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The Nuclear Magnetic Resonance Spectroscopy of ^{15}N-Labelled Cyclophosphazenes

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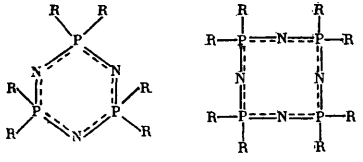
The ^{31}P NMR spectra of ^{15}N-labelled cyclophosphazenes contain additional information compared with the unlabelled compounds, namely, apart from the spin-spin coupling constant J_{PN}, it is also possible to obtain information, in the case of homosubstituted compounds, about the spin-spin coupling constants J_{PP} and J_{NN}. The ^{15}N NMR spectra of these compounds yield the same information and in addition the chemical shift of the ^{15}N signal. All these NMR parameters are sensitive to changes in the electronic structure of the cyclic P-N systems, which depend on the type and number of substituents and also on the ring size. Studies on labelled halides, amino-derivatives, ethers, thioethers, and alkyl-substituted derivatives of cyclic phosphazenes containing between three and six P-N structural units are examined. The NMR data are interpreted on the basis of empirical relations and also with the aid of semiempirical quantum-chemical methods.
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I. INTRODUCTION

Cyclophosphazenes are inorganic cyclic compounds with alternating phosphorus and nitrogen atoms. Their simplest representatives are cyclotriphosphazenes with three NPR_2 fragments and cyclotetraphosphazenes with four NPR_2 fragments.



The P–N bond length is intermediate between the lengths of single and double bonds. For identical substituents, all the bonds in the ring are likewise identical, i.e. there is no alternation of double and single bonds between the P and N atoms. According to the model of Craig and Paddock,[1] a more or less pronounced cyclic delocalisation of molecular π orbitals is postulated, while Dewar et al.[2] suggest that the conjugation terminates at each phosphorus atom (the island model). In addition some workers[3,4,5] have postulated the presence of transannular P–P bonds, which are particularly evident in hexafluorocyclotriphosphazene.

There exist numerous derivatives of cyclophosphazenes differing from one another by ring size and also by the type, number and positions of the substituents R; NMR has proved to be a convenient method for the identification and investigation of these compounds.

The first measurement of the chemical shift of the ^{31}P signal in the NMR spectra of cyclophosphazenes was made by Van Wazer et al.[6] in 1956. Among 200 phosphorus compounds investigated, there were also hexachlorocyclotriphosphazene and, in addition, according to the authors, a linear phosphazene. In 1959 Becke-Goehring and Koch[7] used ^{31}P NMR to identify cyclophosphazene oligomers and polymers. In the same year ^{31}P NMR was also employed to investigate aminocyclotriphosphazenes with different numbers of substituents.[8] The possibility of investigating the NMR spectra of suitable magnetic nuclei forming part of the composition of the substituent R in order to determine the molecular structure of cyclophosphazene as well as their isomers was first reported in 1961. Ray and Shaw studied the ^{1}H NMR spectra of dimethylaminocyclotriphosphazenes[9] and Chapman et al.[10] as well as Heffernan and White[11] investigated the ^{19}F NMR spectra of trimeric chlorofluoro-derivatives.

In recent years one of the principal methods for the determination of the structures of aminocyclophosphazenes as well as their ethers and thioethers and other phosphazenes with proton-containing substituents has been ^{1}H NMR. In order to simplify the spectra, homonuclear decoupling has been used in some cases.[12] This method made it possible to identify unambiguously in many instances the substitution products (the geminal and *cis*- or *trans*-non-geminal positions of the substituents).

The wide-scale use of ^{31}P NMR for the determination of the structures of cyclophosphazenes did not begin until the middle 1970s. As an example, one may quote a study[13] on aminophosphazenes. As Fourier transform spectroscopy and the associated possibility of measuring the ^{13}C NMR spectra of compounds with the natural abundance of carbon isotopes developed, it became possible to employ this method to investigate cyclophosphazenes with organic substituents.[14-18] Mason et al. published in 1977 a report[19] in which they describe studies of cyclophosphazenes by broad-line ^{14}N NMR. Other nuclei forming part of the composition of the P–N rings were first investigated in this way and the nitrogen chemical shifts were measured for certain triphosphazenes and cyclotetraphosphazenes with the same substituents.

In the majority of investigations of cyclic phosphazenes, NMR is used to identify the reaction products or to investigate the structure of the compound synthesised but not in systematic research permitting an interpretation of the NMR parameters. The aim of our studies was to determine, by investigating the NMR spectra of ^{15}N-labelled cyclophosphazenes, additional parameters which yield much information about these cyclic P–N systems.

Phosphazenes with identical substituents, fully labelled by ^{15}N, are spin systems of the type AA'A"XX'X" in the case of the trimeric compounds and of the type AA'A"A"'XX'X"X"' in the case of tetrameric compounds, provided that spin–spin coupling with the substituents is absent or is suppressed. The higher-order NMR spectra obtained permit the determination of the following parameters: (1) the chemical shifts δ_P and δ_N, (2) the coupling constants $^1J_{PN}$ and $^2J_{PP}$, and (3) the coupling constants $^2J_{NN}$ and $^3J_{PN}$. The latter quantities are very small for cyclophosphazenes and are not resolved in the experimental spectra. This is indicated by the results of studies on cyclophosphazenes with mixed substituents.[20–23] The neglect of these coupling constants greatly simplifies the analysis of the spectra. This also applies to the coupling constants $^4J_{PP}$[20,24–26] and $^4J_{NN}$ for the spectra of tetrameric phosphazenes.

The ^{31}P and ^{15}N NMR spectra of cyclic phosphazenes with identical substituents are symmetrical and the positions of the centres yield information about the chemical shifts (Fig. 1). The coupling constants $^1J_{NN}$ can be obtained from both spectra; the distance between the outer intense lines given by

$$2^1J_{PN}+{}^3J_{PN}$$

is used to determine it. Since $^3J_{PN}$ is negligible, half this distance represents the value of $^1J_{PN}$. In order to obtain the coupling constants $^2J_{PP}$ for cyclotriphosphazenes[27] and cyclotetraphosphazenes[28] we developed graphical methods based on the continuous variation of the distances between the additional spectral lines as a function of the ratio $^2J_{PP}/{}^1J_{PN}$. In this way it is possible to do without the computer modelling for the simulation of the spectra. We may note that analysis of the spectra in such cases does not yield information about the relative signs of the coupling constants.

^{15}N-Labelled cyclophosphazenes with mixed substituents also give rise to ^{31}P and ^{15}N NMR spectra containing high-order lines. In most cases preliminary data can be extracted from these spectra by means of first-order analysis. Modelling of the spectra enables one to refine these estimates.[20,21,23] In some cases it is then possible to determine the relative signs of the coupling constants.

The empirical interpretation of the NMR parameters permits the conclusion that the atoms of the substituents linked directly to phosphorus, i.e. the oxygen atoms in ethers, the nitrogen atoms in amino-derivatives, etc., exert a direct influence on such spectra. Relations are then observed between the NMR parameters and the positions of the corresponding elements in the Periodic System.[29] This simplified treatment is useful also in the interpretation of NMR data with the aid of semiempirical quantum-mechanical calculations for model compounds.[30,31]

It is therefore of interest to investigate how the NMR parameters vary (a) with the substituents R (in the first place one considers substituents of the same type), (b) with ring size (under the same conditions), and (c) with the degree of substitution (when cyclophosphazenes with mixed substituents are considered). Attention will be concentrated in this review on the possibility of obtaining from NMR data information about the characteristics of the P–N bond system in cyclophosphazenes.

II. THE ^{31}P CHEMICAL SHIFTS

The ^{31}P NMR chemical shifts have been determined for almost all the hexa-substituted cyclotriphosphazenes synthesised, for example, for R = F,[32–35] Cl[6–8,35–41] etc., Br,[32,35,42,43] NCS,[41,44,45] N_3,[46] OMe,[30,39,47] OEt,[30,39,44,47] OPh,[30,39,48,49] SMe,[50] SEt,[37,51] SPh,[20] NH_2,[21,32,41] NHMe,[8,13,30] NHEt,[13,30] NHPr-iso,[13] NHPh,[30] NMe_2,[8,13,30] NEt_2,[13,30] NC_5H_{10},[13] Me,[30,52] and Ph.[41,53,54] This also applies to the octa-substituted cyclotetraphosphazenes with R = F,[32,35] Cl,[7,32,35–37] Br,[32,35,42] NCS,[32,44] OMe,[28,47] OEt,[44] OPh,[28] SEt,[51] NHMe,[13] NHEt,[13,28] NHBu-t,[13] NMe_2,[13,28] Me,[28,52] and Ph,[13] to certain decasubstituted cyclopentaphosphazenes with R = F,[55] Cl,[35,36] OMe,[47,55] NMe_2,[55] and Me,[52] and to dodecasubstituted cyclohexaphosphazenes with R = Cl,[35,36] OMe,[47,55] and NMe_2.[55] Finally we may mention $(NPCl_2)_7$[35,36] and $(NPCl_2)_8$.[36]

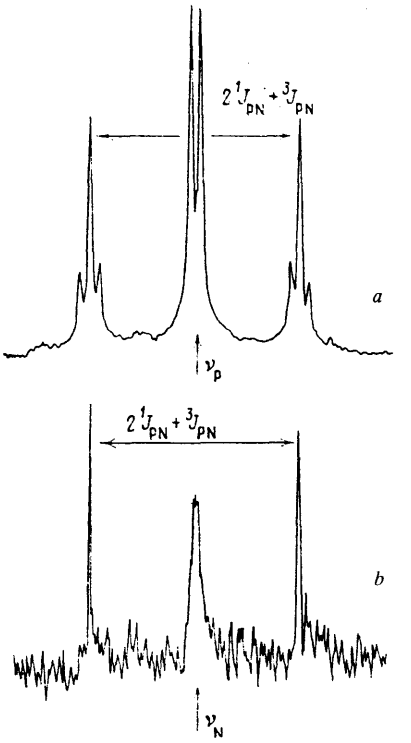


Figure 1. Experimental spectra of the compound $(^{15}NPBr_2)_3$: a) ^{31}P NMR spectrum; b) ^{15}N NMR spectrum.

