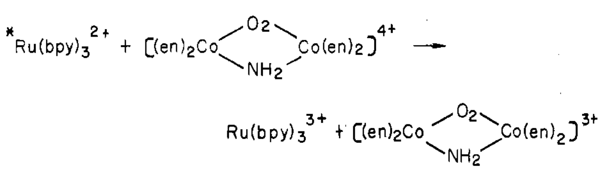
products is not possible from this pathway, and to account for the decomposition reaction some other mechanism has to be proposed. The emitting state of $\mathrm{Ru(bpy)_3}^{2+}$ can also be deactivated by transferring the excited-state energy to the quencher provided the excited state of the quencher lies below that of $\mathrm{Ru(bpy)_3}^{2+}$. Indeed such low-lying states are available in principle as the absorption spectra of cobalt(III) complexes show. Energy transfer to the superoxo dicobalt(III) complex could lead to the decomposition of the complex from the states which are active in direct photolysis. The presence of $\mathrm{Ru(bpy)_3}^{3+}$ in addition to cobaltous ion as a product of the sensitization rules out this process also.

The pathway in which net products of photosensitization are observed is different from the excited-state electron-transfer pathway discussed earlier and is elucidated from the results obtained for the μ-amido-μ-superoxo complexes. In the case of the ethylenediamine dibridged complex and $\mathrm{Ru(bpy)_3}^{2+}$, the excited-state electron-transfer process produces the peroxo dibridged complex and $\mathrm{Ru(bpy)_3}^{3+}$ (see eq 5). Thermal back-reaction between the photoproducts is fast, and there is little accumulation of the peroxo complex or $\mathrm{Ru(bpy)_3}^{3+}$ in the medium. Since the μ-amido-μ-peroxo ethylenediamine complex itself does not decompose in the acidic medium to give the cobaltous ion, the predominant excited-state electron-transfer pathway is not the one which causes formation of the cobaltous ion. Again excited-state electron transfer directly to the metal center is also ruled out considering the fact that one-electron transfer by various reducing agents in thermal reaction involves the dioxygen bridge only and does not involve the metal center.[35] Thus the net products of the photosensitive reaction are to be attributed to an independent pathway, and the following mechanism in Figure 4 is proposed to account for the products.



$$^{*}\mathrm{Ru(bpy)_3}^{2+} + [(\mathrm{en})_2\mathrm{Co}\overset{\mathrm{O_2}}{\underset{\mathrm{NH_2}}{\diamond}}\mathrm{Co(en)_2}]^{4+} \longrightarrow \mathrm{Ru(bpy)_3}^{3+} + [(\mathrm{en})_2\mathrm{Co}\overset{\mathrm{O_2}}{\underset{\mathrm{NH_2}}{\diamond}}\mathrm{Co(en)_2}]^{3+} \quad (5)$$

$\mathrm{Ru(bpy)_3}^{3+}$ externally added to the steady photolysis system does not change the photosensitization quantum yields for $\mathrm{Ru(bpy)_3}^{3+}$ production as well as dicobalt(III) complex decomposition as shown in Table IV. These results indicate that $\mathrm{Ru(bpy)_3}^{3+}$ production is also not coupled with the primary electron-transfer reaction observed in flash photolysis. It is proposed that formation of $\mathrm{Ru(bpy)_3}^{3+}$ is due to the oxidation of $\mathrm{Ru(bpy)_3}^{2+}$ ion by the excited state of the dicobalt(III) cation. In this process the cobalt complex decomposes to give the cobaltous ion as one of the products. $\mathrm{Ru(bpy)_3}^{3+}$, which remains in solution, slowly decays to $\mathrm{Ru(bpy)_3}^{2+}$ with a half-life of more than 1 h, probably reacting with the species present in the medium. On the basis of the above mechanism, the quantum yield for net product formation was related to the quencher concentration by eq 6.

$$\frac{2}{\phi(\mathrm{Co}^{2+})} = \frac{1}{\phi(\mathrm{Ru(bpy)_3}^{3+})} = \frac{1}{k_s\tau[Q]} + \frac{k_q + k_s}{k_s} \quad (6)$$

The intercept vs. the slope in the $1/\phi$ vs. $1/[Q]$ plot gives a measure of the Stern–Volmer constant, and the values of K_{sv} calculated from the plots are given in Table III. Good agreement is seen in cases where secondary reactions do not complicate the measurement of quantum yields. Complications seen for the dibridged ammine complexes are due to the secondary reaction described in Figure 4.

