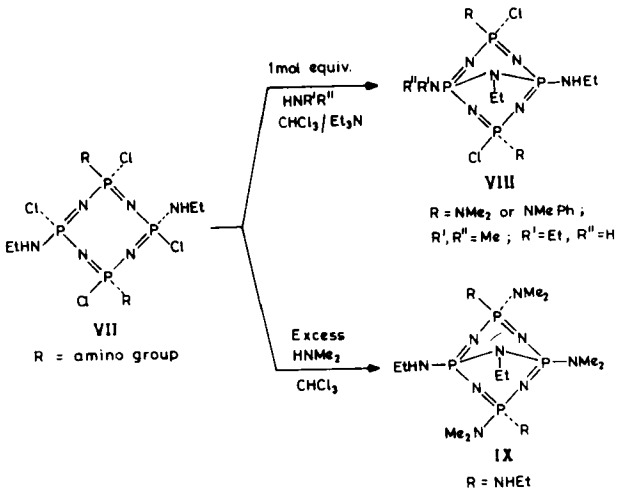
Table I : Effect of solvent and substituents on the relative yields of bicyclic (XI) and cyclotetraphosphazenes(XII).

Phosphazene(X)			Reacting amine	Solvent[a]	Relative yield(%)[b]		Ref
R^1,R^2	R^3	R^4	R^5R^6NH		XI	XII	
Et	NMe_2	NMe_2	Me_2NH	Et_2O	0	100	2,5
Et	NMe_2	NMe_2	Me_2NH	MeCN	15	85	5
Et	NMe_2	NMe_2	Me_2NH	CH_2Cl_2	40	60	5
Et	NMe_2	NMe_2	Me_2NH	$CHCl_3$	70	30	3,5
Me	NMe_2	NMe_2	Me_2NH	$CHCl_3$	40	60	5
Pr^n	NMe_2	NMe_2	Me_2NH	$CHCl_3$	67	33	5
Bu^n	NMe_2	NMe_2	Me_2NH	$CHCl_3$	25[c]	75	5
Bu^t	NMe_2	NMe_2	Me_2NH	$CHCl_3$	0	100	2
CH_2Bu^t	NMe_2	NMe_2	Me_2NH	$CHCl_3$	10	90	11
Et,Bu^t	NMe_2	NMe_2	Me_2NH	$CHCl_3$	67[c]	33	5
Et	NHEt	NHEt	Me_2NH	Et_2O	5	95	11
Et	NHEt	NHEt	Me_2NH	$CHCl_3$	70	30	11
Et	NMe_2	NMe_2	$EtNH_2$	Et_2O	0	100	8
Et	NMe_2	NMe_2	$EtNH_2$	$CHCl_3$	70	30	8
Et	NMePh	NMePh	$EtNH_2$	$CHCl_3$	33[c]	67	11
Et	$N(CH_2Ph)_2$	$N(CH_2Ph)_2$	$EtNH_2$	$CHCl_3$	45[c]	55	11
Et	NHEt	$N(CH_2Ph)_2$	$EtNH_2$	Et_2O	20[c]	80	11
Et	NHEt	$N(CH_2Ph)_2$	$EtNH_2$	MeCN	25[c]	75	11
Et	$NHBu^t$	$NHBu^t$	$EtNH_2$	$CHCl_3$	33[c]	67	11
Et	$NHBu^t$	$NHBu^t$	$EtNH_2$	MeCN	40[c]	60	11
Et,Bu^t	$NHBu^t$	$NHBu^t$	$EtNH_2$	MeCN	55[c]	45	11
Et	NCH_2Bu^t	NCH_2Bu^t	$EtNH_2$	$CHCl_3$	20[c]	80[c]	11
Et	NEt_2	NEt_2	Et_2NH	$CHCl_3$ / MeCN	90	10[c]	10,13
Et	NC_4H_8O	NC_4H_8O	OC_4H_8NH	$CHCl_3$	15	85	10
Et	NC_5H_{10}	NC_5H_{10}	$C_5H_{10}NH$	$CHCl_3$	70[c]	30	10,13
Et	NHC_3H_5	NHC_3H_5	$C_3H_5NH_2$	$CHCl_3$	80	20	10

a Generally, reaction carried out at the boiling point of the solvent ; for reactions in $CHCl_3$, Et_3N was also invariably used.

b Estimated by ^{31}P NMR spectroscopy (± 5%); absolute yields of XI and XII (based on the starting cyclophosphazene) together exceed 75% in most cases.

