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ORGANOSUBSTITUTED PHOSPHAZENES. XII. HE(I) PHOTOELECTRON SPECTR--ETC(U)

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Organosubstituted Phosphosphazenes. XII. He(I)
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p-N,N-Dimethylaminophenylfluorocyclotriphosphazenes

by

Christopher W. Allen and Jennifer C. Green

Prepared for Publication in
Inorganic Chemistry

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Organophosphazenes. XII. He(I) Photoelectron Spectra of
Selected Phenyl- and p-N,N-Dimethylaminophenylfluorocyclotriphosphazenes.¹

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ABSTRACT

He(I) photoelectron Spectra are presented for $P_3N_3F_{6-n}(C_6H_5)_n$ ($n=1,2,4$) and $P_3N_3F_5C_6H_4N(CH_3)_2$. Ionization energies are discussed in terms of perturbations of molecular orbitals of the parent aryl and phosphazene functions. The data confirm the strong electron withdrawing effect of the $P_3N_3F_5$ moiety and show a dramatic decrease in this effect as fluorine atoms are replaced by phenyl groups. One also observes a significant destabilization of the phosphazene out of plane π molecular orbital as the fluorine atoms are replaced by phenyl groups. The ionizations from the phenyl π_{a_2} and π_{b_1} orbitals are unresolved in phenyl phosphazenes thus demonstrating the lack of significant phosphazene - aryl group mesomeric interactions. The electronic effect of the electron donating dimethylamino substituent on the phenyl unit is transmitted to the phosphazene through the sigma bond system.

Introduction

The nature of the electronic interaction between aromatic hydrocarbon groups and directly bonded second row atoms, such as silicon and phosphorus, continues to attract considerable attention. Various spectroscopic probes have been applied to these systems in order to evaluate the relative importance of conjugative, hyperconjugative and inductive effects.³⁻⁵ Aryl substituted cyclophosphazenes have been examined by UV⁶, ESR⁷, NQR⁸ and NMR (¹H⁹, ¹³C¹⁰, ¹⁹F¹¹ and ³¹P¹²) spectroscopy and these results have been variously interpreted as showing no, a small amount, or extensive mesomeric interactions depending on the technique which was utilized. Our recent ¹³C NMR work¹⁰, along with ¹⁹F NMR studies of Chivers and Paddock¹¹, establish that the P₃N₃F₅ group exerts a strong electron withdrawing effect on a phenyl ring. The mechanism for this perturbation is still unclear. The difficulties associated with separation of field and mesomeric contributions to NMR Chemical shifts¹³ suggested to us that an alternative, more definitive, technique should be used if an unambiguous resolution to this problem is to be attained. Since photoelectron (PE) spectroscopy¹⁴ has been successfully applied to problems of this type with other main group compounds^{5,15}, we have chosen to investigate the He(I) photoelectron spectra of a series of phenyl-fluorocyclotriphosphazenes, P₃N₃F_{6-n}(C₆H₅)_n (n=1,2,4) and of p-N,N-dimethylamino-phenylpentafluorocyclotriphosphazene, P₃N₃F₅C₆H₄N(CH₃)₂.

Experimental Section

Materials. The phenyl-substituted fluorocyclotriphosphazenes were prepared and purified by previously reported procedures.^{12,16} The p-N,N-dimethylaminophenyl derivative was prepared by the reaction of p-N,N-dimethylaminophenyl magnesium bromide with hexafluorocyclotriphosphazene (P₃N₃F₆).¹⁷

Measurements. The He(I) PE spectra were recorded on a Perkin-Elmer PS 16/18 instrument modified to take a heated insert. The spectra were calibrated using

xenon and argon. The data are reported in table I.

Results and Discussion

In the subsequent discussion we shall assume the validity of Koopman's theorem.¹⁸ This assumption appears warranted in that one is dealing with electrons in delocalized molecular orbitals. It has been shown¹⁹ however for substituted benzene derivatives that Koopman's theorem only holds to a first approximation. Molecular orbital energy changes in the range of 0.333eV(3.65%) over those expected on the basis of Koopman's theorem are observed. Independent of the strict validity of Koopman's theorem, most of the arguments we shall make are valid if we assume that deviations from this assumption are constant throughout this series of closely related compounds.

