

## Nitrogen Nuclear Magnetic Resonance Spectroscopy. Part 9.<sup>1</sup> Cyclophosphazenes and Related Phosphorus–Nitrogen Compounds

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Nitrogen-14 n.m.r. shifts determined by wide-line methods are reported for the cyclophosphazenes (NPX<sub>2</sub>)<sub>n</sub> (*n* = 3, X = NMe<sub>2</sub>, OMe, F, Cl, Br, or NCS; *n* = 4, X = OMe, F, or Cl) and for the acyclic compounds P(NMe<sub>2</sub>)<sub>3</sub>, As(NMe<sub>2</sub>)<sub>3</sub>, P(NMe<sub>2</sub>)<sub>3</sub>S, and Cl<sub>3</sub>PNPCL<sub>2</sub>O. The cyclophosphazene nitrogen resonances span a range of 90 p.p.m., and are at fairly high field, as for example for S<sub>4</sub>N<sub>4</sub>, in contrast to those of aromatic azines and the cyclothiazonium ion [S<sub>4</sub>N<sub>3</sub>]<sup>+</sup> at medium field. The effects of ring size and perhaps of puckering are fairly small, and the chemical shifts of the ring nitrogens are not very different from those in the acyclic compounds with similar substituents on phosphorus. The shielding of the ring nitrogens in the cyclotriphosphazenes reflects the combined inductive and conjugative effects of the substituent X on phosphorus. Thus the sequence of the (NPX<sub>2</sub>)<sub>3</sub> resonances resembles that observed for acyclic nitrogen groups in which the X substituents are attached directly to nitrogen, and is the same for nitrogen and phosphorus shielding, if the latter is corrected for the variation in the diamagnetic contribution of the ligand X.

WE report <sup>14</sup>N n.m.r. shifts in cyclophosphazenes and acyclic phosphorus–nitrogen compounds (Tables 1 and 2).

### RESULTS AND DISCUSSION

*Cyclophosphazenes* (NPX<sub>2</sub>)<sub>n</sub>.—The nitrogen resonances in these P–N heterocycles are at relatively high field,

(NPPH<sub>2</sub>)<sub>4</sub>, no line could be detected, perhaps because of low solubility. Interestingly, no nitrogen line could be detected for the bromo-trimer with a 90-MHz Fourier-transform spectrometer, the wide-line continuous-wave spectrometer being superior in this respect.

For the compounds in which X = NMe<sub>2</sub> or NCS only one line was observed, and for the thiocyanate this was

TABLE I

Nitrogen and phosphorus shifts (δ) and paramagnetic-shielding terms (σ<sub>p</sub><sup>AL</sup>) in the cyclophosphazenes, compared with the reciprocal energy of the u.v. absorption