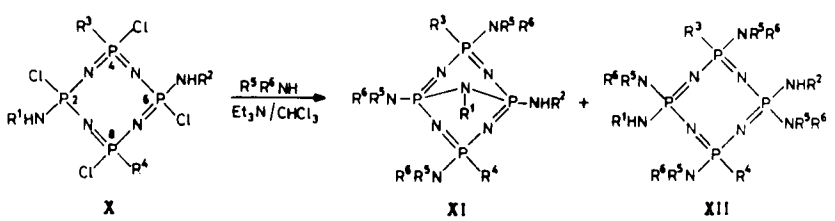
c Pure Product not isolated ; d morpholino ; e piperidino ; f cyclopropylamino



treatment of 2,4,6,8-$N_4P_4Cl_4(NHEt)_2R_2$ (VII, R = NHEt) with dimethylamine in $CHCl_3$ affords the bicyclic phosphazene, $N_4P_4(NHEt)_3(NMe_2)_3(NEt)$(IX)[11].

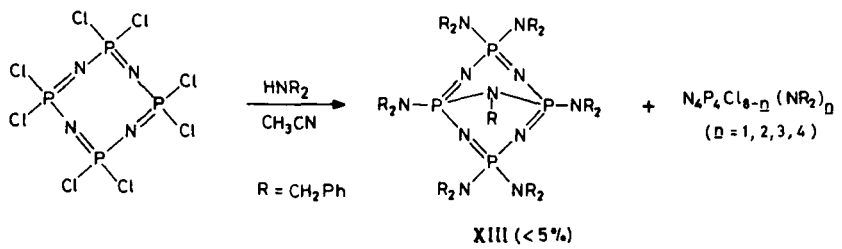
The reactions of 2,6-$N_4P_4Cl_6(NHBu^t)_2$, 2,4-$N_4P_4Cl_6(NHBu^t)_2$, $N_4P_4Cl_7[N(CH_2Ph)_2]$, and 2,6-$N_4P_4Cl_6[N(CH_2Ph)_2]_2$ with ethylamine in chloroform have also been studied and in all cases bicyclic phosphazenes are formed in varying yields. A tetrakis(amino) intermediate such as X may be envisaged in all these reactions[11].

The effect of various substituents attached to the phosphazene ring and the attacking nucleophile on the relative yields of bicyclic phosphazenes(XI) and the corresponding (amino)cyclotetraphosphazenes(XII) is brought out by the data shown in Table I.



The solvent used to carry out the amination reaction exerts a marked influence on the relative yields of bicyclic phosphazenes and (amino)cyclotetraphosphazenes as shown in Table I for the reactions of 2,6-$N_4P_4Cl_6(NHEt)_2$ with dimethylamine. Whereas chloroform and dichloromethane promotes the formation of bicyclic phosphazenes, the bicyclic phosphazenes are not formed at all in diethyl ether or their yields are very low. Methyl cyanide shows an intermediate behaviour[5]. However, when the cyclophosphazene precursor or the attacking nucleophile carries bulky substituents, bicyclic phosphazenes can be formed to a significant extent even in diethyl ether or methyl cyanide (Table I)[9,11].