Registry No. **1**, 12139-91-2; **2**, 12139-90-1; **3**, 73199-19-6; **4**, 12578-75-5; **5**, 12580-23-3; $[(\mathrm{NH_3})_5\mathrm{Co}(\mu\text{-}\mathrm{O_2})\mathrm{Co}(\mathrm{NH_3})_5]^{5+}$, 12259-09-5; $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2})\mathrm{Co}(\mathrm{NH_3})_4]^{4+}$, 12381-36-1; $[(\mathrm{en})_2\mathrm{Co}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2})\mathrm{Co}(\mathrm{en})_2]^{4+}$, 12387-59-6; $[(\mathrm{bpy})_2\mathrm{Co}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2})\mathrm{Co}(\mathrm{bpy})_2]^{4+}$, 11059-95-3; $[(\mathrm{phen})_2\mathrm{Co}(\mu\text{-}\mathrm{NH_2},\mathrm{O_2})\mathrm{Co}(\mathrm{phen})_2]^{4+}$, 11060-43-8; $\mathrm{Ru(bpy)_3}^{2+}$, 15878-95-2; $\mathrm{Ru(bpy)_3}^{3+}$, 19052-39-2; Co^{2+}, 22541-53-3.

---

(35) Recent pulse-radiolysis experiments confirm that reduction by strong organic radicals, unstable metal ions, and hydrated electrons reduces the dioxygen bridge to give the analogous peroxo complexes.[36]

(36) P. Natarajan and N. V. Raghavan, *J. Chem. Soc., Chem. Commun.*, 268 (1980).

Contribution from the Department of Chemistry, University of Vermont, Burlington, Vermont 05405,
and the Inorganic Chemistry Laboratory, Oxford OX1 3QR, England

Organophosphazenes. 12. He I Photoelectron Spectra of Selected Phenyl- and [*p*-(Dimethylamino)phenyl]fluorocyclotriphosphazenes(1)

CHRISTOPHER W. ALLEN*[2a] and JENNIFER C. GREEN[2b]

Received October 22, 1979

He I photoelectron spectra are presented for $\mathrm{P_3N_3F_{6-n}(C_6H_5)_n}$ (n = 1,2,4) and $\mathrm{P_3N_3F_5C_6H_4N(CH_3)_2}$. 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 $\mathrm{P_3N_3F_5}$ 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 phenylphosphazenes, 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 σ-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

---

(1) Part 11: Dupont, J. G.; Allen, C. W. *Macromolecules* **1979**, *12*, 169.

(2) (a) University of Vermont. (b) University of Oxford.

(3) Attridge, C. J. *Organomet. Chem. Rev., Sect. A* **1970**, *5*, 323.

(4) Pitt, C. G. *J. Organomet. Chem.* **1970**, *61*, 49.

(5) Bock, H.; Ramsey, B. G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 734.

0020-1669/80/1319-1719$01.00/0 © 1980 American Chemical Society

Table I. Ionization Energies (eV) for Arylfluorocyclotriphosphazenes

$P_3N_3F_5C_6H_5$	2,2-$P_3N_3F_4(C_6H_5)_2$	*cis*-2,4-$P_3N_3F_4(C_6H_5)_2$	*trans*-2,4-$P_3N_3F_4(C_6H_5)_2$	2,2,4,4-$P_3N_3F_2(C_6H_5)_4$	$P_3N_3F_5C_6H_4N(CH_3)_2$
10.07	9.64	9.62	9.62	8.59 (sh)	7.88
11.25	10.56	10.36	10.25	9.31	9.53
12.20	12.08	11.41	11.28	10.15	10.21
12.98	14.33	12.46	12.03	11.83	10.73
14.72	15.19	13.77	12.49	14.04	11.95
15.42	16.12	14.45	13.75	14.63	12.82
16.35	17.17	15.13	14.43		13.43
		17.19	15.09		14.29
			17.29		14.59
					15.84