Table 1 presents the ^{31}P chemical shifts for certain identically substituted cyclophosphazenes. The results presented were obtained in our laboratory,[28,30,55] since the available literature data for the chemical shifts had been obtained under different conditions which made it difficult to compare them. For example, it is completely impossible to compare the data[41,45] for the compound $[NP(NCS)_2]_3$ and in other cases the difference between the chemical shifts obtained in different studies for the same compounds reach several p.p.m., for example, for $(NPMe_2)_{3,4}$ (Grushkin et al.[54] and Thomas et al.[28,30]), $[NP(NH_2)_2]_3$ (Moeller[32] and Latscha[41]), $(NPPh_2)_3$ (Reddy and Weis[53] and Grushkin et al.[54]), $[NP(OEt)_2]_3$ (Nielsen et al.[44] and Dhathathreyan et al.[47]), $(NPF_2)_3$ (Allen et al.[33] and Moeller[32]), and $(NPBr_2)_3$ (John and Moeller[42] and Engelhardt et al.[43]). These differences can be understood if one takes into account the fact that the measurements were performed on spectrometers of different degrees

of accuracy and, in addition, for different states of the test substance, for example, without a solvent in the fused state, or after dissolution in various solvents such as water, ether, benzene, CS_2, CH_2Cl_2, etc. and that the concentration of the test substance also varied within wide limits. Our measurements were performed at 302 K after dissolving the substance in $CDCl_3$; in most cases the concentration of the substance was kept constant (at ~0.5 M) with the sole exception of the $[NP(NH_2)_2]_3$ solution.

In the first major investigation by Van Wazer et al.[6] devoted to phosphorus compounds, which was already mentioned above, the influence of substituents on the ^{31}P chemical shift was discussed. The following series of substituents was found for tetracoordinate phosphorus:

$$Se > S > C_{aliph} > C_{arom} \cong P > N \cong Cl > O > F.$$

A similar series was established also for cyclophosphazenes with the exception of $[NP(NHPh)_2]_n$ or $[NP(OPh)_2]_n$, where the phenyl substituent at the nitrogen or oxygen atom influences also the chemical shift of phosphorus.

A qualitative correlation between the electronegativity of the group linked to the phosphorus atom and the ^{31}P chemical shift has been established.[40] The electrophilic character of the group R linked to the phosphorus atom is responsible for the partial delocalisation of the free electron pair of the nitrogen atoms in the ring and the formation of additional P–N π-bonds which decreases the chemical shift of phosphorus.

It is seen from the data in Table 1 that the ^{31}P chemical shift for cyclophosphazenes with a given ring size diminishes when the substituents are altered in a way corresponding to moving from left to right along the same Period in Mendeleev's Table (from alkylphosphazenes to the fluoro-derivatives and from the thioethers to the chloro-derivatives) and, when substituents belonging to a single Group are varied, δP increases on passing from an element in the Second Period to one in the Third Period (from ethers to thioethers and from fluoro-derivatives to chloro-derivatives). Like phosphoryl halides, the bromo-derivatives have very low chemical shifts which has not been explained satisfactorily.

On passing from trimeric to tetrameric phosphazenes with retention of the number and nature of the substituents, δP appreciably diminishes, but, on further increase of ring size, the shift decreases more slowly, gradually reaching a limiting value. A decrease of the P–N bond length with increase of ring size corresponds to these changes.[56] This can be explained by the effect which was responsible for the influence of the substituents, i.e. by the more or less effective involvement of the free electron pair of the nitrogen atom in the π-bond system. Thus a correspondence is observed with the results of a quantum-mechanical calculation,[57] according to which there exists a satisfactory correlation between the chemical shifts in the ^{31}P NMR spectra of the compounds $(NPCl_2)_n$ (where n = 3, 4, or 5) and the overall overlap of the π-bonds $\Sigma_\pi(PN)$.

The appreciable difference between the ^{31}P chemical shifts, and, as will be shown below, between other NMR parameters for cyclotriphosphazenes and cyclotetraphosphazenes is in our view caused by the difference between the molecular geometries. Whereas cyclotriphosphazenes have a virtually planar ring structure, higher oligomers consist of non-planar rings. This unusual structure of cyclotriphosphazenes is reflected in other properties of these compounds, for example, in their dipole moments,[58] which is manifested in its turn by the corresponding behaviour in the chromatographic separation of the test substance.[29,59]

For a more detailed interpretation of the relation between the δP, δN, $^1J_{PN}$, and $^2J_{PP}$ parameters of the cyclophosphazenes investigated and the properties of the substituents influencing the geometry and the P–N bond system of the ring, semiempirical quantum-chemical calculations have been carried out for model compounds by the CNDO/2 method and the paramagnetic contributions of the shielding constants as well as the interaction constants were calculated.[29–31,35] The calculations were performed in terms of the parametrisation of Pople[60] and Santry;[61] account was taken of the *d* orbitals for phosphorus, whereas only the *s* and *p* orbitals were used for substituents comprising the elements in the Third Period (chlorine and sulphur).

The shielding constant σ_A for a nucleus A in the molecule can be represented, according to Ramsay,[62] by the sum of two contributions, which depend on the choice of the origin of coordinates:

$$\sigma_A = \sigma_{dia,A} + \sigma_{para,A} . \qquad (1)$$

The paramagnetic contribution in this equation can be estimated in accordance with the approximation proposed by Pople.[63] The changes in the diamagnetic contributions on passing from one compound to another are small and can therefore be disregarded. According to Pople's approximation mentioned above, the paramagnetic contribution by the given nucleus A can be calculated as follows:

$$\sigma_{para,A} = -\frac{e^2\hbar^2}{2m^2c^2} \cdot \frac{1}{\Delta E} \cdot \langle r_p^{-3} \rangle \cdot \sum_B Q_{AB} , \qquad (2)$$

where

$$Q_{AB} = \frac{4}{3}\delta_{AB}(p_{x_Ax_B} + p_{y_Ay_B} + p_{z_Az_B}) - \frac{2}{3}(p_{y_Ay_B}p_{z_Az_B} + p_{z_Az_B}p_{x_Ax_B} + p_{x_Ax_B}p_{y_Ay_B}) + \frac{2}{3}(p_{y_Az_B}p_{z_Ay_B} + p_{z_Ax_B}p_{z_Bx_A} + p_{x_Ay_B}p_{y_Ax_B}) . \qquad (3)$$

Here B is any atom in the molecule, δ_{AB} is the Kronecker delta, p_{ij} are the elements of the density matrix, and $\langle r_P^{-3} \rangle$ is the expected value of the reciprocal of the cube of the radius of the 3*p* orbital of phosphorus or the 2*p* orbital of nitrogen. The latter values were calculated from the Hartree–Fock atomic functions[64,65] using a linear interpolation for the non-integral charges.

The 3*d* orbitals of the phosphorus atom are probably also important for the description of the chemical bonds in cyclophosphazene but their influence on the chemical shift is small, because the expected value of the reciprocal of the cube of the radius of the 3*d* orbitals of phosphorus is smaller by several orders of magnitude than the corresponding value for the 3*p* orbitals; the contribution of the 3*d* orbitals is not therefore taken into account in Eqn.(2).

In the calculations of the ^{31}P chemical shift in the NMR spectra of cyclophosphazenes, the quantity ΔE may be regarded as constant and one can thus compare the experimental chemical shifts with the products $\langle r_P^{-3} \rangle \sum_B Q_{AB}$.

It is then found that allowance for the distribution of the charge on the phosphorus atom $\langle r_P^{-3} \rangle Q_{PP}$ alone leads to results which are not in sufficiently good agreement with experimental data. Evidently the bond between phosphorus and the neighbouring nitrogen atoms, taken into account by the quantity $2Q_{PN}$, makes a large contribution to the ^{31}P chemical shift, so that comparison of the experimental chemical shifts with the product $\langle r_P^{-3} \rangle (Q_{PP} + 2Q_{PN})$ leads to satisfactory results.[35] Additional allowance for the influence of the atoms of the substituents, expressed in terms of $2Q_{PX}$, does not entail an appreciable improvement of the agreement between the calculation and experiment.

Quantum-chemical calculations have been performed for the following compounds: $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_3$. $[NP(OH)_2]_3$, $[NP(OH_2]_4$, $[NP(SH)_2]_3$, $[NP(NH_2)_2]_3$, and $[NP(NH_2)_2]_4$ were chosen as model compounds for the ethers, thioethers, and amino-derivatives.[30,31] The planar molecular structure was adopted for cyclotriphosphazenes and the tetrameric fluoro-derivative, while the structures of other cyclotetraphosphazenes were assumed to be in the form of a saddle with approximately D_{2d} symmetry.[29] The bond lengths and bond angles were taken from the literature (for example, Allcock[56]) or were estimated for model compounds.