A unique bicyclic compound, $N_4P_4[N(CH_2Ph)_2]_6(NCH_2Ph)$(XIII) has been isolated in a tiny yield (< 5%) from the reaction of $N_4P_4Cl_8$ with an excess of dibenzylamine in methyl cyanide. There is no crystallographic confirmation of the structure of this compound but it has been characterised by high-resolution mass spectrometry and IR and NMR spectroscopy. Arguments based on steric grounds have been adduced to account for the formation of XIII and the absence of chloro(dibenzylamino)tetraphosphazenes, $N_4P_4Cl_{8-n}[N(CH_2Ph)_2]_n$ ($n > 4$)[14]. The steric hypothesis is supported by recent results on the reactions of $N_4P_4Cl_6(NHEt)_2$(II) with dibenzylamine[10]. The formation of the bicyclic compound XIII must involve a dealkylation step prior to or concomitant with an intramolecular attack. The generality of this type of reaction has not been explored and we shall not discuss this further.



XIII (< 5%)

MECHANISM OF FORMATION OF BICYCLIC PHOSPHAZENES(XII)

The following observations are pertinent to an understanding of the mechanism of formation of bicyclic phosphazenes from chloro(primary amino)cyclophosphazenes[5,9,10,11].

(i) A bicyclic phosphazene is not formed when $N_4P_4Cl_7(NHEt)$ is treated with an excess of dimethylamine in $CHCl_3$ nor in the reaction of 2-trans-6-$N_4P_4(NMe_2)_6Cl_2$ with an excess of ethylamine in the same solvent.

(ii) Addition of a tertiary base (Et_3N) in moderate amounts enhances the yield of bicyclic phosphazenes.

(iii) Whereas a bicyclic phosphazene is formed in the reaction of 2-trans-6-$N_4P_4Cl_6(NMePh)_2$[15] (structure known from X-ray analysis) with ethylamine in chloroform, an analogous reaction with 2-trans-4-$N_4P_4Cl_6(NMePh_2)$ (structure also known from X-ray crystallography) yields only an octakis(amino)cyclotetraphosphazene. Undoubtedly a tetrakis(amino)intermediate, $N_4P_4(NMePh)_2(NHEt)_2Cl_4$ is involved in these reactions but the disposition of the NHEt groups for the two isomers will be different (antipodal phosphorus centres for the former and adjacent phosphorus centres for the latter).

(iv) The reaction of 2,6-$N_4P_4Cl_6(NHBu^t)_2$ or 2,6-$N_4P_4(NHPh)_2Cl_6$ with dimethylamine does not afford a bicyclic phosphazene; however, the reaction of the former with ethylamine or that of the mixed amino derivative, 2,6-$N_4P_4Cl_6(NHBu^t)(NHEt)$ with dimethylamine gives a bicyclic phosphazene in which the bridging nitrogen carries an ethyl group.

It is thus clear that the trans-annular P-N-P bridge is formed only when both the antipodal phosphorus centres carry a PCl(NHR) group and one or both of the R groups is capable of being accommodated at the bridging nitrogen atom. Bridging of adjacent phosphorus atoms does not occur as it would entail the formation of a strained four-membered ring.

Turning to more specific details of the mechanism[5,11], the initial step from the tetrakis(amino) intermediate XIV (Figure 1) would be the base-assisted double proton abstraction - chloride elimination steps to give a three-coordinated P^V intermediate B (pathway (i) in Figure 1). This species then readily adds a molecule of the reacting amine (R^3R^4NH) followed by the intramolecular addition of the resulting NHR^2 group on one phosphorus to the exocyclic double bond at the antipodal phosphorus to give the bicyclic phosphazene D which is still left with P-Cl bonds.