The PE spectrum of $P_3N_3F_5C_6H_5$ is shown in figure 1. One can approach the assignment of the spectrum by the composite molecule approach¹⁴ starting from the known spectra of benzene¹⁴ and hexafluorocyclotriphosphazene,²⁰ $P_3N_3F_6$. The first ionization potential (IP) of benzene occurs in the region of 9.25eV²¹ and is raised by the presence of electron withdrawing substituents e.g. the first aryl π ionization in nitrobenzene occurs at 10.03eV^{14,22}. Since NMR measurements have suggested that the electron withdrawing effect of the $P_3N_3F_5$ moiety approximates that of a nitro group,^{9,10} the first band in the PE spectrum of $P_3N_3F_5C_6H_5$ (10.07eV) is logically assigned to ionization from molecular orbitals derived primarily from the highest energy π molecular orbitals (a_2, b_1) of the aryl unit. The first IP of $P_3N_3F_6$ occurs at 11.4eV and drops steadily as fluorine atoms are replaced by less electronegative substituents.²⁰ We therefore assign the band at 11.25eV to an analogous ionization process. On the basis of X α calculations²³ this band (in $P_3N_3F_6$) has been assigned to ionization from an orbital of the out of plane π system which is only weakly bonding. Reversal of

the assignment of the first two peaks would place the aryl ionization well above those recorded for other monosubstituted benzene derivatives¹⁴ and the aryl ionization would not be in the range expected on the basis of the σ^+ constant (calculated from ¹³C NMR shifts) of the P₃N₃F₅ moiety.¹⁰

The next set of peaks (12.20 and 12.98 eV) would be expected to contain contributions from both arene and phosphazene based molecular orbitals. The in plane π ionization which occurs at 13.1eV in P₃N₃F₆¹⁸ and the π_{a2u} benzene ionization are reasonably assigned to this region.¹⁴ The σ_{eg} ionization of the aryl unit occurs at 11.70eV¹⁴ in benzene and would be expected to be raised into the region in question by the strong electron withdrawing effect of the phosphazene unit.

The remaining peaks in the spectrum begin at 14.72eV and fall in the region of σ bond ionizations in both the arene¹⁴ and phosphazene systems²⁰ and will not be discussed.

The partial assignment of the PE spectrum of P₃N₃F₅C₆H₅ allows one to answer some basic questions about electronic interactions in this molecule. The observation of a large increase in the ionization energy (relative to benzene) of the highest filled arene based molecular orbitals is consistent with previous nmr studies⁹⁻¹¹ which have established the P₃N₃F₅ moiety as a strong electron withdrawing group. The data from the PE spectrum demonstrates that the magnitude of this effect is competitive with traditional strong electron withdrawing units such as the nitro or cyano groups.¹⁴ Having established the electron withdrawing nature of the P₃N₃F₅ function, the next question is: by what mechanism is this process accomplished? On going from benzene to monosubstituted benzene derivatives, the resulting lowering of symmetry removes the degeneracy of the two highest filled arene molecular orbitals. The disposition of the two molecular orbitals is such that one (b_1) is in a position to undergo mesomeric interaction with the substituent while the

other (a_2) is not. The magnitude of the splitting of the b_1 and a_2 ionizations is thus a direct measure of the amount of mesomeric interaction of a substituent with the benzene ring.²⁴ The observation of a relatively narrow, unsplit band for the arene b_1, a_2 set establishes that any removal of degeneracy of b_1 and a_2 orbitals must be small enough to be within the band envelope and hence the electron withdrawing process is essentially through the σ system.

Although hyperconjugative models^{4,5,15} have been widely and successfully applied to the interpretation of the electronic structure of organosilicon compounds, such effects do not appear to be significant for the aryl phosphazenes. A σ/π mixing of phosphorus-nitrogen bonds and the phenyl π system will not be significant since the appropriate σ bond energy is well removed (below 15eV) from the phenyl π system. This effect, if present, would destabilize the phenyl $\pi a_2, b_1$ molecular orbitals. In view of the large observed stabilization, any σ/π mixing is small compared to the σ electron withdrawing effect. A hyperconjugative mixing of the phenyl and phosphazene π molecular orbitals would lead to a destabilization of the phenyl and stabilization of the phosphazene molecular orbitals. Since the opposite effect is observed, one can conclude that this effect is not operative to any significant degree.