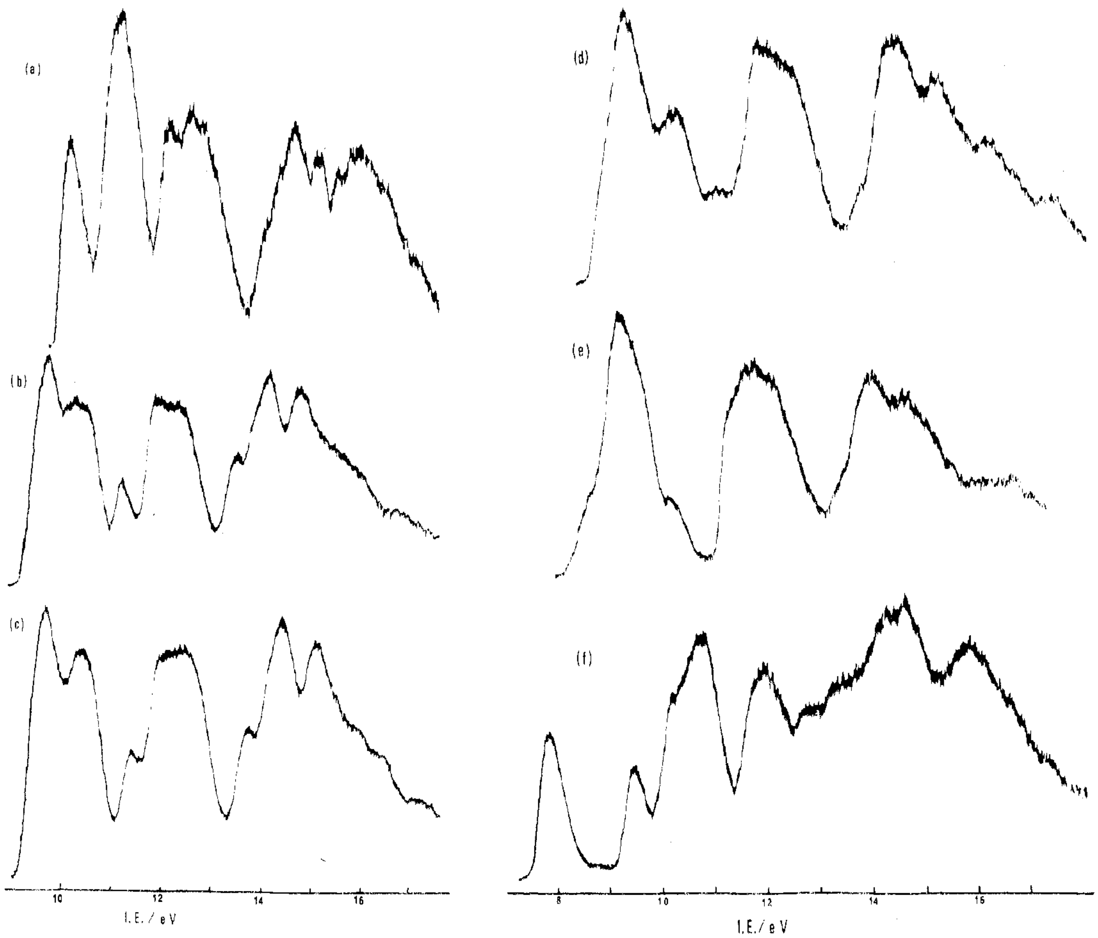


Figure 1. PE spectra of (a) $P_3N_3F_5C_6H_5$, (b) *trans*-2,4-$P_3N_3F_4(C_6H_5)_2$, (c) *cis*-2,4-$P_3N_3F_4(C_6H_5)_2$, (d) 2,2-$P_3N_3F_4(C_6H_5)_2$, (e) 2,2,4,4-$P_3N_3F_2(C_6H_5)_4$, and (f) $P_3N_3F_5C_6H_4N(CH_3)_2$.