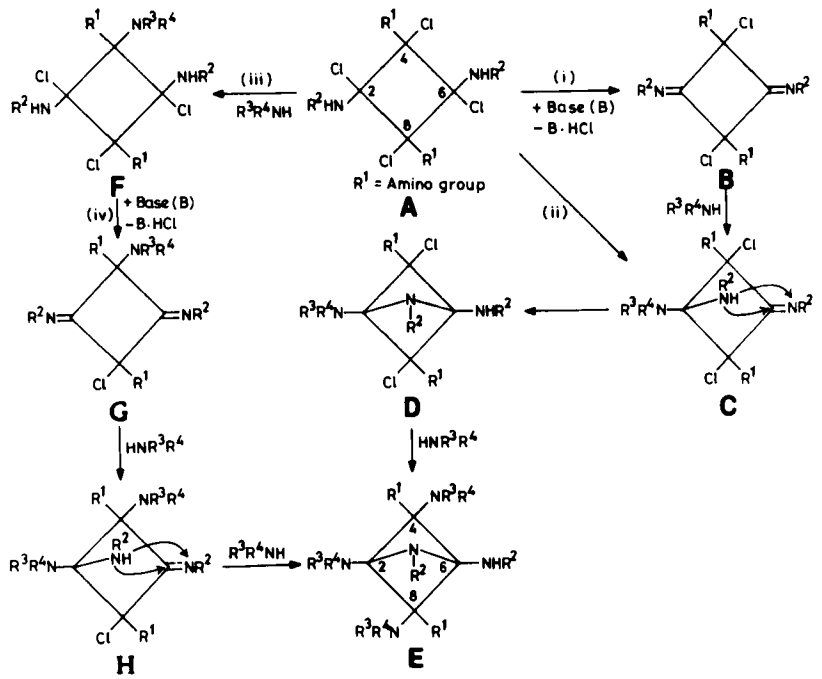


FIGURE 1 Mechanism of formation of bicyclic phosphazenes: (i) Pathway (i), S_N1 c.b mechanism; (ii) Pathway(ii), $S_N2(P)$ attack by R^3R^4NH followed by S_N1 c.b at the antipodal phosphorus ; (iii) Pathway(iii), $S_N1(P)$ or $S_N2(P)$ attack; (iv) S_N1 c.b mechanism (corners of the squares represent P atoms; ring N atoms on the periphery not shown).

Further amination leads to the final product E. Pathway (ii) slightly differs from pathway(i) in that C would be formed by a direct $SN^2(P)$ attack by the reacting amino group at one of the phosphorus centres. The rest of the steps are the same as in pathway(i). Whether the two steps B⟶C and C⟶D are sequential or synchronous is at present uncertain.

Formation of (amino)chlorocyclotetraphosphazenes by normal chlorine atom replacement is shown in pathway(iii). The intermediate F can be converted either into a bicyclic derivative via the sequence F⟶G⟶H⟶E or octakis (amino)cyclotetraphosphazenes (not shown in the Figure). Species C can also give octakis(amino)cyclotetraphosphazenes. The proposed structure for D is tentative; an alternative structure with the chlorines at P(6) and P(8) cannot be discounted[10] though unlikely particularly when NR_2 is a secondary amino group in view of the ease of amine attack at a PCl(NHR) centre and also because of the greater electrophilicity of the junction phosphorus atoms [P(2) and P(6)][10].

The operation of a S_N1 c.b. (proton abstraction - chloride elimination) mechanism in cyclophosphazene chemistry was first proposed by Shaw and coworkers and later elaborated by Goldschmidt and coworkers[16]. We have recently provided kinetic evidence for such a mechanism in cyclotriphosphazene chemistry[17]. Furthermore, the intermediacy of a planar three-coordinated P^V species has been established by trapping it with methanol and also by the isolation of the unusual products, [gem-$N_3P_3Cl_4(NHC_6H_4R)(O)]^-(NHEt_3)^+$ [17]. We have also shown that in the reaction of $N_3P_3Cl_6$ with dimethylamine, there is a change-over from an associative $S_N2(P)$ to a dissociative $S_N1(P)$ mechanism after three chlorine atoms are replaced in a nongeminal pathway[18]. It is likely that the dissociative pathway gains ascendency in the reactions of $N_4P_4Cl_8$ after one chlorine from each P is replaced by an amino group.