Compound	δ( <sup>14</sup> N) <sup>a</sup> p.p.m.	<i>w</i> <sup>b</sup> Hz	S : N	σ <sub>p</sub> <sup>AL</sup> (N) <sup>c</sup> p.p.m.	λ <sub>max</sub> <sup>d</sup> nm	Ref. (u.v.)	δ( <sup>31</sup> P) <sup>e</sup> p.p.m.	σ <sub>p</sub> <sup>AL</sup> (P) <sup>c</sup> p.p.m.
[NP(NMe <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> (l)	27 <sup>f</sup>	410	10 : 1	−312 <sup>g</sup>	193 (4)	12	25	−796
[NP(OMe) <sub>2</sub> ] <sub>3</sub> (in OEt <sub>2</sub> )	35	440	10 : 1	−322	<192 (>2.7)	12	21.7	−810
[NP(OMe) <sub>2</sub> ] <sub>4</sub> (in OEt <sub>2</sub> )	56	570	6 : 1	−343	<192 (>2.7)	12	−3.5	−785
(NPF <sub>2</sub> ) <sub>4</sub> (l)	55 <sup>h</sup>	285	20 : 1	−349	147.5 (>4)	11	−17	−791
(NPF <sub>2</sub> ) <sub>3</sub> (l)	59	165	>100 : 1	−347	149.4 (>4)	11	13.9	−819
[NP(NCS) <sub>2</sub> ] <sub>3</sub> (in OEt <sub>2</sub> )	100 <sup>f</sup>	750	10 : 1	−386 <sup>g</sup>	196 (5.1) 250 (3.4)	12	30	−802
(NPCL <sub>2</sub> ) <sub>4</sub> (in OEt <sub>2</sub> )	97	495	10 : 1	−384	173 (4) <sup>i</sup>	12	−7.4	−854
(NPCL <sub>2</sub> ) <sub>3</sub> (l)	106	224	12 : 1	−394	175 (4) <sup>i</sup>	12	20	−872
(NPBr <sub>2</sub> ) <sub>3</sub> (in CHCl <sub>3</sub> or C <sub>6</sub> H <sub>6</sub> )	115	460	2.5 : 1	−402	201.5 (4.4)	12	−45.4	−950
<i>sym</i> -Triazine (in dioxan)	257 <sup>j</sup>			−447	272 (3)	<i>k</i>		

<sup>a</sup> Relative to [NH<sub>4</sub>]<sup>+</sup> (aq), positive downfield. The precision depends on the linewidth and is usually better than ±5 p.p.m. <sup>b</sup> Peak-to-peak width (±5–10%) of the derivative line, with modulation at 20–40 Hz. The lines are modulation-broadened, particularly at low signal-to-noise ratios. <sup>c</sup> Atom-plus-ligand paramagnetic term (see text). <sup>d</sup> log (ε/dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>) is given in parentheses. <sup>e</sup> Relative to 85% H<sub>3</sub>PO<sub>4</sub>(aq), positive downfield. The values were taken from ref. 9. <sup>f</sup> Unresolved. <sup>g</sup> Diamagnetic correction as for the ring nitrogen. <sup>h</sup> Measured at 50 °C so as to melt the crystals. <sup>i</sup> Estimated. <sup>j</sup> Ref. 2. <sup>k</sup> S. F. Mason, *J. Chem. Soc.*, 1959, 1240.

in contrast to those of aromatic heterocycles (such as *sym*-triazine<sup>2</sup>) which are at medium field, and the range is quite large if one considers that it reflects the substitution at phosphorus not nitrogen. The lines are very broad, as expected for a quadrupolar nucleus in an environment of low symmetry, but some of the broadening is due to overmodulation that is necessary to make the resonance appear at all. The narrower lines for the fluoro-compounds reflect the low viscosity of these liquids. For the bromo-trimer the line is near the limit of detection, and for the corresponding tetramer, and for

very broad indeed (Table 1). In these two compounds the observed chemical shifts may perhaps be more characteristic of the exocyclic nitrogen, the higher local symmetry of which should sharpen the resonance. Thus the nitrogen lines are close together for [NP(NMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub>, P(NMe<sub>2</sub>)<sub>3</sub>, and NHMe<sub>2</sub><sup>3</sup> and also for [NP(NCS)<sub>2</sub>]<sub>3</sub> and EtNCS<sup>4</sup> (150 p.p.m. upfield of that of EtSCN,<sup>5</sup> confirming that the ligand is bound to phosphorus through nitrogen rather than sulphur). Nevertheless, the lines of [NP(NCS)<sub>2</sub>]<sub>3</sub> and [NP(NMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub> are in the range spanned by the cyclophosphazenes, so the contours probably contain the resonances for the ring and exo-

<sup>1</sup> Part 8, J. Mason, *J.C.S. Faraday II*, 1977, 1464.

<sup>2</sup> M. Witanowski, L. Stefaniak, H. Januszewski, and G. A. Webb, *Tetrahedron*, 1971, **27**, 3129.

