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Core Electron Binding Energies of Cyclotriphosphazenes and Cyclotetraphosphazenes

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The core electron binding energies of $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_4$ have been determined in the gas phase by x-ray photoelectron spectroscopy. The data show a reasonable correlation with the eleconegativities of the substituent groups. On going from $(NPF_2)_4$ to $(NPF_2)_3$ or from $(NPCl_2)_4$ to $(NPCl_2)_3$, the binding energies increase by only 0.22 eV or less. This near-constancy of the binding energies suggests that the degree π bonding is similar in the trimers and tetramers.

The cyclophosphazenes are often cited as examples of inorganic aromatic systems.[3] A large number of experimental data, including structural parameters,[4] ionization potentials,[5,6] and mass spectrometric fragmentation patterns,[7] have been interpreted in terms of the presence of delocalized π bonding in the rings. Any increase in the degree of this π bonding involves the transfer of negative formal charge from the ring nitrogen atoms to the phosphorus atoms or to substituent groups on the phosphorus atoms. Therefore the atomic core electron binding energies should be sensitive to the degree of π bonding.

In this study we have used x-ray photoelectron spectroscopy to determine the core electron binding energies of $(NPF_2)_3$, $(NPF_2)_4$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_4$ in the gas phase in an attempt to provide experimental information related to the bonding arrangements in these compounds.

Results and Discussion

The core binding energies of the phosphazenes and, for comparison, some phosphorus halides and oxyhalides, are listed in Table I. Most of the differences in the core binding energies of the compounds in Table I can be qualitatively interpreted in terms of differences in atomic charges. For example, the increases in the P $2p_{3/2}$ and N 1s binding energies in the series $[NP(CH_3)_2]_4 < (NPCl_2)_{3,4} < (NPF_2)_{3,4}$ probably correspond to increasing positive charge on the phosphorus atoms and decreasing negative charge on the nitrogen atoms and reflect relative electronegativities of the methyl group, chlorine, and fluorine. Similarly, the P $2p_{3/2}$ binding energy shifts between $(PNX_2)_{3,4}$ and the compounds PX_3 and POX_3 can be rationalized in terms of electronegativities. The similarity of the P $2p_{3/2}$ binding energies of the fluorophosphazenes and PF_3 shows that the two nitrogen atoms attached to a phosphorus atom in a cyclophosphazene are essentially equivalent in their combined electron-withdrawing power to one fluorine atom. Although the phosphorus atom in POF_3 has the same coordination number as that in a fluorophosphazene, the four highly electronegative ligand atoms in POF_3 make the phosphorus atom much more positively charged than a phosphorus atom in a fluorophosphazene, where two of the ligand atoms are nitrogen atoms (with relatively low electronegativities). Thus we can understand why the P $2p_{3/2}$ binding energy of POF_3 is by far the highest listed in Table I. The two nitrogen atoms bonded to a phosphorus atom in a phosphazene have slightly more combined electron-withdrawing power than one chlorine atom; hence the P $2p_{3/2}$ binding energy of PCl_3 is slightly less than that of the chlorophosphazenes. As expected, the high electronegativity of oxygen causes the P $2p_{3/2}$ binding energy of $POCl_3$ to be considerably greater than that of the chlorophosphazenes.

The shifts in the phosphorus, nitrogen, and halogen binding energies on going from a tetrameric phosphazene to the corresponding trimer are quite small (0.22 eV or less), and the significance of these shifts is not as obvious as in the cases just discussed. It has been shown that a core binding energy, E_B, can be represented as a sum of three terms[8,9]

$$E_B = (kQ + l) + V - E_R$$

The first term is a linear function of the atomic charge, Q; the second term, V, is the electrostatic potential due to the other charged atoms in the molecule, and the third term, $-E_R$, is the negative of the relaxation energy associated with the migration of electron density toward the core hole. The data in Table I show that, in the change from a tetramer to the corresponding trimer, an increase occurs in the binding energies of all the corresponding atoms. Because the charges of *all* the atoms cannot become more positive on going from a tetramer to a trimer (the sum of the charges must remain zero), we infer that the sum of the second and third terms must change in the case of at least one of the atoms. Unfortunately, our present understanding of methods of calculating V and E_R is too poor to account for chemical shifts as small as 0.1 or 0.2 eV. However, if we make the assumption that the observed shifts are entirely due to changes in the values of Q, we can, using estimated k values,[10] calculate that the changes in the atomic charges are the following: for phosphorus, 0.01; for nitrogen, 0.01; for fluorine, 0.01; for chlorine, 0.02. It is reasonable to assume that the actual changes in the charges are not much greater than these values. Therefore, we conclude that the atomic charges in the trimeric cyclophosphazenes differ very little (probably less than 0.02 unit) from those in the corresponding tetrameric compounds.

