X-Ray Photoelectron Spectroscopy of Some Dimethylamino-substituted Cyclotriphosphazenes

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X-Ray photoelectron spectra of a number of substituted cyclophosphazenes have been measured and the results discussed qualitatively in terms of the charge distributions in these compounds. The ability of the phosphazene ring to redistribute charge appears to be important. Some suggestions are made concerning the basicity of the ring and amine nitrogen atoms.

THE bonding of cyclophosphazenes, and the effects caused by the addition of substituents is still not fully understood. We report here the results of a study of various closely related substituted cyclotriphosphazenes by *X*-ray photoelectron spectroscopy (ESCA), which allow the changes in charge distribution with substitution to be followed.

EXPERIMENTAL

Chloro- and fluoro-dimethylaminocyclotriphosphazenes were prepared as described previously.[1-3] The structures of these compounds have been well established by conventional spectroscopic techniques. The spectra were studied using an A.E.I. ES100 *X*-ray photoelectron spectrometer with Al $K_{\alpha_1\alpha_2}$ radiation. The samples were studied as solids cooled to between 150 and 170 K, because of the high volatility of the solids at room temperature under the high vacuum (5×10^{-8} to 5×10^{-7} mmHg) conditions of the spectrometer. The solids were mounted on double-sided Sellotape which was attached to the copper sample block, and were calibrated by reference to the gold $4f_{7/2}$ level electrons (binding energy = 84·0 eV) from gold powder on the surface of the solids. Two of the compounds [P$_3$N$_3$Cl$_5$(NMe$_2$) and *trans*-P$_3$N$_3$Cl$_2$F$_2$(NMe$_2$)$_2$] were liquids at room temperature but were studied as solids at 170 K by freezing a mixture of the liquid and gold powder spread over a gold plate. In view of the somewhat narrow range of shifts being investigated considerable care was taken over calibration, and other levels from entities such as surface adsorbed water and carbon were used for further calibration checks. The results are considered accurate to ±0·3 eV. Overlapping peaks (electron counts *vs.* binding energy) were deconvoluted using a Dupont curve analyser.

	Binding energies (eV)					
Compound	P(2*s*)	P(2*p*)	N(1*s*)	Cl(2*s*)	Cl(2*p*)	F(1*s*)
P$_3$N$_3$Cl$_6$ (I)	191·0	134·0	398·4	271·4	200·5	
P$_3$N$_3$Cl$_5$(NMe$_2$) (II)	191·0 (*P*Cl$_2$)	133·7	398·2 (ring)		200·7 (P*Cl*$_2$)	
	190·8 [*P*Cl(NMe$_2$)]	133·4	399·6 (*N*Me$_2$)		200·0 [P*Cl*(NMe$_2$)]	
cis-P$_3$N$_3$Cl$_4$(NMe$_2$)$_2$ (III)	190·9 (*P*Cl$_2$)	133·3	398·1 (ring)	270·6 (not resolved)	200·7 (P*Cl*$_2$)	
	190·1 [*P*Cl(NMe$_2$)]	132·9	399·0 (*N*Me$_2$)		200·0 [P*Cl*(NMe$_2$)]	
trans-P$_3$N$_3$Cl$_4$(NMe$_2$)$_2$ (IV)	190·8 (*P*Cl$_2$)	133·2	397·7 (ring)	270·5 (not resolved)	200·6 (P*Cl*$_2$)	
	190·0 [*P*Cl(NMe$_2$)]	132·5	399·3 (*N*Me$_2$)		199·9 [P*Cl*(NMe$_2$)]	
trans-P$_3$N$_3$Cl$_2$F$_2$(NMe$_2$)$_2$ (V) (1,3-difluoride)	191·2	133·8	398·4 (ring)	271·2	200·5	687·8
			399·8 (*N*Me$_2$)			
trans-P$_3$N$_3$F$_3$(NMe$_2$)$_3$ (VI)	191·5	134·0	398·4 (ring)			687·7
			399·8 (*N*Me$_2$)			
cis-P$_3$N$_3$Cl$_3$(NMe$_2$)$_3$ (VII)	190·5	133·1	397·9 (ring)		200·0	
			399·2 (*N*Me$_2$)			
gem-P$_3$N$_3$Cl$_3$(NMe$_2$)$_3$ (VIII)	190·8	133·4	398·3 (ring)		200·5 (P*Cl*$_2$)	
			399·7 (*N*Me$_2$)		199·7 [P*Cl*(NMe$_2$)]	
P$_3$N$_3$(NMe$_2$)$_6$ (IX)	189·8	132·5	397·9 (ring)			
			399·8 (*N*Me$_2$)			

RESULTS AND DISCUSSION

The results of the studies are presented in the Table. P$_3$N$_3$Cl$_6$ (I) has been studied previously, and the binding energies of the electrons ejected from the nitrogen 1*s* core energy level have been found[4] to be 399·5 eV, and from[5] the phosphorus 2*p* core energy level 134·5 eV. The small difference between these and our results are

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[1] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.