<sup>3</sup> M. Alei, A. E. Florin, W. M. Litchman, and J. F. O'Brien, *J. Phys. Chem.*, 1971, **75**, 932.

<sup>4</sup> O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 1964, 3335.

<sup>5</sup> D. Herbison-Evans and R. E. Richards, *Mol. Phys.*, 1964, **8**, 19.

cyclic nitrogens. In the halogenophosphazenes also, the chemical shift of the ring nitrogen closely resembles those of acyclic P-N compounds with similar substituents on phosphorus: *cf.* the chloro-tetramer and  $\text{Cl}_3\text{PNPCL}_2\text{O}$ . The lines of the fluoro-trimer and -tetramer fall between those of  $\text{NH}_2(\text{PF}_2)_2$  <sup>6</sup> and  $\text{NH}(\text{PF}_2)_2$ , <sup>7</sup> but the differences are now larger, between the (III) and (v) oxidation states of phosphorus (Table 2).

The effect of ring size on the nitrogen shifts is fairly small and appears to be unsystematic in the nitrogen

first ionisation energies of the cyclophosphazenes,<sup>9</sup> but the delocalisation of ligand electrons in  $\pi^*$  orbitals tends to raise  $\Delta E$  in the order  $\text{X} = \text{NMe}_2 > \text{OMe} > \text{F} > \text{Cl} > \text{Br}$ . Table 1 shows that the nitrogen resonances do indeed move downfield as the u.v. absorption <sup>11-13</sup> moves to longer wavelengths in the series of halogenocyclophosphazenes, but the absorption is thought <sup>12,13</sup> to be a property of the P-X group rather than of the phosphazene ring.

The observed <sup>31</sup>P resonances in the trimers <sup>9</sup> (given in

TABLE 2

Nitrogen and phosphorus shifts ( $\delta$ ) and paramagnetic-shielding terms ( $\sigma_p^{\text{AL}}$ ) in acyclic phosphorus-nitrogen compounds

Compound	$\delta(\text{N})^a$ p.p.m.	$w^b$ Hz	S : N	Ref.	$\sigma_p^{\text{AL}}(\text{N})^c$ p.p.m.	$\delta(^{31}\text{P})$ p.p.m.	Ref.	$\sigma_p^{\text{AL}}(\text{P})^c$ p.p.m.
$\text{P}(\text{NMe}_2)_3\text{O}$ (l)	2			5	-269	27	17	-798
$\text{P}(\text{NMe}_2)_3\text{S}$ (l)	12	750	12 : 1		-279	78	17	-884
$\text{P}(\text{NMe}_2)_3$ (l)	20	630	20 : 1		-287	122	17	-847
$\text{As}(\text{NMe}_2)_3$ (in $\text{C}_6\text{H}_6$ )	24	600	40 : 1		-380			
$\text{P}(\text{NCO})_3$ (in $\text{C}_6\text{H}_6$ )	31			<i>d</i>	-277			
$\text{NH}_2(\text{PF}_2)$ (in $\text{SiMe}_4\text{-CCl}_3\text{F}$ )	39.5 <sup>e</sup>			6	-252	145.9	6	-901
$\text{NHPh}(\text{PMe}_2)$ (in $\text{C}_6\text{H}_6$ )	46.3 <sup>e</sup>			<i>f</i>	-288	13.4	<i>f</i>	-724
$\text{NHPh}[\text{P}(\text{NMe}_2)_2]$ (in $\text{C}_6\text{H}_6$ )	57.9 <sup>e</sup>			<i>f</i>	-300	103.9	<i>f</i>	-833
$\text{NMe}_2[\text{P}(\text{NHPh})_2]$ (in $\text{C}_6\text{H}_6$ )	58.2 <sup>e</sup>			<i>f</i>	-300	84.5	<i>f</i>	-814
$\text{NHPh}[\text{PMe}(\text{OMe})]$ (in $\text{Me}_2\text{SO}$ )	61.8 <sup>e</sup>			<i>f</i>	-304	31.2	<i>f</i>	-758
$\text{NH}(\text{PF}_2)_2$ (in $\text{SiMe}_4\text{-C}_6\text{D}_6$ )	104.4 <sup>e</sup>			7	-397	144.4	7	-900
$\text{Cl}_3\text{PNPCL}_2\text{O}$ (in $\text{OEt}_2$ )	111	1100	10 : 1		-392	-0.1	<i>g</i>	-892
						-14.2	<i>g</i>	-846
$\text{N}(\text{PF}_2)_3$ (in $\text{SiMe}_4\text{-C}_6\text{D}_6$ )	157.1 <sup>e</sup>			7	-546	150.3	7	-909