The modest destabilization (from $P_3N_3F_6$) of the out of plane π phosphazene molecular orbital is consistent with previous ionization potential measurements on cyclophosphazenes.²⁰ The origin of this effect lies in the fact that replacement of the highly electronegative fluorine atom by an electron releasing substituent lowers the ability of the phosphorus center to attract, and hence effect delocalization, of π electrons. In that one would expect a σ phosphorus-carbon bond to be higher in energy than a σ phosphorus-fluorine bond, one could expect an increase in the σ/π hyperconjugative contribution to the phosphazene π orbital. However, the appropriate σ level is again far removed from the π

level so the magnitude of this interaction would be small.

All three isomers (2,2 , 2,4-cis and 2,4-trans) in the diphenyltetrafluorocyclotriphosphazene series have similar PE spectra (figure 1) which can be analyzed in terms of the model proposed for the monosubstituted derivative. The lowest energy ionization (ca 9.6eV) is again most logically assigned to the aryl π_{a_1, b_2} ionization. The next ionization occurs in the region of 10.3 to 10.5eV (depending on the isomer in question). If this were to be an aryl π ionization, it would require an increase in the phosphazene electron withdrawing effect when a fluorine atom is replaced by the electron donating phenyl group. Consequently the 10.3-10.5eV band is assigned to the phosphazene out of plane π system. The intensity of the 9.6eV band relative to the 10.3-10.5eV increases on going from the mono to the disubstituted derivative. This observation is in keeping with the proposed assignments since it reflects the increase in the number of phenyl groups in the system.

As in the case of the monophenyl derivative, ionizations from the two highest filled aryl molecular orbitals are not resolved in the spectra of any of the three diphenyl isomers thus indicating the minimal importance of aryl-phosphorus mesomeric interactions in these compounds.

Bands in the region of 11.3-11.4eV and 13.7eV appear in the PE spectra of the non-geminal isomers. These bands do not appear in the spectrum of the geminal isomer and hence are diagnostic of the non-geminal species. It would of interest to see if those bands occur in the spectrum of the monosubstituted material but the region in question is dominated by the out of plane π phosphazene and other ionizations. The origin of these new bands is unclear but the fact that they appear in the spectra of the species of lower symmetry suggests that they may arise from the removal of degeneracy of some of the many degenerate phosphazene

molecular orbitals.²³

The bands in the 12-13eV region exhibit severe overlapping however the broad band width and asymmetry of the peaks suggest at least two ionizations (as in the monosubstituted derivative) are contained in the band envelope.

The PE spectrum of the geminally substituted tetraphenyl derivative, 2,2,4,4 - $P_3N_3F_2(C_6H_5)_4$, exhibits most of the general features observed in the other derivatives. As expected, the aryl π ionization band (9.31eV) has increased in intensity and moved to lower energy while the phosphazene π ionization band (10.15eV) exhibits a relative decrease in intensity and also has moved to lower energy. The most interesting spectral feature is the shoulder (8.5eV) on the aryl π ionization band. Similar PE spectra have been observed for phenyl substituted methanes and the additional ionization has been ascribed to π/π interactions between adjacent phenyl rings.²⁵ A similar process could be envisioned as occurring in the tetraphenyl phosphazene under consideration. The electron withdrawing effect of the phosphazene unit is significantly reduced in the tetraphenyl derivative and the aryl π ionization energy is near that of benzene itself. As a consequence of this decreased π stabilization, intramolecular π/π interactions can occur in a more facile fashion than in the other, more electron withdrawing, phenylphosphazenes.