The efficacy of chloroform to promote the formation of bicyclic phosphazenes can be rationalised by assuming that it stabilizes the transition state in the intramolecular attack by hydrogen bonding to the incipient electron-rich $\overset{\ominus}{N}R$ centre[5,10]. Donor solvents such as Et_2O or MeCN can reduce the electrophilicity of the phosphorus centres for the trans-annular attack by the weaker P-NHR nucleophile whilst the reactivity towards a stronger nucleophile such as amines is not impaired to any significant extent. However, when the cyclotetraphosphazene precursor bears a bulky amino group (e.g. $NHBu^t$, $N(CH_2Ph)_2$) or when the reacting nucleophile is sterically demanding [e.g. $HNEt_2$, $HN(CH_2Ph)_2$], an associative pathway would be accessible only with difficulty and the trans-annular bridge formation, in as much as it entails a dissociate pathway, will be facilitated. Under these circumstances, bicyclic phosphazenes are formed in significant amounts in methyl cyanide or even in diethyl ether[10,11] (Table 1).

SEPARATION AND ANALYSIS OF BICYCLIC PHOSPHAZENES

Bicyclic phosphazenes are invariably formed as mixtures with (amino)cyclotetraphosphazenes and the separation of the two types of products poses considerable difficulties. Separation can be achieved by repeated fractional crystallization or preparative scale thin-layer chromatography over silica gel[10]. Even so, in several instances, a separation of the two types of compounds cannot be effected. Recently we have explored the utility of High Performance Liquid Chromatography (HPLC) for this purpose. An efficient separation can be achieved on an analytical scale over a reverse-phase silica column by using a methanol-water mixture containing 0.1% trifluoroacetic acid as the eluent[12]. Typical chromatograms are shown in Figure 2. The use of a reverse phase column enables the elution of the more elusive bicyclic compound first.

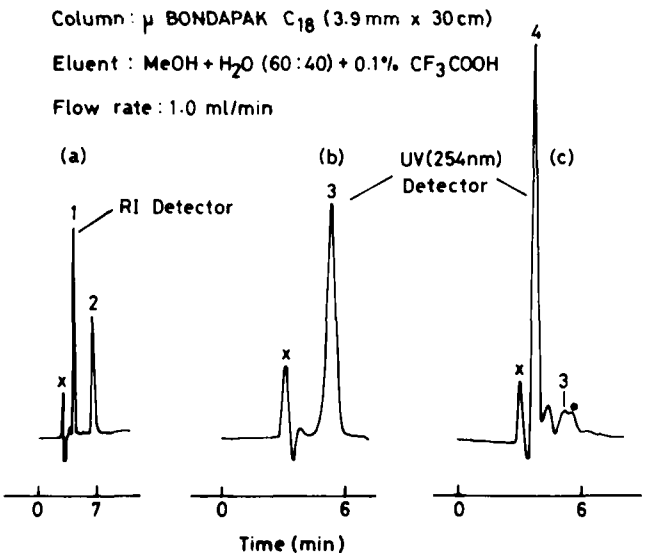


FIGURE 2 HPLC separation of bicyclic phosphazenes and (amino)cyclotetraphosphazenes : (a) a mixture of $N_4P_4(NHEt)_6(NEt)$(1) and $N_4P_4(NHEt)_8$(2); (b) a pure sample of 2-trans-6-$N_4P_4(NMePh)_2(NHEt)_6$(3); (c) a mixture of (3) and bicyclic $N_4P_4(NMePh)_2(NHEt)_4(NEt)$(4) (x - solvent peaks; ● benzene).

NMR SPECTRA OF BICYCLIC PHOSPHAZENES

The ^{31}P chemical shifts for bicyclic phosphazenes lie in a range which is ~10 ppm downfield from that characteristic of the related (amino)cyclotetraphosphazenes. Hence ^{31}P NMR spectroscopy has proved a powerful analytical tool for the identification and estimation of the relative yields of bicyclic phosphazenes and (amino)cyclotetraphosphazenes, particularly in those instances where the two cannot be readily separated from reaction mixtures[5,7,9,10]. The spectra of two typical reaction mixtures are shown in Figure 3.