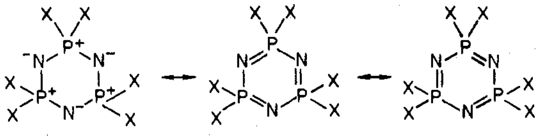
One model of the bonding in cyclophosphazenes is based on the assumption that the $2p\pi$ orbitals of the nitrogen atoms and the $3d\pi$ (and perhaps the $4p\pi$) orbitals of the phosphorus atoms are at least partly involved in ring π bonding and that the 3s and 3p orbitals of each phosphorus atom are completely

Table I. Core Electron Binding Energies and Line Widths, eV

	P $2p_{3/2}$		F 1s		Cl $2p_{3/2}$		N 1s	
Compd	E_B	Fwhm	E_B	Fwhm	E_B	Fwhm	E_B	Fwhm
$(NPF_2)_3$[a]	141.73 (5)[b]	1.06	694.71 (5)	1.49			405.29 (5)	1.07
$NNPF_2)_4$[a]	141.62 (6)	1.19	694.51 (5)	1.52			405.08 (5)	1.15
$(NPCl_2)_3$[a]	140.25 (6)	1.17			206.76 (6)	1.43	404.38 (5)	1.15
$(NPCl_2)_4$[a]	140.17 (6)	1.23			206.54 (6)	1.44	404.25 (4)	1.13
$[NP(CH_3)_2]_4$[a]	137.20 (8)	1.39					402.07 (7)	1.33
PF_3[c]	141.78 (7)	1.23	694.09 (6)	1.50				
PCl_3[c]	139.75 (6)	1.30			206.42 (6)	1.42		
POF_3[c]	143.0 (1)	1.43	695.6 (1)	1.51				
$POCl_3$[c]	141.02 (5)	1.07			207.31 (6)	1.32		

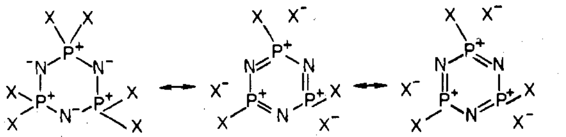
[a] The binding energies for these compounds were determined relative to that for the Ne 1s level (870.31 eV). [b] The uncertainty in the last digit is given in parentheses. [c] The binding energies for these compounds were determined relative to that for the Ar $2p_{3/2}$ level (248.60 eV).[14] The binding energies differ slightly from previously published values because of the change in the value taken for the reference level and because of the use of a revised spectrometer constant.

involved in σ bonding to two substituent groups and two nitrogen atoms. According to this model, a cyclotriphosphazene can be represented in the simplest sense as a resonance hybrid of the structures I, IIa, and IIb. Structure I corresponds



I IIa IIb

to no involvement of the phosphorus 3d or 4p orbitals but assumes localization of six pairs of nonbonding electrons on the more electronegative nitrogen atoms. Structures IIa,b correspond to maximum involvement of the higher phosphorus orbitals in ring π bonding. Another speculative model of the bonding assumes little or no use of phosphorus 3d orbitals and assumes that the π bonding is formed by the overlap of pπ orbitals on the nitrogen and phosphorus atoms.[3] It is assumed that the formation of pπ–pπ bonding in the ring would be accompanied by a corresponding reduction in the σ bonding in the P–X bonds. This bonding model is equivalent to the consideration of resonance structures such as structures I, IIIa,



