ized lines at 167 ($q = \pi/a$), 110 ($q = \pi/3a$), 54 ($q = 4\pi/L$), and 25 cm^{-1} ($q = 2\pi/L$). From the similarity of the spectra, it seems probable that the chromophores in the [KBr + I_2]-amylose complex consist of a linear chain of iodine atoms randomly interspersed by a small number of bromine atoms. The Raman spectrum of [KBr + IBr]-amylose also contains four polarized lines at 181, 152, 54, and 27 cm^{-1}, with probable assignments as in the KI + I_2 sample. In that case the larger frequency shifts for the $q = \pi/a$ and $q = \pi/3a$ in the KBr + IBr adduct compared with the KBr + I_2 complex reflect an increased bromine distribution in the former. However, it is possible that the 181 cm^{-1} in [KBr + IBr]-amylose is a local Br mode and that the $q = \pi/3a$ mode is not visible.

In conclusion, resonance-enhanced Raman spectra of the trihalide ions I_3^-, I_2Br^-, and IBr_2^- are presented. Although a complete excitation profile (Raman line intensity *vs.* exciting frequency) was not obtained, the relative intensity of ν_3 was found to decrease with respect to that of ν_1 as the excitation was tuned from the red (6328 Å) toward the blue (5308 Å). The length of the iodine chain in both amylose and PVA was calculated to be approximately 28 atoms. In the amylose complex, however, it appears that the iodine chain has clamped end points, whereas in the PVA complex the terminal iodine atoms are unclamped. In the natural organic polymers (amylose, agarose, and amylopectin) and the synthetic amylose polymers (DP = 100 and 800) studies, the inclusion matrix of the iodine chain had no observable effect on the Raman spectra. It was, therefore, concluded that there is a preferred iodine chain length of approximately 28 atoms in all these iodine-complexing polymers. The Raman spectra of the iodine-amylose complex in ethanol and of the iodine-polymer complexes in water (independent of KI concentration) displayed a line at approximately one-third of the π/a zone. The $q = \pi/3a$ line is interpreted as an indication of the presence of I_3 units in these complexes. The incorporation of iodine into gel-forming solutions of PVA and agarose and into oriented PVA films had no effect on the iodine chain length.

Acknowledgment. We are indebted to Professor W. Prins for the gel-forming PVA and agarose samples and for stimulating discussions.

X-Ray Photoelectron Spectroscopic Study of Some Bis(triphenylphosphine)iminium Salts

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Abstract: X-Ray photoelectron spectroscopy (ESCA) has been used to measure the phosphorus 2p and nitrogen 1s electron binding energies in the bis(triphenylphosphine)iminium cation (abbreviated, PPN). The magnitudes of the binding energies, *ca.* 133 eV for the P(2p) electrons and *ca.* 397 eV for the N(1s) electrons, imply that the phosphorus atoms in the PPN cation bear some degree of positive charge while the nitrogen atom has some negative character. Variation of the anion in the lattice is found to have little or no effect on the binding energies in the PPN cation.

The bis(triphenylphosphine)iminium cation, $\{[(C_6H_5)_3P]_2N\}^+$ (hereafter abbreviated PPN), was first synthesized by Appel and Hauss[1] as a bromide salt. More recently, Ruff and Schlientz[2] prepared the chloride salt by a much simpler method in close to quantitative yield. They were then able to convert the chloride salt in a straightforward manner to salts containing other simple inorganic anions such as bromide, iodide, cyanate, thiocyanate, azide, and nitrate. Ruff[3-6] has shown that the PPN cation imparts a remarkable degree of stability to mono- and polynuclear metal carbonyl anions. Handy, *et al.*,[7] have reported the structure of the PPN cation as determined by X-ray crystallographic analysis for $\{[(C_6H_5)_3P]_2N\}^+$ $\{Cr_2(CO)_{10}\cdot CH_2Cl_2\}^-$ and related polynuclear metal carbonyl salts.