Fig.2 illustrates the correlation between the chemical shift δP and the quantity

$$\langle r_p^{-3}\rangle \sum_B Q_{AB}$$

for cyclotriphosphazene. With an increase of the positive charge on the phosphorus atom, the paramagnetic component as a rule diminishes, which is evident from the comparison of data for substituents in the series C, N, O, F and also Cl, F and S, O. However, when the substituents C and Cl are compared, an increase of the paramagnetic contribution is observed. The coefficient of the correlation between the chemical shift and the calculated paramagnetic contribution, amounting to 0.74, is not satisfactory. The points for the chloro-derivative and the thioether in Fig.2 deviate markedly from the regression line. If account is taken only of compounds in which the substituent atoms are those of elements in the Second Period in Mendeleev's table, a better correlation coefficient is obtained (0.88). This is also observed for the correlations with other NMR parameters (see below). The deviations observed for substituent atoms which are those of elements in the Third Period, arise owing to the lack of validity of the method of approximation employed. Fig.2 does not include compounds containing a phenyl group (the anilino-, phenoxy-, and phenylthio-derivatives), since the phenyl group has a strong influence on the ^{31}P chemical shift.

An analogous correlation has been observed for cyclotetraphosphazenes between the ^{31}P chemical shift and the quantity

$$\langle r_p^{-3}\rangle \sum_B Q_{AB}.$$

The change in δP in the upfield direction with increase of ring size and specially the marked change in δP on passing from cyclotriphosphazene to cyclotetraphosphazene cannot be explained by the distribution of electrons at the phosphorus atom alone, because it is virtually the same for the trimers and tetramers; in these cases too it is essential to take into account the contributions of the bonds with the neighbouring nitrogen atoms. The cause of the change in the chemical shift should be sought primarily in the change of the contribution of the bonding $3p-2p$ orbitals on passing from the planar trimeric compounds to the nonplanar tetrameric compounds.[35] In the case of the fluoroderivative the large change in δP on passing from cyclotriphosphazenes to cyclotetraphosphazenes must have other causes, because the planar structure is retained in this instance.[29] Indeed it is found that the change in δP is not adequately described by the values of

$$\langle r_p^{-3}\rangle \sum_B Q_{AB},$$

if it is assumed that

$$\sum_B Q_{AB} = Q_{PP} + 2Q_{PN}.$$

This change in δP can be described more adequately if account is taken of transannular bonds with other phosphorus atoms ($2Q_{P\ldots P}$). These transannular bonds are particularly marked in hexafluorocyclotriphosphazene.[35]

Numerous studies have been devoted to cyclophosphazenes with mixed substituents. Data on the ^{31}P chemical shifts are presented in monographs[56,67-70] and numerous later publications. Cyclotriphosphazenes with mixed substituents, giving rise to spectra of the A_2X, A_2B, AMX, ABX, or ABC

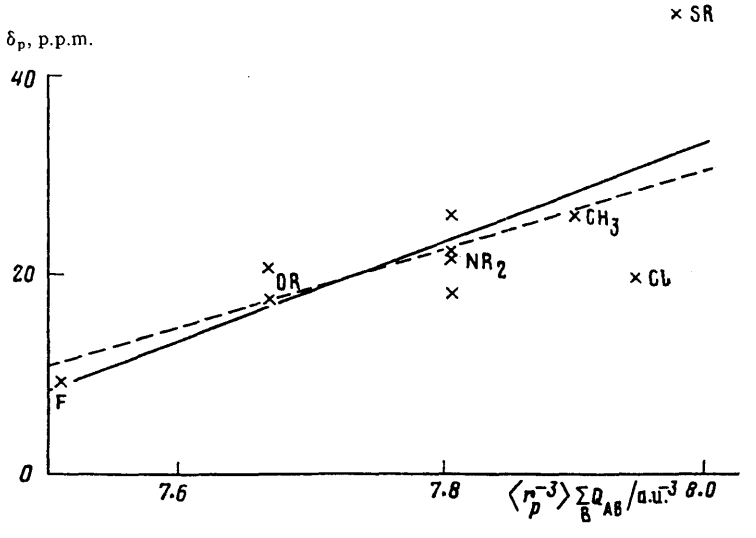


Figure 2. Correlation between the ^{31}P chemical shift in the NMR spectra of compounds of the type $(^{15}NPR_2)_3$ and the quantity $\langle r_p^{-3}\rangle \sum_B Q_{AB}$; the correlation coefficients are $r = 0.74$ (continuous line) and $r = 0.88$ (dashed line); the crosses represent experimental points.

types, as well as a series of cyclotetraphosphazenes with mixed substituents for which there is a possibility of spectra of types A_2X_2, A_2B_2, AA'XX', A_2MX, A_2BX, A_2BC, ABMX, ABXY, ABCX, ABCD, and AA'BB', were investigated in the first place. Since higher-order spectra are observed in many cases, the exact chemical shifts and interaction constants can be obtained only by modelling the spectra.

The available ^{31}P chemical shifts provide answers to the questions how the chemical shift changes when two different substituents are attached to the same phosphorus atom and what is the influence of the substituents at the other phosphorus atoms. Answers to these questions have been provided in relation to the series $N_3P_3Cl_{6-n}(SEt)_n$ (n = 0–6) and $N_4P_4Cl_{8-n}(SEt)_n$ (n = 0–8), in which geminally substituted compounds are formed exclusively.[51] In the selected examples the chemical shifts for the phosphorus atoms with two identical substituents, i.e. for PX_2 and PY_2, differ markedly and the chemical shifts for phosphorus atoms with mixed substituents (PXY) are always intermediate between these values (but are not their averages). In the case of aminochlorophosphazenes, where the shifts change only slightly on passing from PX_2 to PY_2 (Table 1), the δp for PXY are sometimes not intermediate between these values.[13,22] Thus the fact, known for other phosphorus compounds, that the dependence of the chemical shift of phosphorus on the contributions of the substituents is not additive, has been confirmed also for cyclophosphazenes. For this reason attempts are no longer made to create a system of increments for the empirical calculation of the chemical shifts similar to the systems which exist for ^{1}H and ^{13}C. The finding[72] that the chemical shift for phosphorus atoms with mixed substituents is usually displaced downfield compared with the average value holds also for cyclophosphazenes (Tables 2 and 3).

Table 1. ^{31}P Chemical shifts (in p.p.m.*) for cyclophosphazenes of the type $(NPR_2)_n$.

Compound	n=3	n=4	n=5	n=6
$(NPMe_2)_n$	26.1	19.9	14.9	—
$[NP(NH_2)_2]_n$	15.9**	—	—	—
$[NP(NHMe)_2]_n$	22.3	10.2	—	—
$[NP(NHEt)_2]_n$	18.1	6.4	—	—
$[NP(NHPh)_2]_n$	4.9***	—	—	—
$[NP(NMe_2)_2]_n$	26.0	10.2	3.1****	0.5****
$[NP(NEt_2)_2]_n$	21.9	6.2	—	—
$[NP(OMe)_2]_n$	20.8	2.4	−2.0	−4.3
$[NP(OEt)_2]_n$	17.6	0.8	—	—
$[NP(OPh)_2]_n$	8.7	−12.4	—	—
$[NP(SEt)_2]_n$	46.3	25.1	—	—
$[NP(SPh)_2]_n$	43.4	—	—	—
$(NPF_2)_n$	9.3	−17.7	−21.9	—
$(NPCl_2)_n$	20.0	−6.5	−15.5	−17.5
$(NPBr_2)_n$	−44.2	−69.9	−78.1	—

*Standard—85% phosphoric acid; positive values denote a downfield shift.

**In aqueous solution.

***Saturated solution in $CDCl_3$.

****The value of δp depends strongly on the solvent.

The effect of substituents at other phosphorus atoms on the δp is also evident from the data presented in Tables 2 and 3. The change in δp is by several p.p.m. for the identical immediate environment of the phosphorus atom and a distinct regularity is not observed. It is known that the bond lengths and angles in cyclophosphazenes vary quite markedly when substituents are introduced. The change in the geometry of the environment of the phosphorus atom can be to some extent responsible for the change in δp.

Table 2. ^{31}P Chemical shifts (in p.p.m.) for chloro(ethylthio)cyclotriphosphazenes.

Compound	Structural groups at P atoms		
	$\equiv PCl_2$	$\equiv PClSEt$	$\equiv P(SEt)_2$
$N_3P_3Cl_6$	20.0	—	—
$N_3P_3Cl_5SEt$	21.0	33.1	—
$N_3P_3Cl_4(SEt)_2$	18.7	—	51.3
$N_3P_3Cl_3(SEt)_3$	18.1	38.5	50.6
$N_3P_3Cl_2(SEt)_4$	17.4	—	49.2
$N_3P_3Cl(SEt)_5$	—	37.1	48.0
$N_3P_3(SEt)_6$	—	—	46.5
Mean value	19.0	36.2	49.1

Table 3. ^{31}P Chemical shift (in p.p.m.) for chloro(ethylthio)cyclotetraphosphazenes.

Compound	Structural groups at P atoms		
	$\equiv PCl_2$	$\equiv PClSEt$	$\equiv P(SEt)_2$
$N_4P_4Cl_8$	−6.5	—	—
$N_4P_4Cl_6(SEt)_2$	−7.1; −8.2	—	30.4
2,2,4-$N_4P_4Cl_5(SEt)_3$	−8.0; −8.9	13.5	29.7
2,2,6-$N_4P_4Cl_5(SEt)_3$	−8.2	14.6	29.4
2,2,4,4-$N_4P_4Cl_4(SEt)_4$	−8.7	—	27.9
2,2,6,6-$N_4P_4Cl_4(SEt)_4$	−8.8	—	29.4
2,2,4,4,6-$N_4P_4Cl_3(SEt)_5$	−9.4	12.7	26.9
2,2,4,6,6-$N_4P_4Cl_3(SEt)_5$	−9.5	12.2	28.1
$N_4P_4Cl_2(SEt)_6$	−9.5	—	26.9; 26.0
$N_4P_4(SEt)_8$	—	—	25.1
Mean value	−8.4	13.3	28.0

An attempt has been made recently[74] to calculate the ^{31}P chemical shifts for a series of geminally disubstituted tetrachlorocyclotriphosphazenes from the increments in the shifts caused by substituents. Very satisfactory results have been obtained for the dialkyl derivatives probably because the changes in the chemical shifts in this group of compounds are small. In the case of compounds with mixed alkyl and halogeno-substituents, appreciable deviations are observed unless special corrections are applied. For *para*-substituted monoarylphosphazenes, Harris[74] observed a satisfactory correlation with the Hammet σ parameters.