<sup>a-c</sup> As in Table 1. <sup>d</sup> K. F. Chew, W. Derbyshire, N. Logan, A. H. Norbury, and A. I. P. Sinha, *Chem. Comm.*, 1970, 1708. <sup>e</sup> <sup>15</sup>N-measurements. <sup>f</sup> W. McFarlane and B. Wrackmeyer, *J.C.S. Dalton*, 1976, 2351. <sup>g</sup> J. Emsley and P. B. Udy, *J. Chem. Soc. (A)*, 1970, 3025.

resonance, in contrast to the phosphorus resonance for which the tetramer appears upfield of the trimer. The differences are small for the fluoro- and chloro-compounds, 4 and 9 p.p.m. respectively, perhaps because all the rings are flat (or nearly so) <sup>8,9</sup> in the liquid phase. The ring is flat in the methoxy-trimer, but the tetramer ring is puckered in the solid, as is the bromo-trimer (when  $\text{X} = \text{NMe}_2$  or  $\text{NCS}$  the trimers are slightly puckered).

*Substituent effects on the nitrogen shielding.* With variation of the X group on phosphorus the shielding of the ring nitrogen in the trimers decreases in the order  $\text{X} = \text{NMe}_2 > \text{OMe} > \text{F} > \text{NCS} > \text{Cl} > \text{Br}$  (Table 1). This resembles the sequences observed in nitrogen shielding for groups X attached directly to nitrogen,<sup>10</sup> interpreted as the decreasing order of effective excitation energy  $\Delta E$  for excitations of the  $p_x \rightarrow p_y$  type (such as  $n \rightarrow \pi^*$ ,  $\sigma \leftarrow \pi$ ). The  $\sigma$ -inductive effect tends to increase  $\Delta E$  (shifting the line upfield) in the approximate order  $\text{X} = \text{F} > \text{Cl} > \text{Br} > \text{OMe} > \text{NMe}_2$  as given by the

<sup>6</sup> D. W. W. Anderson, J. E. Bentham, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 1215.

<sup>7</sup> D. E. J. Arnold and D. W. H. Rankin, *J.C.S. Dalton*, 1975, 889.

<sup>8</sup> N. Zumbulyadis and B. P. Dailey, *J. Magnetic Resonance*, 1974, 13, 189.

<sup>9</sup> H. R. Allcock, 'Phosphorus-Nitrogen Compounds,' Academic Press, New York, 1972, ch. 3 and refs. therein.

<sup>10</sup> L.-O. Andersson, J. Mason, and W. van Bronswijk, *J. Chem. Soc. (A)*, 1970, 296.

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<sup>12</sup> B. Lakatos, Á. Hesz, Zs. Vetéssy, and G. Horváth, *Acta Chim. Acad. Sci. Hung.*, 1969, 60, 309.

<sup>13</sup> D. P. Craig and N. L. Paddock in 'Non-benzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1971, p. 349.