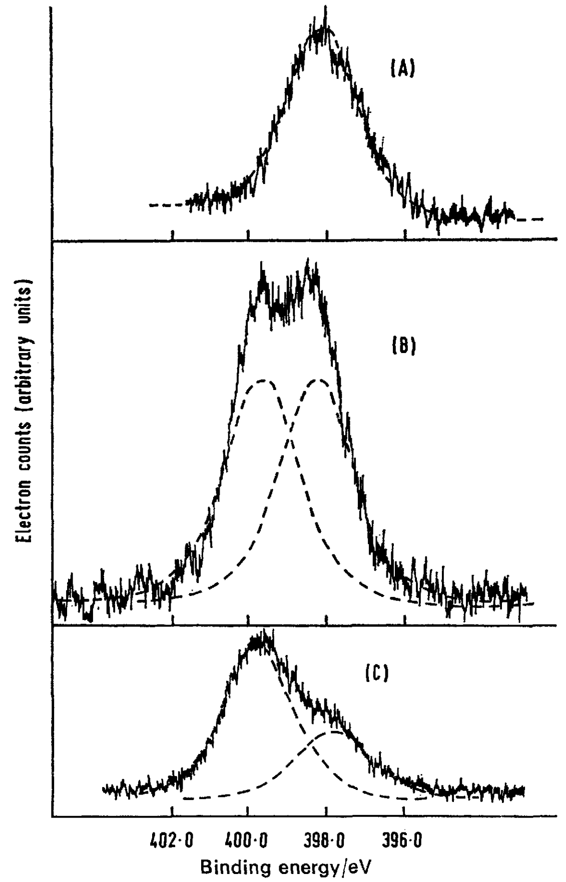
[2] B. Green and D. B. Sowerby, *J. Chem. Soc.* (*A*), 1970, 987.

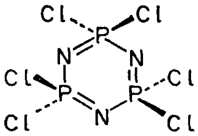
[3] B. Green, D. B. Sowerby, and P. Clare, *J. Chem. Soc.* (*A*), 1971, 3487.

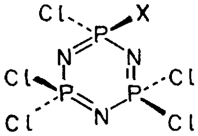
[4] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 1969, **8**, 2642.

[5] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, 1970, **74**, 1116.

probably due to calibration differences. Figure (A) shows the N(1*s*) binding energy for $P_3N_3Cl_6$. The width of this peak was taken as a standard for the other compounds. Typical spectra deconvoluted on this basis are shown in Figure (B) and (C). Figure B shows the compound $P_3N_3F_3(NMe_2)_3$ where two peaks of intensity ratio 1 : 1 may be deconvoluted. Figure (C) shows the compound $P_3N_3(NMe_2)_6$ where two peaks of intensity ratio 2 : 1 may be deconvoluted. Other deconvolutions were done on the same basis. The values for *cis*-$P_3N_3Cl_4(NMe_2)_2$ (III) and *trans*-$P_3N_3Cl_4(NMe_2)_2$ (IV) provide a good indication of the accuracy of the calibration, for in these compounds the stereochemical difference would be expected to give little change in chemical environment. The results show the binding energies for these two compounds to be within $\pm 0{\cdot}3$ eV. The results show that the overall effect of replacing the six chlorine atoms by six (NMe_2) groups to give $P_3N_3(NMe_2)_6$ (IX) is to reduce the binding energy of the 2*p* electrons of the phosphorus to which these groups are attached. This result is quite expected for the replacement of an electron-withdrawing group by an electron-donating group. The 1*s* electrons of the ring nitrogen atom have a lower binding energy in the amino-compound consistent with a decrease in overall electron-withdrawing character of the ring substituents [Figure (C)]. As expected from its electron-donating character, the NMe_2 group has the highest nitrogen 1*s* binding energy.




(I)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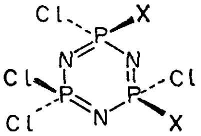
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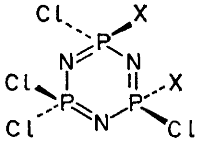
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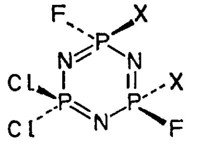
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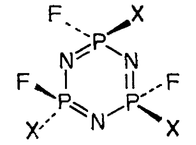
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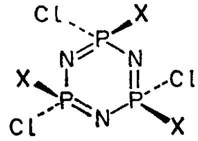
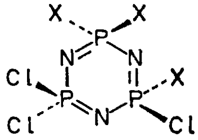
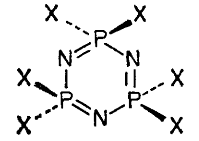

(VII)


(VIII)


(IX)