III. ^{15}N CHEMICAL SHIFTS

Chemical shift data for endocyclic nitrogen atoms were published by ourselves for ^{15}N-labelled cyclophosphazenes.[20–23,28,30,35,55] Apart from these data, the results of Mason and co-workers,[19] who used the broad line ^{14}N NMR, are available in the literature. These results are not accurate, since they were obtained under different conditions (without a solvent, in the melt, and in various solvents) and, furthermore, the line width is in the range 165–700 Hz. A detailed analysis of the experimental chemical shifts of nitrogen is possible only when ^{15}N NMR is used.

Table 4 presents the nitrogen chemical shifts for cyclophosphazenes with identical substituents, which we obtained in the study of endocyclic ^{15}N-labelled compounds. The

measurements were performed for solutions of the compound in $CDCl_3$; the exceptions will be indicated separately.

Mason et al.[19] obtained the following series based on the influence of the substituents at the phosphorus atom on the nitrogen chemical shift:

$$NMe_2 > OMe > F > NCS > Cl > Br .$$

This sequence does not coincide either with that observed for the ^{31}P shift or with the reverse of the latter. The authors[19] attempted to give a semiempirical explanation of the phosphorus and nitrogen chemical shifts; they were able to establish a correlation by comparing the paramagnetic contributions of the atom–ligand system for phosphorus and nitrogen, i.e. the contributions which include the diamagnetic component of the ligand.[75]

Table 4. ^{15}N Chemical shifts (in p.p.m. relative to nitromethane) for cyclophosphazenes with substituents of one kind and different ring sizes.

Compound	n=3	n=4	n=5	n=6
$(^{15}NPMe_2)_n$	−319.5	−300.0	—	—
$(^{15}NP(NH_2)_2)_n$	−298.3*	—	—	—
$(^{15}NP(NHMe)_2)_n$	−315.1	—	—	—
$(^{15}NP(NHEt)_2)_n$	−312.4	−306.7	—	—
$(^{15}NP(NMe_2)_2)_n$	−320.8	−314.8	−317.0	−317.6
$(^{15}NP(NEt_2)_2)_n$	−316.3	—	—	—
$(^{15}NP(OMe)_2)_n$	−317.8	−313.7	−318.9	−320.0
$(^{15}NP(OEt)_2)_n$	−314.3	—	—	—
$(^{15}NP(OPh)_2)_n$	−305.9	−302.5	—	—
$(^{15}NP(SEl)_2)_n$	−284.2	−270	—	—
$(^{15}NP(SPh)_2)_n$	−285.0	—	—	—
$(^{15}NPF_2)_n$	−314.5	−314.4	−322.8	—
$(^{15}NPCl_2)_n$	−258.8	−248.0	−253.1	−253.3
$(^{15}NPBr_2)_n$	−240.1	−230.8	—	—

*Solution in water; in the remaining cases—solution in $CDCl_3$.

The virtual absence of a difference in the δ_N for different substituent atoms of elements in the Second Period attached to the phosphorus atom is striking in the study of the nitrogen chemical shift. For example, on passing from alkylphosphazene to the fluoro-derivative in the series of cyclotriphosphazenes, the chemical shift δ_N changes by only 5 p.p.m. This finding is particularly surprising in view of the fact that the basicities of the above phosphazenes differ markedly[76] and the basicity centres are in fact located at the ring nitrogen atoms. Evidently there is no direct relation between the basicity and the nitrogen chemical shift.

The ^{15}N chemical shift varies markedly for phosphazenes with substituents involving elements belonging to the same Group. For example, on passing from fluoro- to bromocyclotriphosphazene, the chemical shift increases by 74.4 p.p.m., while in the case of the corresponding cyclotetraphosphazenes the increase is by 83.6 p.p.m. In order to account for these changes, one cannot assume that ΔE is constant in the series of similar compounds, because the nodal planes of the π orbitals or the non-bonding p orbitals pass through the ^{15}N nucleus or in its vicinity.[35] Such orbitals exert a major influence on the shielding of the nucleus.[77] As in the interpretation of the ^{17}O chemical shifts by one of the present authors and his co-workers,[78] the difference between the energies of the lowest unoccupied and the highest occupied orbitals, where the π electrons of nitrogen are mainly localised, was adopted as a measure of ΔE:

$$\Delta E = \epsilon_{LUMO} - \epsilon_{HOMO} .$$

The relation between δ_N and ΔE is illustrated in Fig. 3. The slight change in δ_N in the presence of substituents comprising elements of the Second Period corresponds to a slight change in ΔE and a marked change in δ_N within the Groups and also corresponds to a marked change in ΔE.

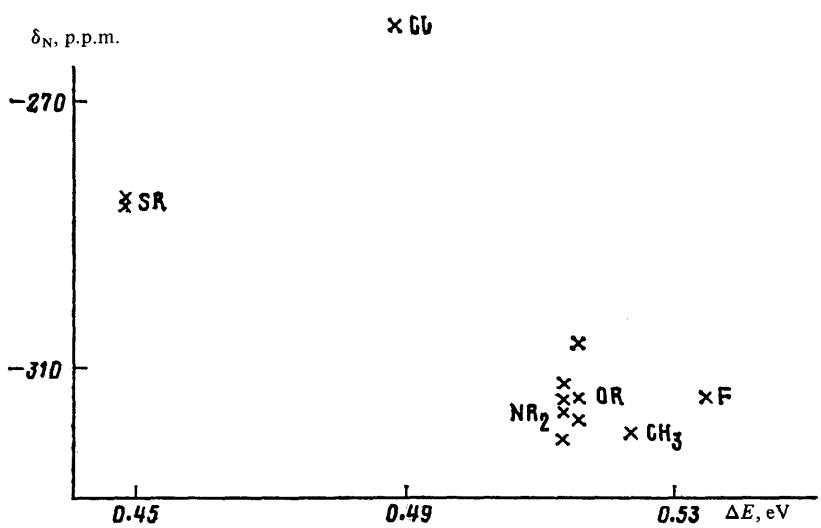


Figure 3. Dependence of the ^{15}N chemical shift on the calculated value of ΔE for cyclophosphazenes of the type $(^{15}NPR_2)_3$.

However, the ΔE for the thioethers is smaller than would be expected from the upfield displacement of δ_N relative to the chloro-derivative. This deviation can be caused by the fairly considerable contribution of the sulphur orbitals to the HOMO.

The ^{15}N chemical shift in the NMR spectra of cyclotetraphosphazenes has undergone a downfield displacement compared with the spectrum of cyclotriphosphazenes. This is probably caused by the change in molecular structure to a non-planar form, indicated by the identical chemical shifts for the compounds $(^{15}NPF_2)_3$ and $(^{15}NPF_2)_4$. The ^{15}N chemical shift for the pentameric cyclophosphazenes has undergone an upfield displacement compared with the spectrum of the tetrameric cyclophosphazenes, which can be accounted for by the fact that, on passing from $(NPR_2)_4$ to $(NPR_2)_5$, the quantity ΔE should change only slightly, while Q_{PN} should diminish, which agrees with the change in the ^{31}P chemical shift. In the calculation of the paramagnetic contribution in the case of ^{15}N account is also taken of the values of Q_{PN}, as for ^{31}P, and the above analogy in the instances quoted is understandable. On further increase of ring size, δ_N undergoes a slight upfield shift and probably approaches a limiting value.[55]

Cyclophosphazenes with mixed substituents but with identical substituents at the phosphorus atoms adjoining the nitrogen atom are characterised by a ^{15}N chemical shift which is almost independent of the substituents at the phosphorus atom remote from the ring nitrogen atom. In this case a simpler picture is observed than for the ^{31}P NMR spectra. The shifts δ_N for the phenylamino-derivatives of cyclotriphosphazene and cyclotetraphosphazene are presented as an example in Tables 5 and 6.

Table 5. ^{15}N Chemical shifts (in p.p.m.) for chloro(phenylamino)cyclotriphosphazenes.

Compound	PCl_2-N-PCl_2	PCl_2-N-PClNHPh	PCl_2-N-P(NHPh)$_2$
$^{15}N_3P_3Cl_6$	−258.8	—	—
$^{15}N_3P_3Cl_5NHPh$	−256.3	−268.1	—
$^{15}N_3P_3Cl_4(NHPh)_2$*	−255.1	—	−279.1
Mean value	−256.7	—	—

*Geminal substitution.

Table 6. ^{15}N Chemical shifts (in p.p.m.) for chloro(phenylamino)cyclotetraphosphazenes.[23]

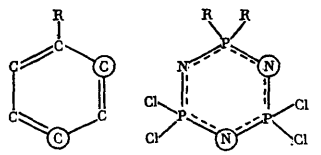
Compound	PCl_2–N–PCl_2	PCl_2–N–PClNHPh	PClNHPh–N–PClNHPh
$^{15}N_4P_4Cl_8$	−248.0	—	—
$^{15}N_4P_4Cl_7NHPh$	−246.7	−260.1	—
6,8-$^{15}N_4P_4Cl_6(NHPh)_2$	−244.5	−259.2	−275.5
4,8-$^{15}N_4P_4Cl_6(NHPh)_2$	—	−259.2*	—
Mean value	−246.4	−259.5	—

*Solution in $(CD_3)_2CO$.