Aside from carbon and sulfur, the most extensive X-ray photoelectron spectroscopic (ESCA) studies have been reported on nitrogen[8-10] and phosphorus[11,12] compounds. Since the PPN salts were suggested to contain a quaternary nitrogen atom and two P-N double bonds, ESCA studies, of the P(2p) and N(1s) electron binding energies, were undertaken with the aim of elucidating bonding characteristics in the simple salts PPN(X) (where X = F^-, Cl^-, Br^-, I^-, SCN^-, N_3^-, NO_3^-, OCN^-, and $V(CO)_6^-$).

The magnitudes of the binding energies, *ca.* 133 eV for the P(2p) electrons and *ca.* 397 eV for the N(1s) electrons, imply that the phosphorus atoms in the PPN

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cations carry a degree of positive charge, while the nitrogen atom is largely negative in character. Variation of the anion is found to have little or no effect on the P(2p) and N(1s) binding energies in the PPN cation.

Experimental Section

Apparatus. The photoelectron spectra were obtained using an AEI ES-100 electrostatic electron spectrometer. The X-ray powder data were obtained using a standard Norelco X-ray diffraction apparatus equipped with a copper X-ray tube and a Bruerger X-ray powder camera.

Reagents. All of the bis(triphenylphosphine)iminium salts were prepared and purified by the method of Ruff and Schlientz.[2]

Procedure. In all cases, the aluminum $K\alpha_{1,2}$ X-ray line ($h\nu$ = 1486.6 eV) was used for photoelectron excitation. All samples were run at room temperature as powders dusted onto double-backed cellophane tape. To compensate for any sample charging effects, calibration of the spectra was accomplished using the C(1s) electron line from the phenyl carbons present in the PPN cation. Aliphatic and aromatic carbons give rise to a C(1s) line at 285.0 eV.[8] The X-ray powder data were determined on samples mounted in 0.3-mm capillary tubes. Each sample was exposed for approximately 24 hr.

Results and Discussion

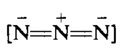
Table I. P(2p) and N(1s) Binding Energies (E_b) for the (PPN)X Salts

Anion	P(2p) E_b, eV[a]	N(1s) E_b, eV[a]
F^-	132.8 ± 0.3	397.6 ± 0.2
Cl^-	133.0 ± 0.2	397.6 ± 0.3
Br^-	133.2 ± 0.2	397.4 ± 0.3
I^-	132.9 ± 0.3	397.5 ± 0.2
OCN^-	133.0 ± 0.2	397.2 ± 0.1
		400.5 ± 0.2[b]
SCN^-	133.3 ± 0.3	397.3 ± 0.3
		400.2 ± 0.3[c]
NO_3^-	132.5 ± 0.2	397.2 ± 0.2
		404.8 ± 0.2[d]
N_3^-	133.2	397.2
		405.3[e,f]
$V(CO)_6^-$	133.3 ± 0.2	397.5 ± 0.2

[a] Error limits indicated are standard deviations. [b] $OC\mathit{N}^-$ nitrogen. [c] $SC\mathit{N}$ nitrogen. [d] $\mathit{N}O_3^-$ nitrogen. [e] $(N{=}\mathit{N}{=}N)^-$ nitrogen. [f] Lines variable due to sample decomposition.

The measured phosphorus 2p and nitrogen 1s electron binding energies for the bis(triphenylphosphine)iminium salts obtained in this work are listed in Table I. At least three replicate samples were used to determine each binding energy. In all cases, only one P(2p) electron line appeared in the spectra of the PPN salts with a full-width half-height (FWHH) of approximately 2.3 eV. The N(1s) electron lines were on the order of 1.8 eV wide. The P(2p) lines are naturally wider than the N(1s) lines since the P(2p) line represents a weighted average of the unresolved $2p^1/_2 - 2p^3/_2$ doublet.