In order to probe the effects of variations in the aryl group on the electronic structure of the phosphorus-aryl bond, the PE spectrum of p-N,N-dimethylaminophenylpentafluorocyclotriphosphazene, $P_3N_3F_5C_6H_4N(CH_3)_2$, was examined. It was of particular interest to see what perturbations of the aryl group would result from the presence of both strong electron withdrawing ($P_3N_3F_5$) and electron donating ($N(CH_3)_2$) groups on aryl ring. The assignment of the spectrum was accomplished via the composite molecule approach using the known spectra of N,N-dimethylaniline²² and hexafluorocyclotriphosphazene²⁰ (figure 2). The lowest energy (7.88eV) ionization is well removed from the aryl π and phosphazene regions

and is assigned to the dimethylamino nitrogen lone pair ionization.²² The next band (9.53 eV) is assigned to the aryl π_{a_2} molecular orbital. The aryl π_{b_1} band is assigned to the 10.21eV ionization while the 10.73eV band is assigned to the phosphazene out of plane π ionization. A reversal of assignment of the latter two bands is unreasonable on intensity grounds. The pattern of relative intensities using the proposed assignment fits that observed for $P_3N_3F_5C_6H_5$. Furthermore, reversal of the π_{b_1} and phosphazene π band assignments would lead to an unacceptable diversity in intensity between the π_{a_2} and π_{b_1} bands.

There are several interesting features in the PE spectrum of $P_3N_3F_5C_6H_4N(CH_3)_2$. The dimethylamino nitrogen lone pair ionization has been stabilized by 0.51eV on going from N,N-dimethylaniline to the phosphazene derivative. Thus, the strong electron withdrawing effect of the phosphazene unit is manifested several atoms distant from the phosphorus center. The splitting of the π_{a_2} and π_{b_1} aryl bands observed in N,N-dimethylaniline is due to the mesomeric interaction of the dimethylamino nitrogen lone pair with the aryl π system. In para-disubstituted benzene derivatives, the π_{a_2}, π_{b_1} separation is approximately the sum of the separations for the appropriate monosubstituted derivatives.²⁴ On going from N,N-dimethylaniline to $P_3N_3F_5C_6H_4N(CH_3)_2$, one actually observes a decrease in the a_2, b_1 splitting which is consistent with the results obtained for the phenylphosphazenes in indicating that no significant phosphazene/aryl conjugative interactions occur. The energy of the phosphazene in plane π ionization is reduced from that observed for the analogous phenyl derivative. This shift reflects the increased electron releasing character of the N,N-dimethylaminophenyl group compared to the phenyl group. This observation demonstrates that π electronic perturbations of the aryl group are transmitted to the phosphazene. Since phosphazene/aryl π conjugative interactions are not significant, this transmission of electronic information must be through the σ bond system.