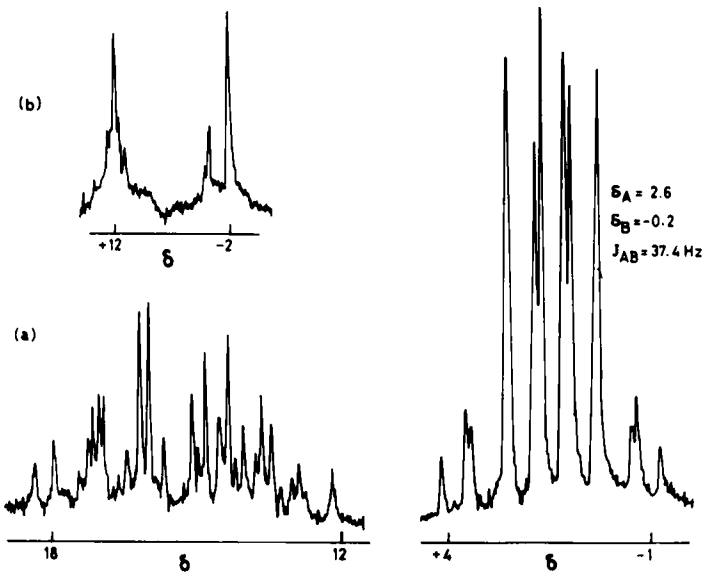


FIGURE 3 The $^{31}P\{^{1}H\}$ NMR spectra (32.4 MHz, $CHCl_3$) of mixtures of (amino)cyclotetraphosphazenes and bicyclic phosphazenes (a) product of the reaction of $N_4P_4(NMePh)_2Cl_6$ with an excess of $EtNH_2$, (b) reaction of $N_4P_4(NMePh)_2(NHEt)_2Cl_4$ with 1 molar equiv. of $ETNH_2$ in $CHCl_3/Et_3N$.

Table II : Phosphorus-31 NMR data for selected bicyclic phosphazenes

Bicyclic phosphazene	δ P(2)[a]	δ P(6)[a]	δ P(4),P(8)	^2J(PNP)/Hz P(2),P(4)	P(4),P(6)	P(2),P(6)	Ref
$N_4P_4(NHMe)_6(NMe)$	—— 18.5 ——		21.5	39.0			4
$N_4P_4(NHEt)_6(NEt)$	—— 18.6 ——		15.3	40.9			3
$N_4P_4(NHC_3H_5)_6(NC_3H_5)$	—— 14.9 ——		18.2	39.7			10
$N_4P_4(NMe_2)_5(NHEt)(NEt)$	19.7[b]	18.9	22.5	42.7	42.7	33.0	3
$N_4P_4(NMe_2)_5(NHBu^t)(NEt)$	19.6[b]	16.1	20.6	46.5	41.2	34.6	7
$N_4P_4(NMe_2)_2(NHEt)_4(NEt)$[d]	—— 18.6 ——						8
$N_4P_4(NC_4H_8)_5(NHEt)(NEt)$	13.9[c]	18.9	14.7	50.0	38.0	35.0	10

a P atoms involved in the P-N-P bridge

b $P(NMe_2)$ c $P(NC_4H_8)$ d NMe_2 at P(4) and P(8) ; single line observed (A_2BC spin system approaching the A_4 limit).