UV,[6] ESR,[7] NQR,[8] and NMR (^1H,[9] ^{13}C,[10] ^{19}F,[11] and ^{31}P[12]) spectroscopy, and these results have been variously interpreted as showing no, a few, or extensive mesomeric interactions depending on the technique which was utilized. Our recent ^{13}C NMR work,[10] along with ^{19}F NMR studies of Chivers and Paddock,[11] establish that the $P_3N_3F_5$ 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 shifts[13] 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) spectroscopy[14] 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 phenylfluorocyclotriphosphazenes, $P_3N_3F_{6-n}(C_6H_5)_n$ (n = 1, 2, 4), and of [*p*-(dimethylamino)phenyl]pentafluorocyclotriphosphazene, $P_3N_3F_5C_6H_4N(CH_3)_2$.

Experimental Section

Materials. The phenyl-substituted fluorocyclotriphosphazenes were prepared and purified by previously reported procedures.[12,16] The *p*-(dimethylamino)phenyl derivative was prepared by the reaction of

---

[6] Wagner, A. J.; Moeller, T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1307.

[7] Allcock, H. R.; Birdsall, W. J. *Inorg. Chem.* **1971**, *10*, 2495.

[8] Whitehead, M. A. *Can. J. Chem.* **1964**, *42*, 1212.

[9] Allen, C. W.; White, A. J. *Inorg. Chem.* **1974**, *13*, 1220.

[10] Allen, C. W. *J. Organomet. Chem.* **1977**, *125*, 215.

[11] Chivers, T.; Paddock, N. L. *Inorg. Chem.* **1972**, *11*, 848.

[12] Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177. Allen, C. W.; Tsang, F. Y.; Moeller, T. *Ibid.* **1968**, *7*, 2183.

[13] Adcock, W.; Gupta, B. D. *J. Am. Chem. Soc.* **1975**, *97*, 6871. Adcock, W.; Khor, T. C. *Ibid.* **1978**, *100*, 7799.

[14] Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1970. Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy"; Wiley-Interscience: New York, 1977.

[15] Ramsey, B. G. *J. Organomet. Chem.* **1977**, *135*, 307.

[16] Allen, C. W.; Moeller, T. *Inorg. Synth.* **1970**, *12*, 293.

[*p*-(dimethylamino)phenyl]magnesium bromide with hexafluorocyclotriphosphazene ($P_3N_3F_6$).[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 by using xenon and argon. The data are reported in Table I.

Results and Discussion

In the subsequent discussion we shall assume the validity of Koopmans' theorem.[18] This assumption appears warranted in that one is dealing with electrons in delocalized molecular orbitals. It has been shown[19] however for substituted benzene derivatives that Koopmans' theorem only holds to a first approximation. Independent of the strict validity of Koopmans' 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 approach[14] starting from the known spectra of benzene[14] and hexafluorocyclotriphosphazene,[20] $P_3N_3F_6$. Given the complex nature of the molecules in question, these assignments are tentative in nature. The first-ionization potential (IP) of benzene occurs in the region of 9.25 eV[21] and is raised by the presence of electron-withdrawing substituents; e.g., the first aryl π ionization in nitrobenzene occurs at 9.93 eV.[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 $P_3N_3F_5C_6H_5$ (10.07 eV) 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 11.4 eV and drops steadily as fluorine atoms are replaced by less electronegative substituents.[20] We therefore assign the band at 11.25 eV to an analogous ionization process. On the basis of Xα calculations[23] 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 monosubstitued benzene derivatives,[14] and the aryl ionization would not be in the range expected on the basis of the σ^+ constant (calculated from ^{13}C NMR shifts) of the $P_3N_3F_5$ 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 13.1 eV in $P_3N_3F_6$[18] and the $\pi_{a_{2u}}$ benzene ionization are reasonably assigned to this region.[14] The σ_{e_g} ionization of the aryl unit occurs at 11.70 eV[14] 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 14.72 eV and fall in the region of σ-bond ionizations in both the arene[14] and the phosphazene systems[20] and will not be discussed.