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Table I

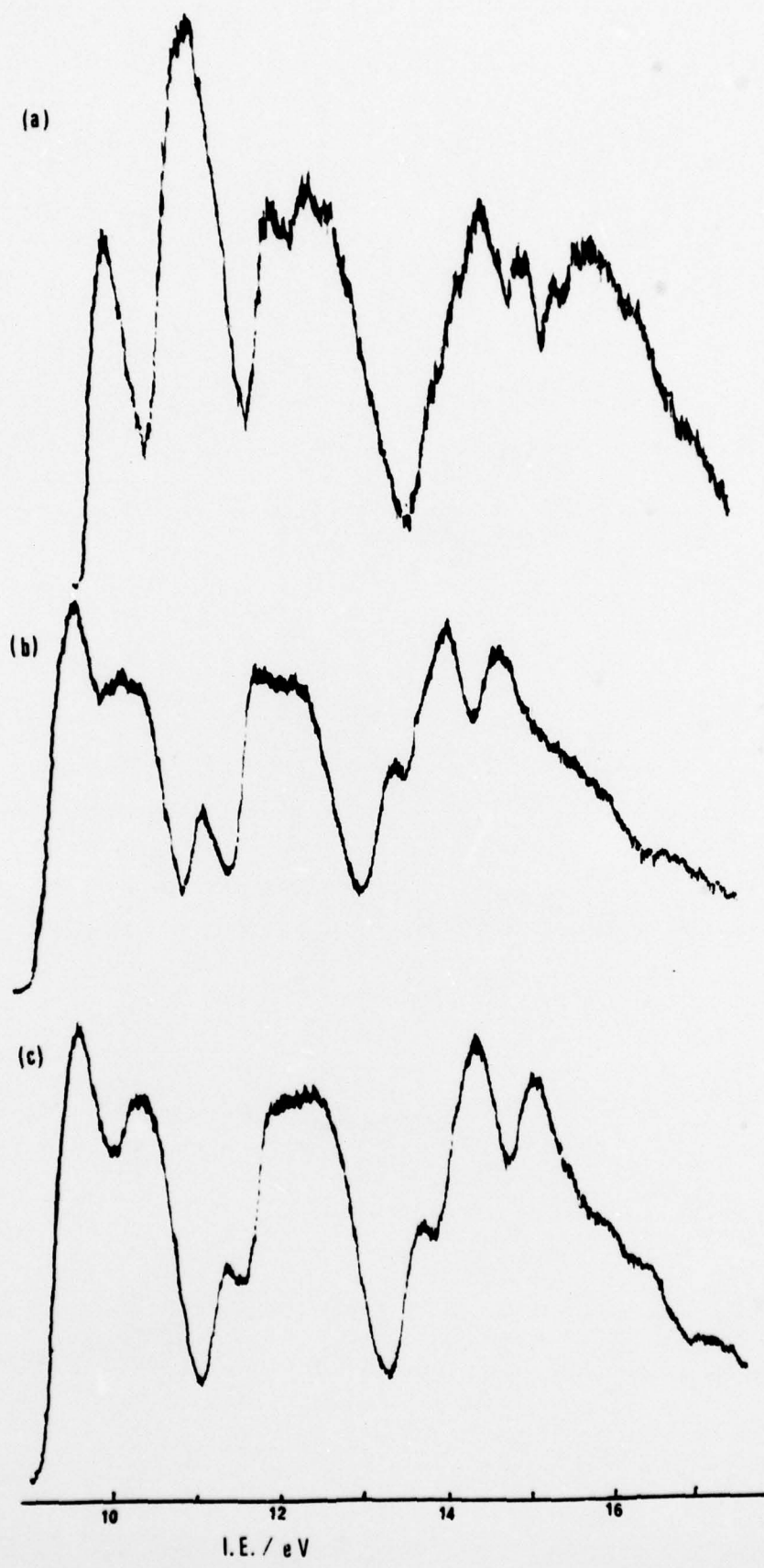
Ionization Energies (eV) for Aryl fluorocyclotriposphazenes

| $P_3N_3F_5C_6H_5$ | $2,2-P_3N_3F_4(C_6H_5)_2$ | $cis-2,4-P_3N_3F_4(C_6H_5)_2$ | $trans-2,4-P_3N_3F_4(C_6H_5)_2$ |
|-------------------|---------------------------|-------------------------------|---------------------------------|
| 10.07             | 9.64                      | 9.62                          | 9.62                            |
| 11.25             | 10.56                     | 10.36                         | 10.25                           |
| 12.20             | 12.08                     | 11.41                         | 11.28                           |
| 12.98             | 14.33                     | 12.46                         | 12.03                           |
| 14.72             | 15.19                     | 13.77                         | 12.49                           |
| 15.42             | 16.12                     | 14.45                         | 13.75                           |
| 16.35             | 17.17                     | 15.13                         | 14.43                           |
|                   |                           | 17.19                         | 15.09                           |
|                   |                           |                               | 17.29                           |

| $2,2,4,4-P_3N_3F_4(C_6H_5)_4$ | $P_3N_3F_5C_6H_4N(CH_3)_2$ |
|-------------------------------|----------------------------|
| 8.59 (sh)                     | 7.88                       |
| 9.31                          | 9.53                       |
| 10.15                         | 10.21                      |
| 11.83                         | 10.73                      |
| 14.04                         | 11.95                      |
| 14.63                         | 12.82                      |
|                               | 13.43                      |
|                               | 14.29                      |
|                               | 14.59                      |
|                               | 15.84                      |

Figure 1. PE spectra of (a)  $P_3N_3F_5C_6H_5$ , (b) *trans*-2,4- $P_3N_3F_4(C_6H_5)_2$ , (c) *cis*-2,4- $P_3N_3F_4(C_6H_5)_2$ , (d) 2,2- $P_3N_3F_4(C_6H_5)_2$ , (e) 2,2,4,4- $P_3N_3F_2(C_6H_5)_2$ , and (f)  $P_3N_3F_5C_6H_4N(CH_3)_2$ .