The data indicate that the N(1s) electron binding energies in the PPN cation are all *ca.* 397 eV. In reviewing the extensive X-ray photoelectron spectroscopic data reported for nitrogen compounds,[8, 10] it was noted that the N(1s) binding energies of *ca.* 397 eV in the PPN salts were lower than any other N(1s) electrons reported to date. Siegbahn, *et al.*,[8] have reported the nitrogen 1s binding energies for sodium azide. The azide ion is commonly represented as 1, according to resonance theory. For the nitrogen atoms bearing large fractional negative charges, Siegbahn reports a N(1s) binding energy of 399.2 eV, while the nitrogen atom with positive character has a 1s binding energy of 403.7 eV. We determine the N(1s) binding energies in NaN_3 to be 403.6 and 399.3 eV, relative to the C(1s) electron line from hydrocarbon contamination, for the positively and negatively charged nitrogen atoms, respectively. Since the N(1s) binding energy of *ca.* 397 eV in the PPN cation is *ca.* 2 eV smaller than that for the negatively charged nitrogen in the azide ion, the PPN nitrogen atom must necessarily have a higher electron density. Thus, the PPN nitrogen must have a higher degree of negative character than do the nitrogens in the azide ion which are normally considered to bear a large negative charge.



$[\overset{-}{N}{=}\overset{+}{N}{=}\overset{-}{N}]$

1

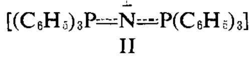
Table II. P(2p) Binding Energies (E_b) for Quaternary Phosphonium Salts

Compound	P(2p) E_b, eV[a]
$CH_3P(C_6H_5)_3Br$	133.2 ± 0.2
$(CH_3OCH_2)P(C_6H_5)_3Cl$	132.7 ± 0.2
$(ClCH_2)P(C_6H_5)_3Cl$	133.6 ± 0.3
$(C_6H_5)_4PBr$	133.7 ± 0.3
$(C_6H_5)_3P$	131.2 ± 0.2

[a] Error limits indicated are standard deviations.

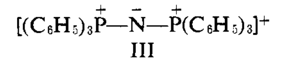
The magnitude of the P(2p) binding energies in the PPN cation of *ca.* 133 eV are also very interesting. When the P(2p) binding energies in the PPN salts are compared to the P(2p) binding energies for several quaternary phosphonium salts (Table II), they are found to be essentially equivalent.[13] Since the phosphorus atom in quaternary phosphonium salts is known to be positively charged, the essential equivalence of P(2p) binding energies implies that the phosphorus atoms in the PPN cation also carry a high degree of positive charge. Since only one P(2p) electron line appears in all the PPN spectra, both phosphorus atoms are equivalent; thus, both bear a large degree of positive character. Appel and Hauss[1] have also found the phosphorus atoms to be equivalent by finding only one resonance line in the ^{31}P nmr spectrum of the bromide salt.

Appel and Hauss[1] suggested several possible structures for the PPN salts. Once they eliminated all "unsymmetrical" structures in which the phosphorus atoms were unequivalent, *via* nmr spectroscopy, they settled on structures II and III as the most likely possibilities. The authors[1] suggested that due to the large electronegativity of nitrogen, ionic structures such as III must be considered. However, they felt the chemical properties of the bromide salt were more readily explained if the molecule contains a quaternary nitrogen as in II. The ESCA data suggest that the ionic



$[(C_6H_5)_3P{=}\overset{+}{N}{=}P(C_6H_5)_3]$

II



$[(C_6H_5)_3\overset{+}{P}{-}\overset{-}{N}{-}\overset{+}{P}(C_6H_5)_3]^+$

III

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(13) In an earlier study (ref 12) of quaternary phosphonium salts a constant difference is found with the present data. This difference could arise from several factors and this discrepancy is currently under investigation.

structure III is a better approximation, since the nitrogen atom bears a large fractional negative charge while the phosphorus appears related to a phosphorus in a phosphonium salt.