I IIIa IIIb

and IIIb. Again structure I corresponds to the absence of π bonding, and structures IIIa,b correspond to complete pπ–pπ bonding. It is significant that, according to both models, changes in the amount of π bonding are accompanied by changes in the atomic charges. Therefore, changes in the *amount* of π bonding, if large enough, should be detectable as core binding energy shifts. The fact that the observed shifts between the trimers and tetramers are very small suggests that the P–N bond orders are practically the same in the trimers and tetramers. This conclusion is probably correct if the P–N π bonding is of the type illustrated by structures IIIa,b, in which the substituent (X) atom charges are affected by changes in the P–N π-bond order and in which all atoms rigorously obey the octet rule. However, if the P–N π bonding is of the type illustrated by structures IIa,b, in which π bonding is accompanied by a shift of negative formal charge only from nitrogen to phosphorus, it is conceivable that rehybridization of the nitrogen orbitals would cause a small increase in the P→N σ-bond polarity, compensated by an increase in the N→P π-bond polarity and accompanied by an increase in the P–N π-bond order. Indeed, structural data show that on going from the trimers to the tetramers, the P–N–P bond angles increase and the P–N bond distances decrease slightly, corresponding to an increase in the s character of the nitrogen σ-bonding orbitals.[4] We prefer to interpret these structural changes as evidence for a slight increase in the *strength*, not the bond order, of the P–N bonds. Such interpretation is quite consistent with the π bonding represented by structures IIIa,b—i.e., the hyperconjugative model. The N–P–N and X–P–X bond angles are essentially the same in all the phosphazenes under consideration (~120 and ~100°, respectively), indicating that the hybridization of the phosphorus orbitals is relatively constant. The N–P–N bond angles cannot be increased further without decreasing the X–P–X bond angles, which are already so small that X–X repulsions are very great.

Experimental Section

The gas-phase x-ray photoelectron spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer.[11] Vapors of the compounds $(NPF_2)_3$ and $(NPF_2)_4$ were introduced into the irradiation chamber at room temperature. Solid samples of $(NPCl_2)_3$, $(NPCl_2)_4$, and $[NP(CH_3)_2]_4$ were placed in a gold-plated gas cell[12] which was heated just enough to provide sufficient vapor pressure (ca. 2×10^{-2} Torr) to obtain good spectra. Magnesium Kα x rays (1253.6 eV) were used for all spectra. Binding energies were determined by a least-squares fitting of the data to Lorentzian line shapes. The uncertaintities listed parenthetically in Table I are twice the standard deviations in the peak position as determined by the least-squares fit. All core binding energies of the cyclophosphazenes were referenced against the Ne 1s line (E_B = 870.31 eV).[13] The reported binding energies are absolute free-molecule ionization potentials.

Core electron binding energies for atoms not listed in Table I include those for O 1s [POF_3, 539.0 (1) eV; $POCl_3$, 537.95 (4) eV] and C 1s [$N_4P_4(CH_3)_8$, 289.8 (1) eV].

The $(NPF_2)_3$ was prepared by a literature procedure[14] from $(NPCl_2)_3$ and sodium fluoride in acetonitrile solvent. The product (bp 50 °C (760 Torr)) was purified by column fractional distillation. The $(NPCl_2)_3$ was prepared according to the literature;[15] the sample melted at 112.1–112.8 °C (uncor) (lit.[15] mp 113.5–114.5 °C).

Octafluorocyclotetraphosphazene, $(NPF_2)_4$, was prepared by the interaction of $(NPCl_2)_4$ with sodium fluoride in nitrobenzene according to the method reported by Moeller and Tsang.[16] Specifically, the reaction took place between $(NPCl_2)_4$ (93 g, ~0.2 mol) and sodium fluoride (76 g, ~1.8 mol) in nitrobenzene (250 mL) to which had been added ~0.1 g of water. An exothermic reaction took place when the mixture was heated to 40 °C. After a 30-min reaction at temperatures in the range of 40–50 °C, the mixture was heated to 112 °C with refluxing for 17 h. A fraction with bp 83–89 °C was then distilled from the reaction mixture. This was $(NPF_2)_4$ (lit. bp 89.7 °C (760 Torr)); yield 33%.

Mixtures of the compounds $[NP(CH_3)_2]_3$ and $[NP(CH_3)_2]_4$ were synthesized from dimethyltrichlorophosphorane either by a direct reaction with ammonium chloride or by reaction with ammonia to yield $(CH_3)_2P(NH_2)_2Cl$, followed by sublimation of the pyrolysis products from this compound. The tetramer, mp 160–161 °C, was obtained by recrystallization from heptane. The detailed procedures were described in a recent paper.[17]

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Registry No. $(NPF_2)_3$, 15599-91-4; $(NPF_2)_4$, 14700-00-6; $(NPCl_2)_3$, 940-71-6; $(NPCl_2)_4$, 2950-45-0; $[NP(CH_3)_2]_4$, 4299-49-4; PF_3, 7783-55-3; PCl_3, 7719-12-2; POF_3, 13478-20-1; $POCl_3$, 10025-87-3.