The values of δ_N for the same ring size depends mainly on the nature of the substituents at the neighbouring phosphorus atoms. A fairly linear relation between δ_N and the degree of substitution is observed regardless of whether the substitution is geminal or non-geminal. It is easily seen that the shifts quoted in the middle columns of Tables 5 and 6 are approximately equal to the arithmetical means of the values in the extreme columns. The same type of behaviour has been observed also for linear phosphazenes; for example, in the series of compounds $(EtO)_nCl_{3-n}P=N-P(O)(OEt)_mCl_{2-m}$, where $n = 0-3$ and $m = 0$ or $n = 3$ and $m = 1$ or 2, the gradual substitution of chlorine by ether groups entails a uniform upfield displacement of δ_N.[79] The additivity of the influence of substituents on the chemical shift of nitrogen holds also for all other cyclophosphazenes which we investigated: $^{15}N_3P_3Cl_4F_2$,[21] $^{15}N_3P_3Cl_4(SEt)_2$,[20,21] $^{15}N_3P_3Cl_4(SPh)_2$ and $^{15}N_3P_3Cl_2(SPh)_4$,[20] and $^{15}N_4P_4Cl_4(SEt)_4$[20] and $^{15}N_3P_3Cl_4.(NH_2)_2$.[21]

The effect of substituents at phosphorus atoms which do not adjoin the given nitrogen atom on δ_N is insignificant in all the cases investigated. The electronic structure of cyclophosphazenes differs clearly from the delocalised aromatic bond system in cyclic organic compounds (Table 7). An appreciable influence of substituents on the ^{13}C NMR chemical shift has been observed in many instances in the case of monosubstituted benzenes for atoms in both *ortho*- and *para*-positions (transmission of the influence of substituents via the delocalised system of ring π electrons), while for the geminally disubstituted cyclotriphosphazenes a marked influence only the neighbouring nitrogen atom is observed. The absence of an appreciable long-range influence is evidence against the ring delocalisation of π electrons in cyclophosphazenes (see also, Thomas et al[22]).

Table 7. ^{13}C Chemical shifts for monosubstituted benzenes[80] and the ^{15}N chemical shifts for geminally disubstituted cyclotriphosphazenes.[21]



R	δ_C	$\Delta\delta_C$	δ_N	$\Delta\delta_N$	$\Delta\delta_{N/n\,R}$
			o-Position		
Cl	128.9	0	−258.0	0	0
F	115.1	−13.8	−286.9	−28.1	−14.05
NH_2	115.5	−13.4	−272.8	−14.1	−7.05
SEt	129.2	0.3	−270.0	−12.1	−6.05
			p-Position		
Cl	126.6	0	−258.8	0	0
F	124.1	−2.5	−259.8	−1.0	−0.5
NH_2	118.5	−8.1	−255.5	3.3	1.65
SEt	125.9	−0.7	−255.9	2.9	1.45

IV. $^{31}P-^{15}N$ SPIN–SPIN COUPLING CONSTANTS

The spin–spin coupling constants $^1J_{PN}$ have been determined in recent years for individual compounds and also for a series of different classes of compounds (mainly for organophosphorus compounds), using both ^{15}N-enriched materials and compounds with the natural abundance of isotopes.[81-90] We determined the $^1J_{PN}$ coupling constants for ^{15}N-labelled cyclophosphazenes.[20-23,27,28,30,35,55] The interaction constants for different cyclophosphazenes with substituents of one kind are compared in Table 8.

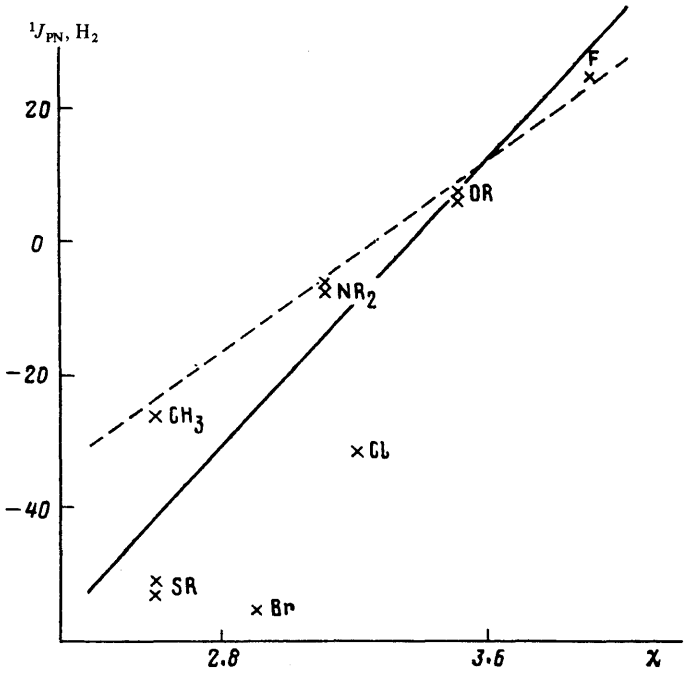


Figure 4. Correlation between the coupling constant $^1J_{PN}$ for compounds of the type $(^{15}NPR_2)_3$ and the electronegativity of the substituent atoms χ; the correlation coefficients are $r = 0.83$ (continuous line) and $r = 0.99$ (dashed line).

Table 8. Coupling constants $^1J_{PN}$ (in Hz) for cyclophosphazenes with substituents of one kind and different ring sizes.*

Compound	$n=3$	$n=4$	$n=5$	$n=6$
$(^{15}NPMe_2)_n$	−26.1	−23.8	—	—
$[^{15}NP(NH_2)_2]_n$	1.6**	—	—	—
$[^{15}NP(NHMe)_2]_n$	−7.7	—	—	—
$[^{15}NP(NHEt)_2]_n$	−7.8	5.5	—	—
$[^{15}NP(NHPh)_2]_n$	−6.6	—	—	—
$[^{15}NP(NMe_2)_2]_n$	−7.5	14.2	19.4	29.3
$[^{15}NP(NEt_2)_2]_n$	−6.1	—	—	—
$[^{15}NP(OMe)_2]_n$	7.5	32.7	39.0	41.5
$[^{15}NP(OEt)_2]_n$	6.4	—	—	—
$[^{15}NP(OPh)_2]_n$	7.1	37.5	—	—
$[^{15}NP(SEt)_2]_n$	−51.0	−34.0	—	—
$[^{15}NP(SPh)_2]_n$	−53.3	—	—	—
$(^{15}NPF_2)_n$	24.9	68.8	71.8	—
$(^{15}NPCl_2)_n$	−31.7	−6.9	−3.0	−2.0
$(^{15}NPBr_2)_n$	−55.8	−35.5	—	—

*The signs of the constants were not determined experimentally.

**For such a low value of the constant, it is impossible to predict the sign of the latter.

It was found that the absolute values of the coupling constant $^1J_{PN}$ are not correlated either with the parameters of the P–N bond or with those of the substituent. In order to account for the observed changes in $^1J_{PN}$ as a

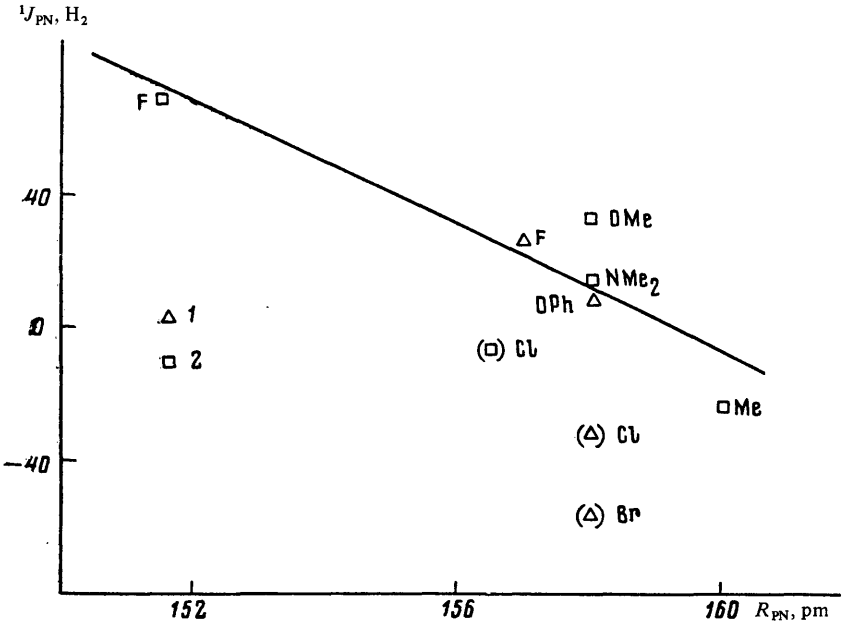


Figure 5. Correlation between $^1J_{PN}$ and the PN bond length (R_{PN}) for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2). The continuous line corresponds to the correlation coefficient $r = 0.91$.

function of the position in the Mendeleev table of substituents linked directly to the phosphorus atom considered, it was necessary to assume that the increase of the atomic number of the substituent element within a Period and within a Group entails the reversal of the sign of $^1J_{PN}$. It is known from the literature[90-92] that $^1J_{PN}$ can be both positive and negative. The sign changes probably within the framework of one class of compounds. Since in most cases it was impossible to determine experimentally the sign of the coupling constants for cyclophosphazenes, the signs were selected in such a way that the changes in $^1J_{PN}$ were reasonable (Table 8). The legitimacy of this approach is confirmed by the results obtained for geminally disubstituted cyclotriphosphazenes[21] and for endocyclically ^{15}N-labelled chloro(phenylamino)cyclotetraphosphazenes[23] (see below).