Bicyclic phosphazenes of type $N_4P_4(NHR)_6(NR)$(V) provide examples of an A_2B_2 spin system[3,7] (considering only the phosphorus nuclei) although accidental coincidence of shifts may cause the A_4 limit to be reached[7,11]. The spectra of the bicyclic phosphazenes of type VI are of the A_2BC or A_2BX type and require iterative computer analysis to determine the spectral parameters[7,10,19]. Data for a few typical compounds are given in Table II. A particularly noteworthy trend is the lower value of P-P coupling across the trans-annular bridge compared to the two-bond P-P coupling along the periphery of the ring. A similar reduction in the ^3J(PNCC) coupling is observed for the bridging ethyl group of $N_4P_4(NHEt)_6(NEt)$ compared to the values for the other NHEt groups[20]. In bicyclic phosphazenes, the bridging nitrogen atom displays a pyramidal geometry (see below). Presumably the reduced s-character of the P-N bonds at the bridge and the consequent decrease in the Fermi-contact contributions causes a reduction of spin couplings across the brdige[19,21].

Consistent with the structures of the bicyclic phosphazenes, their ^1H NMR spectra are quite complex and measurements at high fields (> 5 Tesla) are required to make a complete analysis of the spectrum and assign the various resonances[4,7]. A distinctive feature of the ^1H NMR spectra of bicyclic phosphazenes is the deshielding of the protons of the groups at the junction phosphorus atoms. The ^1H NMR data for two bicyclic phosphazenes are shown in Figure 4 which also includes data for a related cyclophosphazene and an hydrochloride adduct of the bicyclic phosphazene, viz., $N_4P_4(NHMe)_6(NMe).HCl$ in which protonation occurs at the bridging nitrogen atoms[3,4].

X-RAY CRYSTALLOGRAPHIC STUDIES

The structures of four bicyclic phosphazenes - $N_4P_4(NMe_2)_5(NHR)(NR)$ and $N_4P_4(NHR)_6(NR)$ (R = Me or Et) - have been determined by single crystal X-ray analysis [20,22-24]. The molecular shape of

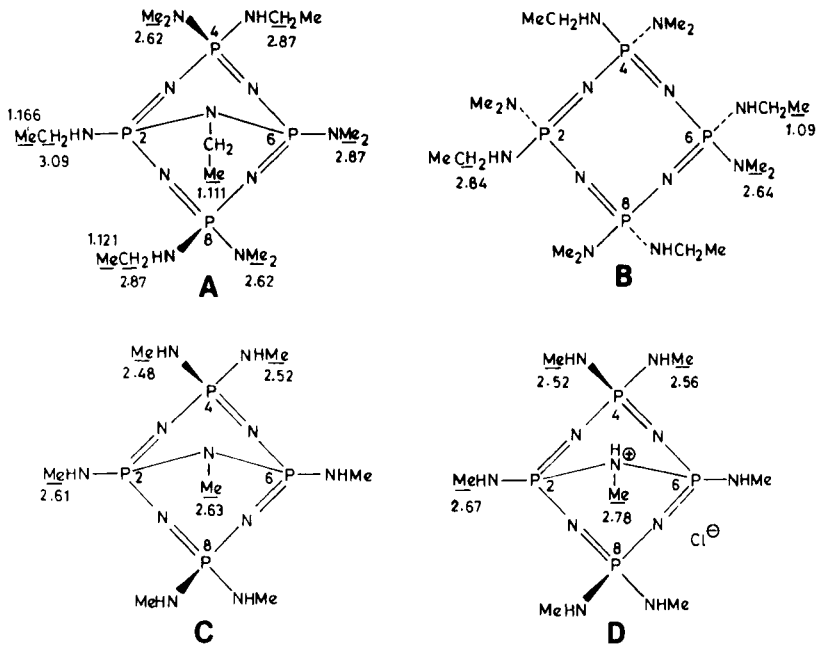


FIGURE 4 Proton NMR data for bicyclic phosphazenes and related octakis(amino)cyclotetraphosphazene [Measurements at 270 MHz in $CDCl_3$ (A and B) and D_2O (C and D)].