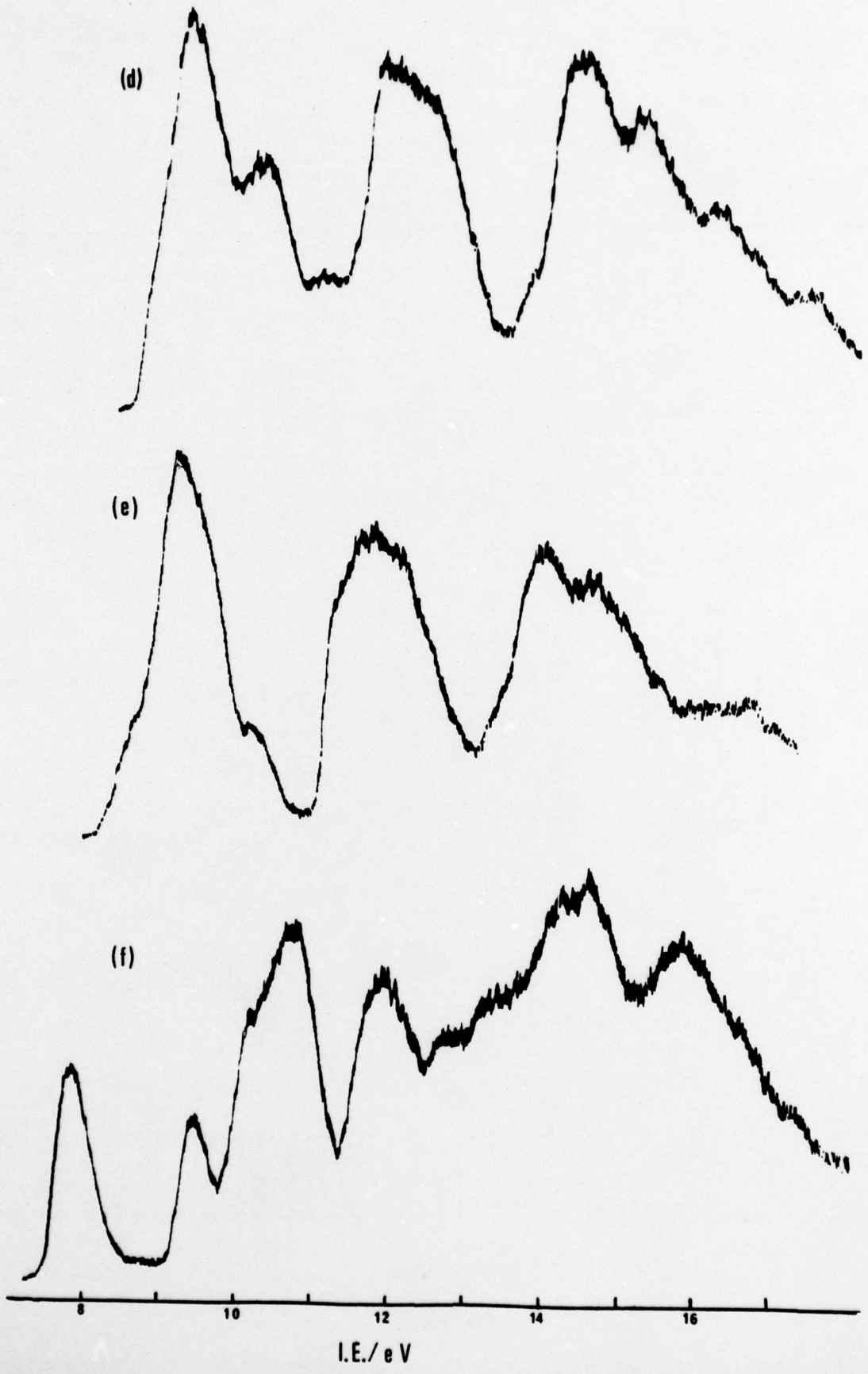
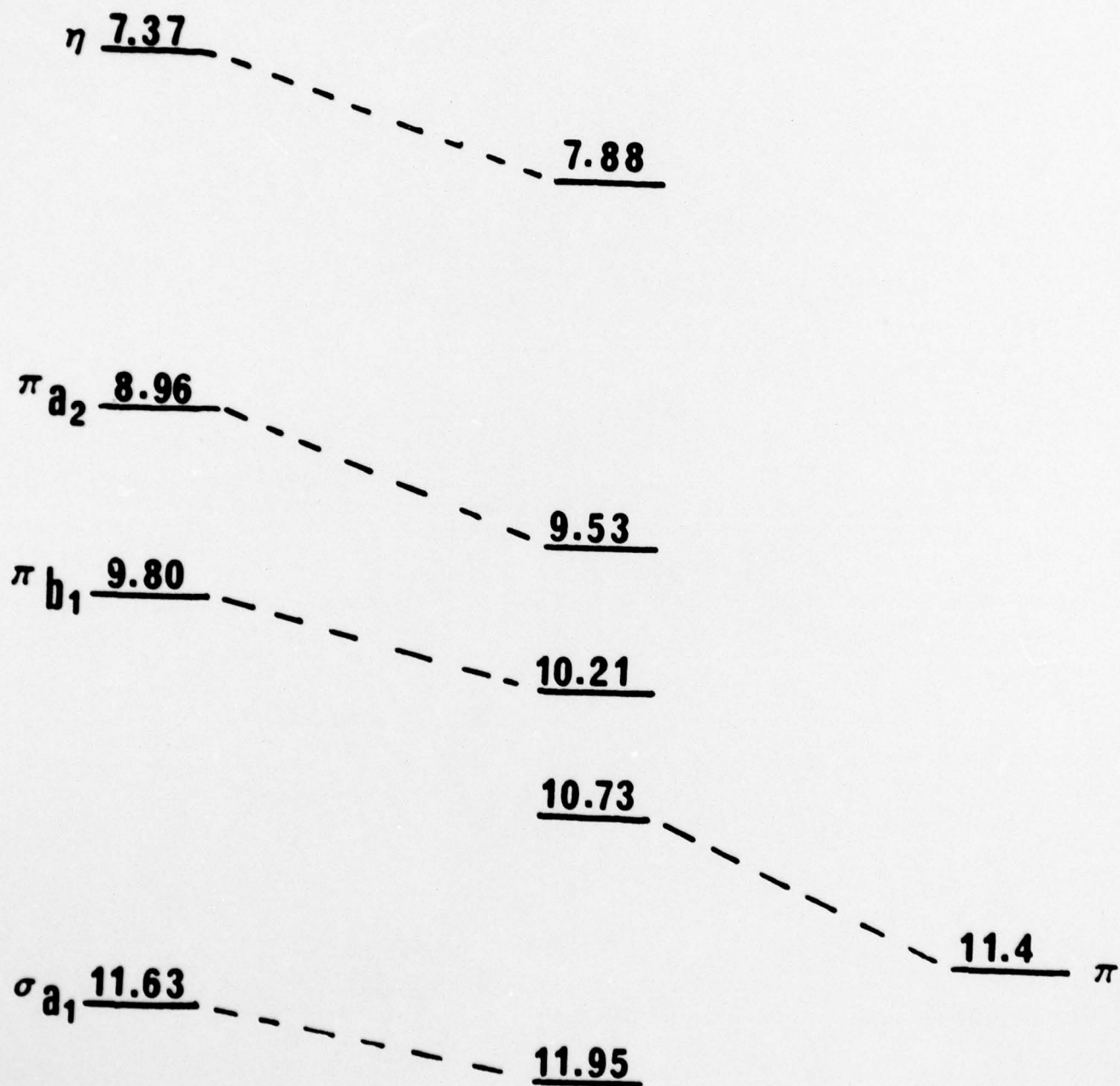
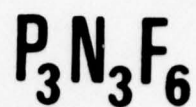
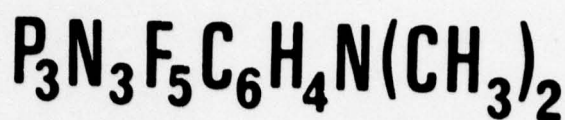
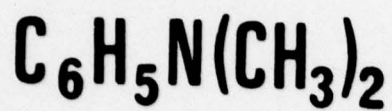


Figure 2. Assignment of the ionization processes in  $P_3N_3F_5C_6H_4N(CH_3)_2$   
(vertical axis in electron volts).



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