The coupling constants thus obtained are satisfactorily correlated with the electronegativity of the substituents atoms linked directly to the phosphorus atom, which can be seen in relation to cyclotriphosphazenes (Fig.4). The correlation coefficient is 0.83; an improved correlation (r = 0.991) can be achieved by considering only the elements of the Second Period as the substituents. The same relations are observed in the series of cyclotetraphosphazenes.[28] The correlation established between the coupling constants $^1J_{PN}$ and the electronegativity of the substituent atoms is as expected, since the structure of the P–N bond systems in cyclophosphazenes depends to a large extent on the nature of the substituents.

In addition, Table 8 shows that $^1J_{PN}$ increases with increasing ring size when cyclophosphazenes with substituents of only one kind are considered and in most cases the greatest change is observed on passing from trimeric to tetrameric phosphazenes.

The examples presented below show that there is a linear correlation between the P–N coupling constant and other experimental data for the molecules. When the $^1J_{PN}$ and the P–N bond lengths for cyclotriphosphazenes and cyclotetraphosphazenes are compared (Fig.5), it is again striking that a satisfactory correlation is observed when account is taken only of the substituents whose atoms, linked to the phosphorus atom, are those of elements in the Second Period. The scatter of the points around the regression line can be accounted for to some extent as, on the one hand, the bond lengths are specified only to within 0.5 pm or even 1 pm (in the main the literature data were taken from the 1960s) and, on the other hand, the bond lengths can change somewhat on passing from a solid to a solution.

The constants $^1J_{PN}$ for cyclophosphazenes are in the given instance extremely sensitive to changes in the P–N bond lengths: when d_{PN} changes from 151 pm in $N_4P_4F_8$ to 160 pm in $N_4P_4Me_8$, the P–N coupling constant changes from +68.8 Hz to -23.8 Hz. Compared with this, the change in the coupling constant $^1J_{CC}$ resulting from the marked alteration of the C–C bond length on passing from ethane (153 pm) to ethylene (134 pm) and acetylene (121 pm) is relatively small—from 34.6 Hz[94] to 67.6 Hz[95] and 171.5 Hz.[95]

Comparison of the P–N interaction constants with the frequencies of the antisymmetric stretching vibrations obtained from the infrared spectra reveals a very satisfactory correlation for substituents in which an element of the Second Period is linked to phosphorus (Fig.6). For other substituents, an appreciable deviation from this relation is observed; however, Fig.6 shows that some regularities can be observed for these elements too (this is indicated by dashed lines connecting points for substituent elements of the Third Period and the halogens).

It has been observed for pyridine and the pyridinium ion[93] that the free electron pair localised at the nitrogen atom influences the interaction constant $^1J_{NC}$. Since the free electron pair localised at the nitrogen atom in cyclophosphazenes is responsible for their basic properties, there should have been a direct relation between $^1J_{PN}$ and the basicities of the corresponding compounds. In fact such a relation is observed only within the limits of a single Period. An increase in the basicity of cyclophosphazenes[76] corresponds to a decrease of the P–N interaction constant.

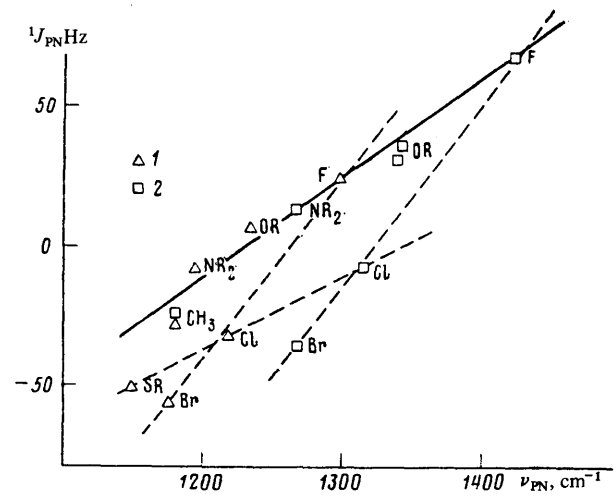


Figure 6. Correlation between $^1J_{PN}$ and the antisymmetric stretching vibration frequency for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2); the correlation coefficient r = 0.87 in all cases.

For a qualitative interpretation of the coupling constants, quantum-chemical model calculations were performed by the CNDO/2 method. The indirect spin–spin coupling constant is determined by three contributions: the Fermi contact contribution (*FC*), the orbital contributions (*OD*), and the spin–dipole contribution (*SD*). For coupling via one bond, the last two contributions are much smaller than that of the Fermi contact interaction and it is therefore possible to consider only the latter. Our calculations did indeed show that the *FC* contribution is greater by two orders of magnitude than the others, which is also confirmed by the data of a number of other investigators. For example, a linear correlation has been observed[83,84] between the experimental coupling constants and the *FC* contributions, also calculated by the CNDO/2 method using the theory of finite perturbations. On the other hand, Duangthai and Webb,[96] who used the INDO method, found, that, although the *SD* contribution remains small, nevertheless the orbital *OD* contribution plays an appreciable role, particularly when it is necessary to obtain the absolute values of the coupling constant.

According to Pople, the expression for the *FC* contribution in terms of the ΔE approximation is

$$J_{AB}^{FC} = \frac{32}{9}\pi\hbar\gamma_A\gamma_B\beta^2\,(^3\Delta E)^{-1}\langle s_A|\delta(r_A)|s_A\rangle\langle s_B|\delta(r_B)|s_B\rangle\, p^2_{s_As_B}\,, \quad (4)$$

where γ_A and γ_B are the gyromagnetic ratios of the interacting nuclei, β is the Bohr magneton, $^3\Delta E$ the "average triplet excitation energy", $\langle s|\delta(r)|s\rangle$ the expected value

of the 2s or 3s function at the location of the nucleus, and $p_{s_A s_B}$ the order of the s-bond. Assuming that

$$K_{AB} = \frac{2\pi}{\hbar\gamma_A\gamma_B} J_{AB} , \quad (5)$$

it is possible to obtain the conventional coupling constant K_{AB}:

$$K_{AB}^{FC} = \frac{64}{9}\pi^2\beta^2 (^3\Delta E)^{-1} \langle s_A|\delta(r_A)|s_A\rangle\langle s_B|\delta(r_B)|s_B\rangle p^2_{s_A s_B} . \quad (6)$$

If it is assumed that ΔE and the expected values of the s-function do not vary, then the interpretation of the experimental coupling constants reduces to their comparison with the square of the s-bond order.

Examination of the experimental coupling constant $^1J_{PN}$ as a function of the calculated *FC* contribution jointly for cyclotriphosphazenes and cyclotetraphosphazenes yields the relation in the form of a regression line (Fig.7). For compounds with substituent elements of the Second Period, a very satisfactory correlation coefficient, amounting to 0.990, has been obtained. The inclusion in the consideration of compounds with substituent elements of the Third Period results in an appreciable worsening of the correlation.

Our method of calculation does not allow the observation of a change in the sign of the coupling constant. The quantum-chemical methods of calculation used in other studies[83,96] lead to different signs of $^1J_{PN}$. However, the changes in the signs of the coupling constants observed in these investigations[83,96] are due to the appreciable differences between the structures of the compounds considered. It has been found[90] that $^1J_{PN}$ depends greatly on the coordination number and hence on the bond system of the phosphorus atom involved in the coupling. These observations were subsequently confirmed. In a later study[96] devoted to the interpretation of the coupling constants $^1J_{PN}$ known at the time, certain refinements were introduced: the constant for coupling with tricoordinate phosphorus was found to be positive, electronegative substituents at the interacting P or N atoms increasing the s-electron density at the nuclei and hence increasing the coupling constant. For tetracoordinate phosphorus, negative coupling constants are frequently observed. Here the decisive factor, determining the sign of the constants, becomes the s character of the free electron pair at the nitrogen atom.

In cyclophosphazenes with identical ring sizes, a marked variation of the geometry is not observed when the nature of the substituent is altered; an exception is the fluorotetramer, having, in contrast to other cyclotetraphosphazenes, a planar ring structure. The marked change in the coupling constant on passing from $(^{15}NPF_2)_3$, for which J_{PN} = +24.9 Hz, to $(^{15}NPBr_2)_3$ with J_{PN} = −55.8 Hz must be caused by the different electron negativities of the substituents at the phosphorus atoms (Fig.4).

Table 9. Coupling constants $^1J_{PN}$ (in Hz)* for compounds of the type $^{15}N_3P_3Cl_{6-n}(SPh)_n$ (where n = 0, 2, 4, or 6).

Compound	Type of P–N bond**			
	I	II	III	IV
$N_3P_3Cl_6$	−31.7	—	—	—
$N_3P_3Cl_4(SPh)_2$	−33.7	−39.4	−50.6	—
$N_3P_3Cl_2(SPh)_4$	—	−39.7	−50.9	−53.5
$N_3P_3(SPh)_6$	—	—	—	−53.3
Mean value	−32.7	−39.55	−50.75	−53.4

*The sign of the constants were not determined experimentally.

**The P–N bond types I, II, III, and IV correspond to isolated P–N bonds in the fragments $Cl_3P{-}N{-}PCl_2$, $Cl_2P{-}NP(SPh)_2$, $Cl_2PN{-}P(SPh)_2$, and $(PhS)_2P{-}N{-}P(SPh)_2$ respectively.