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Raman and Infrared Spectra of Cyanodifluorophosphine

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The Raman spectra of gaseous, liquid, and solid cyanodifluorophosphine and the infrared spectra of the gas and solid have been recorded. The nine fundamental vibrations have been assigned on the basis of the depolarization values, infrared band contours, and group frequencies. A normal-coordinate calculation was carried out. Extensive mixing was found between the PF_2 wag and PF_2 scissors but the other fundamentals appeared to be relatively "pure" motions. In the solid state, there appear to be two molecules per primitive cell. A large number of "hot bands" were observed on both the C≡N and P—C stretching modes.

Introduction

From an investigation of the microwave spectrum of cyanodifluorophosphine, Schwendeman and co-workers[2] found the PCN moiety to be nonlinear with an angle of 171.2 ± 0.8°. These authors found and assigned transitions for the first and second excited vibrational state of about 125 cm^{-1}. They also observed rotational transitions arising from molecules in the first excited state of a second vibrational mode whose relative intensity indicated that the vibration was intermediate between those of the first and the second excited states of the lowest frequency fundamental.

Rudolph et al.[3] reported the infrared spectrum above 200 cm^{-1} but they did not observe the two lowest frequency fundamentals in the expected region (250–320 cm^{-1}). Additionally, these authors,[3] although stating that it was possible that the two fundamentals might occur below 200 cm^{-1}, tentatively assigned the two PCN bending modes at 549 and 460.5 cm^{-1} which is too high in frequency for these normal motions compared to their values in related molecules.[4] Also, the "hot bands" on the CN stretching mode indicated a very low frequency fundamental and the effect of the nonlinearity of the PCN moiety on the CN out-of-plane bending mode is questionable. Since no Raman data have been reported for this molecule, we have recorded the Raman spectra of gaseous, liquid, and solid F_2PCN. We have also obtained the far-infrared spectrum of the gas and solid and the results of our study are reported herein.

Experimental Section

All preparative work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Difluorocyanophosphine was prepared as reported previously[5] from PF_2I and AgCN (Columbia Organic Chemical Co.). Difluoriodophosphine was also prepared by a published procedure.[6] The purification of PF_2CN was achieved by means of a low-temperature vacuum fractionation column[7] and the purity was monitored by ^{31}P NMR (XL-100, 40.5 MHz) and mass spectroscopy (Perkin-Elmer RMU-6, 70 eV).[3]

Infrared spectra were obtained using a Digilab FTS-15 B Fourier transform interferometer.[8] A germanium beamsplitter on a KBr substrate and a glower source covered the 3800–400-cm^{-1} region while a 12.5 μ Mylar beamsplitter and a high-pressure Hg arc lamp source were used for the 400–80 cm^{-1} region. Spectra of the gaseous phase were obtained using a 10-cm glass cell with KBr and high-density polyethylene windows for the mid-infrared and the far-infrared, respectively. Sample pressures were approximately 5 Torr for the mid-infrared and 100 Torr for the far-infrared spectra.

Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The FTS uses a He–Ne laser as a frequency reference of high stability. Calibration is achieved by adjusting a software parameter, the laser wavelength, to reproduce an observed vibrational transition of a suitable standard at its correct frequency. As a result, the accuracy of a measured frequency can be expected to be better than the available resolution throughout the spectrum. The spectra were run at an effective resolution of better than 0.5 cm^{-1} using a modified "boxcar" apodization function.

The Raman spectra were obtained with a Cary Model 82 Raman spectrophotometer equipped with a Spectra Physics Model 171 argon ion laser with excitation wavelength of 5145 Å. The laser could provide approximately 2 W of power at the sample. Spectra of the gas phase were recorded using the Cary multipass accessory at sample pressures of $\simeq$200 Torr. Spectra of the liquid at −15 °C and the solid at −160 °C were obtained using a method similar to that described by Miller and Harney[9] with the sample sealed in a glass capillary. Polarization measurements were made using the standard Cary accessories. Frequencies measured for sharp, resolvable bands are expected to be accurate to at least ±2 cm^{-1}.

Vibrational Spectrum and Assignment

Using the molecular structure and dipole moment components determined in a microwave study of cyanodifluorophosphine by Lee et al.,[2] the molecule is seen to exhibit C_s symmetry and should have nine infrared and Raman active fundamentals, distributed as six a′ and three a″. Infrared spectra of the sample in the gaseous phase should exhibit A/C