the bicyclic phosphazenes may be regarded as that of a basket and bears resemblance to that of adamantane and the $P_4(NMe)_6$ cage compound. The fragments on either side of the bridge are approximately planar and the dihedral angle between the two planes is 120^{o}. Structural parameters for one compound is shown in Figure 5. Three types of P-N bonds are observed; the peripheral ones (1.57 - 1.61 Å) retain their phosphazenic character; the exocyclic P-N bonds (1.63 - 1.66 Å) are slightly longer; the P-N bonds at the bridgehead (1.71, 1.73 Å) are close to the value associated with a P-N single bond. The bridging nitrogen has a pronounced pyramidal character (sum of interbond angles 335^{o}) whilst the geometry around the exocyclic nitrogen atoms is

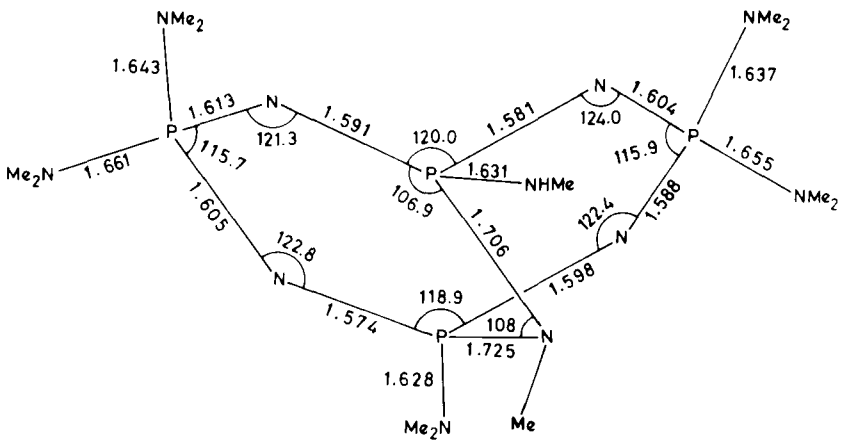


FIGURE 5 Bond distances (Å) and bond angles (°) for the bicyclic phosphazene, $N_4P_4(NMe_2)_5(NHMe)(NMe)$; two phosphazene and two water molecules are held together by hydrogen bonds in the crystal. The parameters for both the molecules are similar.

distinctly planar. The trans-annular P-N-P bridge in bicyclic phosphazenes thus partakes of the characteristics of a phosphazane.

CONCLUDING REMARKS

Stemming from a chance observation, the study of bicyclic phosphazenes has bloosomed into an interesting area in cyclophosphazene chemistry. There are still several intricate details of the mechanism of formation of the trans-annular bridge that require further study to assess the individual importance of factors such as the nature of the solvent, temperature of the reaction and the steric and electronic effects of substituents attached to the phosphazene ring in tilting the balance between associative and dissociative pathways. The isolation of bicyclic phosphazenes containing P-Cl bonds in a crystalline form and their structural elucidation

remains a considerable challenge. When we consider $^{31}P\ \{^{1}H\}$ NMR spectra, bicyclic phosphazenes and their cyclotetraphosphazene precursors constitute excellent examples of a variety of four spin systems including A_2B_2 systems wherein there is true magnetic equivalence of pairs of A and B nuclei[19]. The separation of bicyclic phosphazenes by liquid chromatography and high field ^{1}H and ^{31}P NMR measurements on pure samples should prove rewarding.

Acknowledgement I wish to pay tribute to my numerous research scholars whose names appear in the References Section for their painstaking and skillful experimental work on which this paper is based. Much of the initial work in the area was carried out under a Binational Project between our Department and Birkbeck College, London with support from University Grants Commission, New Delhi and Overseas Development Administration, London which is acknowledged. I thank Prof. R.A. Shaw, Prof. A.R. Vasudeva Murthy and Dr. M. Woods, the Co-investigators of the Binational Project for collaboration. Thanks are also due to Prof. T.S. Cameron (Dalhousie University, Canada) and Prof. H. Manohar of our Department for collaboration in X-ray crystallography, Council of Scientific and Industrial Research and Department of Science and Technology (New Delhi) for support and Shin Nisso Kako Co. Ltd., Japan for gifts of chlorocyclophosphazenes.

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