The N(1s) spectrum of the azide, PPN(N_3), showed unusual behavior. On the basis of the spectra of NaN_3 and the other PPN salts, one would predict the spectrum of PPN(N_3) to contain three N(1s) lines with a relative intensity ratio 1:2:1. Variable results were observed for PPN(N_3), with the most consistent result being a spectrum containing two N(1s) lines separated by 8.1 eV with an intensity ratio of 1:3. It is not possible to rationalize this spectrum on the basis of the known structure of PPN salts. This, couple dwith the variability observed in the spectrum, led us to conclude the PPN(N_3) was decomposing in the X-ray beam.

Several workers have reported linear correlations between core-electron binding energies and the electronegativity of the ligands bound to the atoms. Siegbahn[8] has reported such a correlation for a large number of carbon compounds. Thomas[14] has correlated the carbon 1s binding energies in the halomethanes with the electronegativity of the halogen. Baker, *et al.*,[15] have found the hydrogen ionization potentials in the halogen acids to vary linearly with the electronegativity of the halide present. Barber, *et al.*,[16] have reported a linear relationship between the Mössbauer isomer shift and the tin 4d binding energies for a series of tin complexes. Since the isomer shift for the complexes is known to vary linearly with ligand electronegativity,[17] this represents a further correlation between core-electron binding energies and ligand electronegativities.

Considering the PPN–halide bond in terms of simple electronegativity concepts, one would expect the binding energies for the PPN halides to be in the order PPNF > PPNCl > PPNBr > PPNI. The more electronegative fluorine would be expected to withdraw electrons from the cation most efficiently, thus reducing the electron density around both the P and N atoms, yielding higher core binding energies. Since all of the P(2p) and N(1s) binding energies for the PPN salts are equivalent, within experimental error, it is obvious that electronegativity is not the only factor influencing core binding energies.

Fadley, *et al.*,[18] have shown that variations in the Madelung correction applied to binding energy calculations can be important. This represents a lattice energy variation with interionic distances or with changes in crystal structure, arising from the point-charge coulombic interactions of the ions in the lattice. Such corrections have accounted for variations in binding energy shifts as large as several electron volts for simple salts. An irregular order of N(1s) binding energies was reported in studies of simple quaternary nitrogen compounds.[9] Binding energies were ordered such that F > Cl $\sim$ I > Br, over a range of *ca.* 0.5 eV. This irregularity was attributed to variations in the lattice potential.

Handy, *et al.*,[7] found little difference between the PPN polynuclear metal carbonyl lattices they investigated. For five salts, they found that the PPN cation dominates the lattice and possesses a fairly uniform conformation of phenyl ligands, essentially invariant to the different packing and size effects of the anions. The two chemically equivalent P–N bond lengths in the P–N–P central fragment of the cation showed average values of 1.575 ± 0.005 Å. Analysis of X-ray powder patterns obtained on the halide salts used in this study indicated they were isomorphorous and suggested that lattice dimensions were increasing as one progressed from the fluoride to the iodide. This implies that the anion–cation distance must be increasing from the fluoride through the iodide. Therefore, in the case of the PPN salts, the change in lattice potential should arise not from an overall change in crystal lattice, but from changes in internuclear distances. Siegbahn, *et al.*,[8] have measured the 1s, 2s, 2p, 3s, and 3p electron binding energies for potassium in the halide salts KCl, KBr, and KI. All of the alkali halides, except those of cesium, are known to crystallize in a face-centered cubic structure; therefore, any variations in the potassium electron binding energies must result from changes in the interionic distance between potassium and the halide. Siegbahn measured differences as large as 2–3 eV for the potassium electrons in the halides. In *all* cases, the potassium binding energies followed the order Br > Cl > I.

Therefore, one may conclude, qualitatively, that constancy of the core-electron binding energies in the PPN halides results from two opposing effects. Because the lattice dimensions change as the halogen atom is varied, a corresponding change in lattice potential must occur at the P–N–P site. However, the electronegativity of the halogen also will change, affecting the partial ionic character of the PPN–halide bond, and thus the net charge associated with the PPN cation. These two effects must be occurring in such a fashion as to offset each other, thus keeping the total potential at the site of the P–N–P bond constant.

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