Table 1) do not follow the order of the nitrogen resonances, but they do so (except for  $\text{X} = \text{NCS}$ ) if they are corrected for the rather large variation in diamagnetic contributions of the ligands.<sup>14</sup> The <sup>31</sup>P shielding then decreases in the order  $\text{X} = \text{NMe}_2 > \text{NCS} > \text{OMe} > \text{F} > \text{Cl} > \text{Br}$ , as given by the atom-plus-ligand paramagnetic term  $\sigma_p^{\text{AL}}$  in the final column of Table 1. This refers to an absolute scale based on the spin-rotation measurement <sup>15</sup> of the paramagnetic term (-387 p.p.m.) for <sup>31</sup>PH<sub>3</sub>, combined with an *ab initio* value (981 p.p.m.) of the diamagnetic term,<sup>16</sup> and the known chemical shift ( $\delta$  -240 p.p.m.).<sup>17</sup> Atom-plus-ligand diamagnetic terms<sup>14</sup> were obtained from Flygare's equation,<sup>18</sup> with a local diamagnetic term estimated from the X-ray photoelectron spectroscopic values of core-electron binding energies, for nitrogen <sup>1,19</sup> (327.5 p.p.m.) and phosphorus <sup>20</sup> (963 p.p.m.).

Thus the shielding sequence is the same in the nitrogen and in the phosphorus resonance (except for  $\text{X} = \text{NCS}$ , for which the resonances of the exocyclic and ring

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<sup>15</sup> P. B. Davies, R. M. Neumann, S. C. Wofsy, and W. Klemperer, *J. Chem. Phys.*, 1971, 55, 3564.

<sup>16</sup> S. Rothenberg, R. H. Young, and H. F. Schaefer, *J. Amer. Chem. Soc.*, 1970, 92, 3243.

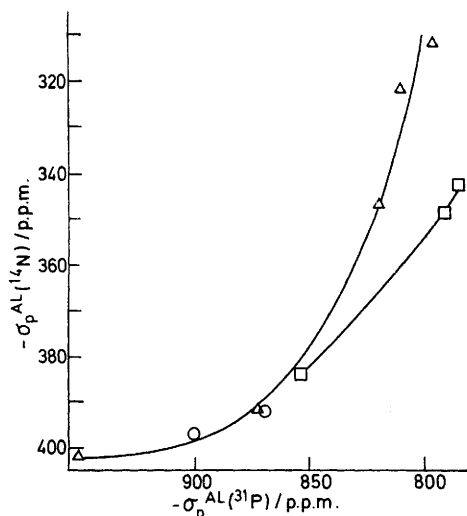
<sup>17</sup> H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, 1954, 22, 162; J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, 1956, 78, 5715.

<sup>18</sup> W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, 1968, 49, 3122; T. D. Gierke and W. H. Flygare, *J. Amer. Chem. Soc.*, 1972, 94, 7277.

<sup>19</sup> D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 1969, 8, 2642.

<sup>20</sup> W. H. Stec, W. E. Morgan, J. R. Van Wazer, and W. G. Proctor, *J. Inorg. Nuclear Chem.*, 1972, 34, 1100.

nitrogens were not resolved), and reflects electronic influences of the groups on phosphorus. A parallel conclusion can be drawn for the more limited series of tetramers, and the Figure shows the relation between the atom-plus-ligand paramagnetic terms for phosphorus and nitrogen in the phosphazenes. A linear relation is not expected since the inductive and conjugative influences are different for phosphorus and nitrogen; thus the nitrogen shifts show larger conjugative than inductive effects, as compared with the phosphorus shifts, and as compared with compounds in which the X group is attached directly to nitrogen.<sup>10</sup> Remote substituent effects (of up to 15 p.p.m.) are observed also in the phosphorus shielding, in cyclophosphazenes in which



Relations between the atom-plus-ligand paramagnetic shielding terms of nitrogen and phosphorus in PNP compounds: (○) acyclic compounds; (△) trimers; and (□) tetramers

different phosphorus atoms bear different substituents.<sup>9</sup> Thus the nuclear magnetic shielding accords with other physical evidence for  $p_n-d_n$  delocalisation in the ring and exocyclic groups. Table 2 indicates that similar conclusions may emerge for appropriate acyclic phosphazenes, but the information is as yet insufficient.