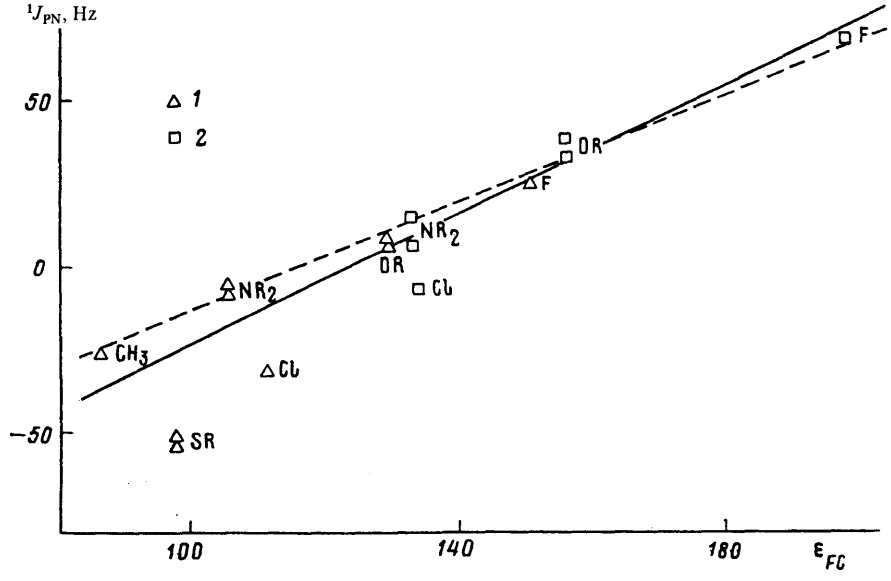


Figure 7. Correlation between $^1J_{PN}$ and the contribution of the Fermi contact interaction ε_{FC} for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2); the correlation coefficients are r = 0.90 (continuous line) and r = 0.990 (dashed line).

Tables 9 and 10 illustrate the influence of the nature of the substituents on the coupling constants $^1J_{PN}$ in relation to chloro(phenylthio)cyclotriphosphazenes[20] and chloro(phenylamino)cyclotetraphosphazenes.[16] The values of $^1J_{PN}$ depend in the first place on the nature of the substituents at the phosphorus atom involved in the P–N coupling considered and only then on the substituents at the other phosphorus atom linked to the given nitrogen atom. It is seen from Tables 9 and 10 that the differences between the coupling constants for bonds of types II and III are much greater than between the constants for bonds of types I and II or III and IV, the differences between the constants for bonds of one type being insignificant.

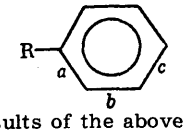
Table 10. Coupling constants $^1J_{PN}$ (in Hz) for chloro(phenylamino)cyclotetraphosphazenes ^{15}N-labelled endocyclically.

Compound	Type of P–N bond*			
	I	II	III	IV
$N_4P_4Cl_8$	−6.9	—	—	—
$N_4P_4Cl_7NHPh$	−6.2; −7.0	−2.9	5.7	—
6,8-$N_4P_4Cl_6(NHPh)_2$	−8.6	−3.0	8.0	6.7
4,8-$N_4P_4Cl_6(NHPh)_2$	—	−3.5	6.6	—
Mean value	−7.2	−3.1	6.8	6.7

*The P–N bond types I, II, III, and IV correspond to isolated P–N bonds in the fragments $Cl_2P–N–PCl_2$, $Cl_2P–NPCl(NHPh)$, $Cl_2PN–PCl(NHPh)$, and (PhNH).ClP–N–PCl(NHPh) respectively.

The observed effect of the nature of substituents on $^1J_{PN}$ enabled us to confirm the change in the sign of $^1J_{PN}$ in relation to the geminal difluoro-derivative $^{15}N_3P_3Cl_4F_2$.[21] For chloro(phenylamino)cyclotetraphosphazenes, it was actually possible to determine directly, by modelling higher-order spectra, the relative sign of $^1J_{PN}$ on the assumption that $^2J_{PP}$ is positive. Thus the signs which we proposed in Table 8 are indeed justified.

It is of interest to compare the influence of substituents on the coupling constants $^1J_{PN}$ for cyclophosphazenes with their influence on the interaction constants $^1J_{CC}$ for monosubstituted benzene derivatives. The constants $^1J_{CC}$ had been determined[97] for C–C bonds occupying different positions in the molecules (see the scheme below) of more than 30 different benzene derivatives.



According to the results of the above study, the maximum changes in the C–C coupling constants for the *a* bond reached 21.3 Hz on passing from R = F to R = SiH_3, up to 4.7 Hz for the *b* bond on passing from R = NHMe to R = I, and 1.9 Hz for the *c* bond on passing from R = NCS to R = CHNOH. The coupling constant $^1J_{CC}$ depends on the electro-negativity of the substituent atom linked to the carbon atom.[96] Thus a profound analogy is observed between the changes in the $^1J_{PN}$ for geminally disubstituted cyclotriphosphazenes[21] and the $^1J_{CC}$ for monosubstituted benzene derivatives. The effect of remote substituents on the coupling constants for compounds with ring-delocalised π-systems is weak, in contrast to the influence on the chemical shift of the ^{13}C signal.

We may note that the endocyclic coupling constants $^3J_{PN}$ are negligible; the exocyclic constants $^3J_{PN}$ for amino-cyclophosphazenes[22,23] will not be considered.

V. ^{31}P–^{31}P SPIN–SPIN COUPLING CONSTANTS

The coupling constants $^2J_{PP}$ were first determined for chlorofluorocyclotriphosphazenes.[10,11] In many cases the determination of $^2J_{PP}$ was complicated by the additional interactions of the ^{31}P nuclei with other magnetic nuclei, in the first place protons. The development of the method involving the proton decoupling of the ^{31}P nuclei was an important step both for the determination of the coupling constants and for the exact determination of the chemical shift δ_P. Numerous constants of this kind are quoted in the literature for cyclotriphosphazenes. The number of such data for cyclotetraphosphazenes is much smaller, since the determination of $^2J_{PP}$ frequently requires model calculations of the spectra. These constants have been determined for certain tetrameric thioethers,[16,37,51,98] ethers,[99] and amino-derivatives.[13,23,100,101]

Analysis of the experimental P–P coupling constants for cyclotriphosphazenes led Finer[102] to the conclusion that $^2J_{PP}$ depends virtually only on the nature of the substituents located about the phosphorus atoms involved in the coupling but is independent of the substituent at the third phosphorus atom. Finer proposed a formula from which it is possible to calculate approximately the P–P coupling constant (in Hz) for any cyclotriphosphazenes:

$$^2J_{PP} = (\lambda_A+\lambda_B)(\lambda_C+\lambda_D). \qquad (7)$$

Table 11. Coupling constants $|^2J_{PP}|$ (in Hz) for chloro(ethylthio)cyclotriphosphazenes.

Compound	Interacting nuclei in fragments				
	PCl_2, PCl_2	PCl_2, $PClSEt$	PCl_2, $P(SEt)_2$	$PClSEt$, $PClSEt$	$P(SEt)_2$, $P(SEt)_2$
$N_3P_3Cl_6$	50*	—	—	—	—
$N_3P_3Cl_5SEt$	—	32.9	—	—	—
$N_3P_3Cl_4(SEt)_2$	54.7*	—	5.0	—	—
$N_3P_3Cl_3(SEt)_3$	—	17.3	3.5	14.1	—
$N_3P_3Cl_2(SEt)_4$	—	—	5.2	—	17.8*
$N_3P_3Cl(SEt)_5$	—	—	—	9.9	—
$N_3P_3(SEt)_6$	—	—	—	—	14.7*
Mean value	52.4	25.1	4.6	12.0	16.3
Calculation by Eqn.(7)	51.0	27.9	4.9	2.7	0.5

*Values obtained from spectra of ^{15}N-labelled compounds.

Here λ_A–λ_D represents specially selected parameters for the substituents attached to the interacting phosphorus atoms. The values of λ are satisfactorily linearly correlated with the electronegativities of the substituent atoms linked directly to phosphorus. The coupling constants $^2J_{PP}$ can be predicted with a satisfactory accuracy in many cases by means of the Finer formula or the set of values of λ for other substituents can be supplemented.[103–105] Our detailed investigation of the constants $^2J_{PP}$ for hetero-substituted chloro(ethylthio)cyclotriphosphazenes showed that the Finer formula does not lead to correct predictions in all cases (Table 11). Sometimes the values of $^2J_{PP}$ for the same combination of interacting nuclei differ markedly. Judging from the average values quoted in Table 11, $^2J_{PP}$ passes through a minimum as the number of SEt groups

substituting chlorine increases. It is difficult to find a satisfactory explanation of this phenomenon. We therefore suggest that in the above series the sign of $^2J_{PP}$ is reversed after the attainment of the minimum. The Finer formula cannot reflect the above feature.

In the case of substituted 2,2,6,6-tetraethylthiocyclotetraphosphazenes,[16] the sign of $^2J_{PP}$ should also change (Table 12). Indeed, different signs of the P–P coupling constants have been obtained for chloro-2,2-diethylthiocyclotetraphosphazene by model calculations of the ^{31}P NMR spectra.[51] The variation of the average constant $^2J_{PP}$ with the degree of substitution for compounds of the type $N_4P_4Cl_{8-n}(SEt)_n$ and $N_3P_3Cl_{6-n}(SEt)_n$ is illustrated in Fig.8. The $^2J_{PP}$ curves for compounds of the trimeric and tetrameric series are parallel if it is assumed that the sign of the constant $^2J_{PP}$ changes on passing from the PCl_2–N–PCl_2 fragment to the $P(SEt)_2$–N–$P(SEt)_2$ fragment. The above constants for cyclotriphosphazenes are somewhat greater than for cyclotetraphosphazenes. The same tendency has been observed for aminochlorocyclophosphazenes[99] and for chlorophenoxycyclophosphazenes[101] (see also, Sulkowski et al.[106] and Samir et al.[107]).