X = NMe_2

The study of the results for compounds of mixed substitution provides interesting examples of the trends in charge distribution between the fully chlorinated and fully aminated cases. In the charge-potential model[6] the binding energy can be expressed in terms of the charge on the atom (Q) and the coulomb potential energy (V) of an electron due to the other atoms of the molecule. Thus:

$$\text{Binding Energy} = \text{Constant}\ Q + V + \text{Constant}.$$

In an ionic compound V includes the contribution from other ions and is thus a Madelung term. In general the neglect of V is most serious for ionic compounds but for the covalent species considered here the binding energy should be dominated by the charge (Q) on the atom concerned. In view of the small shifts observed and of the complex electronic nature of these molecules the relation of binding energy to charge while useful has to be viewed with caution for the reasons stated above. Thus for the compound $P_3N_3Cl_5(NMe_2)$ (II) the phosphorus 2*p* binding energy will be seen to be split, one due to the PCl_2 phosphorus atom, and the other due to the $PCl(NMe_2)$ phosphorus atom. This splitting is small and only results in a broadening of the peak, the component peak positions being obtained by deconvolution.

The phosphorus 2*p* binding energy of the $PCl(NMe_2)$ group is reduced by the electron donation from the NMe_2 group, but this reduction in binding energy is

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[6] K. Siegbahn, C. Nordling, A. Fahlman, K. Nordberg, K. Hamrin, J. Hedman, J. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, 'ESCA Applied to Free Molecules,' North Holland, Amsterdam, 1969.

much less than in the $P(NMe_2)_2$ group of $P_3N_3(NMe_2)_6$, since electron density is being removed from the phosphorus atom by the Cl atom. In agreement the chlorine 2*p* binding energy in $PCl(NMe_2)$ is reduced since this single atom does not have to share electron density with another chlorine atom as in PCl_2 and obtains electron density from the NMe_2 group. Examination of the Table shows such trends being followed on further substitution. In particular it should be noted that in the partially fluorinated compound $P_3N_3Cl_2F_2(NMe_2)_2$ (V) the phosphorus is no longer split, presumably because the charge distribution for the PCl_2 group is the same as that for the $PF(NMe_2)$ group. The situation in the triaminated compounds varies depending upon the possible arrangements of the groups. The simplest case is that of the non-geminal fluorinated compound $P_3N_3F_3(NMe_2)_3$ (VI). The splitting of the N(1*s*) levels into two peaks of equal intensity corresponding to ring and amine nitrogen atoms is shown in Figure (B). In agreement with the suggestion above, that the charge distribution for PCl_2 is similar to $PF(NMe_2)$, the binding energies are close to that of $P_3N_3Cl_6$. These results are consistent with the results for some fluorophenylcyclotriphosphazenes,[7] in which there would be expected to be little movement of electron density to or from the phenyl group. The phosphorus 2*p* binding energy is **133·3** eV for the PPh_2 group, **134·3** eV for the PFPh group, and **135·5** eV for the PF_2 group.

The compound *gem*-$P_3N_3Cl_3(NMe_2)_3$ (VIII) is particularly interesting, since no splitting of the phosphorus levels is observed. Thus while the chlorine binding energies are split to give the expected values for a PCl_2 and $PCl(NMe_2)$ groups, the ring appears to be distributing the electron density to give an equal charge distribution on the phosphorus atoms. This behaviour, though less marked, was observed for the mono- and di-amino compounds.

CONCLUSIONS

We conclude that these results imply that the ability of the triphosphazene ring to distribute charge within the ring has an important effect on the charge distribution in substituted cyclophosphazenes. Thus in the case where the substituents on phosphorus are as different in electron-withdrawing ability as possible, such as in the studies of fluorophenylcyclotriphosphazenes,[7] the shifts in binding energy are relatively small. With a smaller difference between the substituents, as in the case of *gem*-$P_3N_3Cl_3(NMe_2)_3$, there is no shift in the phosphorus 2*p* binding energy for the different phosphorus atoms. Dimethylaminocyclotriphosphazenes contain two potentially basic sites, *viz* a ring nitrogen atom and an amine nitrogen atom. The relative basicities of these sites have been of considerable interest and recent work on this topic has been included in a recent review.[8] It is clear that the N(1*s*) binding energy of the ring nitrogen is greater than that of the amine nitrogen for $P_3N_3(NMe_2)_6$. This implies, notwithstanding the theoretical limitations already discussed, that the total electron density for the amine nitrogen atom is less than for the ring nitrogen atom as Figure (C) clearly illustrates. This suggests that the most basic centre in dimethylamino-substituted cyclotriphosphazenes may be a ring nitrogen atom.

Further interpretation of the results must be treated with caution because of the small shifts observed and the theoretical failings of simple qualitative models, but they should have importance in the consideration of the mechanisms of substitution reactions of cyclophosphazenes.

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[7] W. J. Stec, W. E. Morgan, J. R. Van Wazer, and W. G. Proctor, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1100.

[8] H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315.