It seems, therefore, that the exocyclic groups in the cyclophosphazenes influence excitation energies that are significant both for nitrogen and phosphorus shielding. Such (magnetic-dipole-allowed) excitations are optically forbidden, but can be correlated with u.v. absorption in  $n \rightarrow \pi^*$  bands.<sup>5</sup> For the cyclophosphazenes, however, the longest-wavelength bands (Table 1) are in the vacuum-u.v. region, and are strong, insensitive to protonation, to polar solvents in general, and to ring size.<sup>21,22</sup> The absence of lower-energy  $n \rightarrow \pi^*$  absorption can be attributed to stabilisation of the nitrogen lone-pair electrons relative to the  $\pi^*$  orbital by in-plane  $p_n-d_n$  delocalisation, and by the presence of elec-

tronegative substituents in the ring and in the exocyclic groups. The high energy of the u.v. absorption points to higher  $\pi-\pi^*$  energies in the cyclophosphazenes than in the corresponding azines, and the absence of red shifts with extension of the polyphosphazene systems<sup>12,22</sup> suggests that conjugation is limited to the P-N-P group (and appropriate ligands)<sup>9,12,22,23</sup> since the phosphorus must use  $d_n$  orbitals.

The higher-field disposition of the cyclophosphazene nitrogen resonances (compared to the azines) may be understood in similar terms, although there is an additional factor in the 'heavy-atom' (diamagnetic) effect of the two phosphorus atoms bound to nitrogen. If we allow for this, the upfield shift relative to *sym*-triazine (for example) is much reduced, as Table I shows. A relevant comparison is with the puckered (or cage) cyclothiazene molecule  $\text{S}_4\text{N}_4$ , for which the nitrogen shielding is about the same as in the chloro- and bromo-cyclophosphazenes,<sup>24</sup> in contrast to the planar cyclothiazonium ion  $[\text{S}_4\text{N}_3]^+$  in which the nitrogens are less shielded by *ca.* 250 p.p.m.<sup>25</sup> and there is near-u.v. absorption which can be interpreted as  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  bands arising from a reasonably 'aromatic' system.

*Acyclic P-N Compounds.*—As mentioned above, the substituent shifts in the acyclic compounds (Table 2) are reminiscent of those in the cyclophosphazenes, but more data are needed for useful generalisations to be possible. Interestingly, the increments in  $\sigma_p^{AL}(\text{N})$  for the  $\text{PF}_2$ -substituted amines (which are all planar) are equal for successive substitution, although the increments in  $\delta(\text{N})$  are not (Table 2). The nitrogen and phosphorus paramagnetic shielding terms in the PNP compound  $\text{F}_2\text{P-NH-PF}_2$  are related as in the cyclophosphazenes, as shown in the Figure, and this is true of the other PNP compound  $\text{Cl}_3\text{PNPCL}_2\text{O}$  if one averages the shielding terms for the two phosphorus atoms.

In conclusion, it seems that the nuclear magnetic shielding, like the other physical properties of the cyclophosphazenes, can for the present be described in terms of inductive and conjugative effects without recourse to effects of aromaticity in the phosphazene ring.

#### EXPERIMENTAL

Nitrogen-14 shifts were measured with a Varian 4300B wide-line spectrometer at 3 MHz with phase-sensitive detection of the centre band, typically with 40-Hz modulation. Aqueous ammonium nitrate was used as external reference.

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<sup>24</sup> J. Mason, *J. Chem. Soc. (A)*, 1969, 1567.

<sup>25</sup> N. Logan and W. L. Jolly, *Inorg. Chem.*, 1965, **4**, 1508.