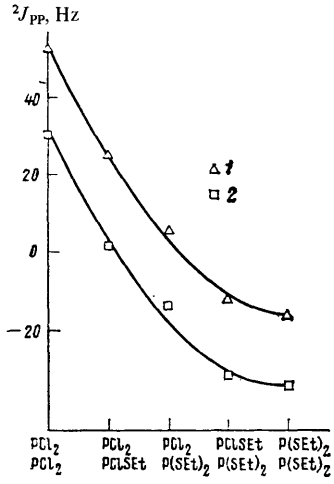


Figure 8. Coupling constants $^2J_{PP}$ for cyclotriphosphazenes (1) and cyclotetraphosphazenes (2) with different numbers of Cl and SEt substituents in fragments of the type R_2PNPR_2.

Table 12. Coupling constants $^2J_{PP}$ for substituted 2,2,6,6-tetraethylthiocyclotetraphosphazenes.

Interacting nuclei in fragments	$\lvert {}^2J_{PP} \rvert$, Hz	Compound
$P(SEt)_2$, $P(SEt)_2$	31.6*	$N_4P_4(SEt)_8$
$P(SEt)_2$, $P(NH_2)_2$	4.0	$N_4P_4(SEt)_4Cl_2(NH_2)_2$
Ditto	4.4	$N_4P_4(SEt)_4(NH_2)_4$
$P(SEt)_2$, PCl_2	11.8	$N_4P_4(SEt)_4Cl_4$
Ditto	11.7	$N_4P_4(SEt)_4Cl_2(NH_2)_2$
$P(SEt)_2$, PClOEt	9.6	*cis*-$N_4P_4(SEt)_4Cl_2(OEt)_2$
Ditto	10.6	*trans*-$N_4P_4(SEt)_4Cl_2(OEt)_2$
»	10.1	$N_4P_4(SEt)_4Cl(OEt)_3$
$P(SEt)_2$, $P(OEt)_2$	18.5	$N_4P_4(SEt)_4Cl(OEt)_3$
Ditto	18.5	$N_4P_4(SEt)_4(OEt)_4$
$P(SEt)_2$, $P(OMe)_2$	20.0	$N_4P_4(SEt)_4(OMe)_4$

*Value obtained from the spectrum of a ^{15}N-labelled compound.

Almost all the P–P coupling constants mentioned hitherto have been obtained for cyclophosphazenes with mixed substituents. The determination of the constant $^2J_{PP}$ for the homosubstituted cyclotriphosphazenes $(NPR_2)_3$ and cyclotetraphosphazenes $(NPR_2)_4$ is possible only when the above compounds contain, apart from phosphorus, other magnetic nuclei with $I = 1/2$, so that higher-order spectra are obtained in which the required constants are reflected. However, Finer et al.[108] were unable to obtain the constants $^2J_{PP}$ from the proton spectra of such compounds by model calculations of the spectra, since the resulting spectra were not sufficiently well resolved.

The possibility of obtaining the P–P coupling constants for ^{15}N-labelled homosubstituted cyclophosphazenes was already mentioned in the introduction. The graphical method for the determination of these compounds has been discussed in detail.[27,28] The constants are presented in Table 13 but only approximate values of some of them could be obtained, since in the case where the ratio $^2J_{PP}/^1J_{PN}$ is large the spectra do not reflect adequately the required constant.[27,28] The spectra of highly symmetrical compounds contain no information about the relative sign of $^2J_{PP}$ compared with $^1J_{PN}$. The signs listed in Table 13 were selected according to the considerations described above.

Table 13. Coupling constants $^2J_{PP}$ (in Hz)* for hexasubstituted cyclotriphosphazenes and octasubstituted cyclotetraphosphazenes.

Compound	n = 3	n = 4
$(^{15}NPMe_2)_n$	4.4	10.7
$[^{15}NP(NHMe)_2]_n$	—	—
$[^{15}NP(NHEt_2)]_n$	—	—
$[^{15}NP(NHPh)_2]_n$	30–70	35–45
$[^{15}NP(NMe_2)_2]_n$	—	—
$[^{15}NP(NEt_2)_2]_n$	—	—
$[^{15}NP(OMe)_2]_n$	—	74.3
$[^{15}NP(OEt)_2]_n$	90–120	—
$[^{15}NP(OPh)_2]_n$	—	80.6
$[^{15}NP(SEt)_2]_n$	−14.7	−31.6
$[^{15}NP(SPh)_2]_n$	−23.5	—
$(^{15}NPF_2)_n$	160–180	155.0
$(^{15}NPCl_2)_n$	45–55	—
$(^{15}NPBr_2)_n$	(−)4.8	−27.2

*The signs of the constants were not determined experimentally.

Fig. 9 illustrates the dependence of $^2J_{PP}$ for cyclotriphosphazenes and cyclotetraphosphazenes on the electronegativity of the substituent atoms; evidently there is a fairly satisfactory correlation between the values, the straight line for the trimeric compound lying above that for the tetrameric compounds.

Quantum-chemical calculation of these coupling constants in accordance with the ΔE approximation does not lead to satisfactory results. The Fermi contact contributions to the P–P coupling calculated by Eqn.(6) proved to be smaller approximately by two orders of magnitude than the contributions to the P–N interaction, while the experimental $^2J_{PP}$ and $^1J_{PN}$ coupling constants are mainly of the same order of magnitude. The additional allowance for other contributions (*OD* and *SD*) did not improve appreciably

the agreement between the experimental and calculated data. The approximate method of calculation of the coupling constants is evidently unsuitable for the spin–spin interactions of atoms separated by two bonds.

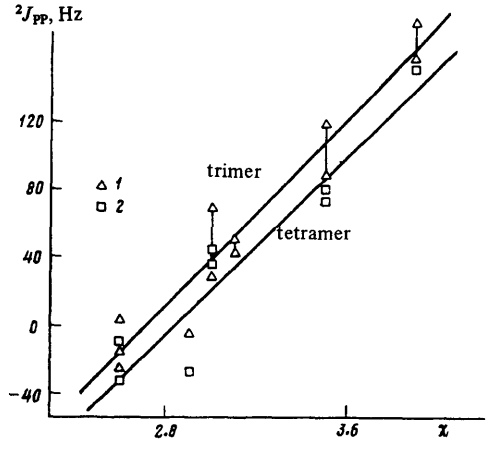


Figure 9. Coupling constants $^2J_{PP}$ for hexasubstituted cyclotriphosphazenes (1) and octasubstituted cyclotetraphosphazenes (2) as a function of the electronegativity of the substituent atom.

The coupling constants $^4J_{PP}$ for cyclotetraphosphazenes are small, as might have been expected. Only in certain cases has it been possible to determine them;[99,101,109] the values obtained for the aminochloro-derivatives, chloroethers, and aminoethers are in the range from −0.7 to −2.2 Hz.

VI. CONCLUSION

The nature of the substituents R at the phosphorus atoms in cyclophosphazenes influences the electronic structure of the $(P–N)_n$ ring as well as the ^{31}P and ^{15}N chemical shifts and the $^1J_{PN}$ and $^2J_{PP}$ coupling constants. A change in ring size also alters the NMR parameters. A correlation is observed between the electronegativity of the substituent atoms and δ_P as well as the $^1J_{PN}$ and $^2J_{PP}$ coupling constants, whereas no such correlation exists for δ_N. This has also been confirmed by calculations by the CNDO/2 method, according to which there is a linear correlation between the δ_P and the part of the paramagnetic contribution which depends on the distribution of electrons, while this type of correlation cannot be traced for δ_N.

In considering the values of the individual parameters, one may reach a number of conclusions. The chemical shift of phosphorus δ_P depends directly on the nature of the substituents attached to the given phosphorus atom. The substituents at the other phosphorus atoms exert only an insignificant influence on δ_P. Despite this, it is impossible to calculate δ_P with an adequate accuracy using a system of increments. With increase of ring size, δ_P undergoes an upfield shift.

The nitrogen chemical shift δ_N depends on the nature of the substituents at both neighbouring phosphorus atoms, but is independent of the substituents at the more remote phosphorus atoms. In this sense, cyclophosphazenes differ markedly from aromatic compounds with a delocalised π-system. The chemical shift δ_N varies linearly with the degree of substitution. On passing from trimeric to tetrameric phosphazenes, δ_N undergoes a downfield shift, while, on further increase of ring size, there is an upfield shift.

The coupling constants $^1J_{PN}$ can be both positive and negative. They depend primarily on the nature of the substituents at the phosphorus atoms involved in the coupling. To a lesser extent, their values are determined by the effect of the substituents at the other phosphorus atom linked to the nitrogen atom considered. The effect of the substituents at the more remote phosphorus atoms has not been observed. With increase of ring size, the constant $^1J_{PN}$ increases. There is an unambiguous relation between $^1J_{PN}$ and the P–N bond length and also the P–N stretching vibration frequency. Semiempirical quantum-chemical calculations have shown that there is a satisfactory correlation between the experimental coupling constants and the Fermi contact contributions. Thus $^1J_{PN}$ is the NMR parameter containing most information from the standpoint of the description of the electronic system of the skeleton of the $(P–N)_n$ rings.

The coupling constants $^2J_{PP}$ can be both positive and negative. They depend mainly on the nature of the substituents at both phosphorus atoms involved in the given coupling and to a lesser extent on the substituents at the other phosphorus atoms. With increase of ring size, $^2J_{PP}$ diminishes.

All the NMR parameters tend to limiting values with increase in ring size.

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