The partial assignment of the PE spectrum of $P_3N_3F_5C_6H_5$ 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 studies[9-11] which have established the $P_3N_3F_5$ 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 $P_3N_3F_5$ 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 arylphosphazenes. 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 15 eV) from the phenyl π system. This effect, if present, would destabilize the phenyl π_{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 destablization 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 destablization (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, cis-2,4, and trans-2,4) 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 9.6 eV) is again most logically assigned to the aryl π_{a_2,b_1} ionization. The next ionization occurs in the region of 10.3–10.5 eV (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 10.3–10.5 eV band is assigned to the phosphazene out-of-plane π system. The intensity of the 9.6 eV band relative to the 10.3–10.5 eV 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

---

(17) Allen, C. W.; Toch, P. L., manuscript in preparation.

(18) Wittel, K.; McGlynn, S. P. *Chem. Rev.* **1977**, *77*, 745.

(19) Marschner, F. *Tetrahedron* **1975**, *31*, 2303.

(20) Branton, G. R.; Brion, C. E.; Frost, D. C.; Mitchell, K. A. R.; Paddock, N. L. *J. Chem. Soc. A* **1970**, 151.

(21) It has been suggested[15] that the energy of the first benzene ionization should be corrected for Jahn–Teller effects to a value of 9.32 eV.

(22) Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2563.

(23) Mitchell, K. A. R.; Noodleman, L.; Paddock, N. L. *Chem. Phys. Lett.* **1977**, *47*, 265. Noodleman, L.; Westwood, N. P. C.; Mitchell, K. A. R. *Ibid.* **1978**, *58*, 252.

(24) Baker, A. D.; May, D. P.; Turner, D. W. *J. Chem. Soc. B* **1968**, 22.

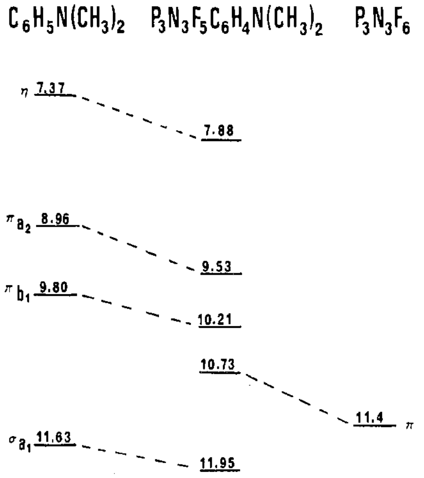


Figure 2. Assignment of the ionization processes in $P_3N_3F_5C_6H_4N(CH_3)_2$ (vertical axis in electronvolts).

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 11.3–11.4 eV and 13.7 eV appear in the PE spectra of the nongeminal isomers. These bands do not appear in the spectrum of the geminal isomer and hence are diagnostic of the nongeminal 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 12–13-eV region exhibit severe overlapping; however, the broad bandwidth and asymmetry of the peaks suggest that 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 (9.31 eV) has increased in intensity and moved to lower energy while the phosphazene π-ionization band (10.15 eV) exhibits a relative decrease in intensity and also has moved to lower energy. The most interesting spectral feature is the shoulder (8.5 eV) 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 tetraphenylphosphazene 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 stabilizaton, 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, we examined the PE spectrum of [*p*-(dimethylamino)phenyl]pentafluorocyclotriphosphazene, $P_3N_3F_5C_6H_4N(CH_3)_2$. 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 by using the known spectra of *N*,*N*-dimethylaniline[22] and hexafluorocyclotriphosphazene[20] (Figure 2). The lowest energy (7.88 eV) ionization is assigned to an orbital which is a mixture of nitrogen lone-pair and aryl π_{b_1} orbitals with the largest contribution associated with the nitrogen lone-pair orbital. The next band (9.53 eV) is assigned to the aryl π_{a_2} ionization. The other aryl π_{b_1}/nitrogen lone-pair band is assigned to the region around 10.21 eV. Since this band is a poorly resolved shoulder, the value of the ionization energy must be taken as an approximation. The 10.73-eV 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 $P_3N_3F_5C_6H_5$ and is consistent with the intensity variations of the aryl vs. phosphazene bands throughout the entire series of phenylphosphazenes. 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 strong electron-withdrawing effect of the phosphazene unit is manifested on all three high-energy aryl molecular orbitals. 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*-dimethylamino)phenyl 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.

Acknowledgment. Research in phosphazene chemistry at the University of Vermont is supported, in part, by the Office of Naval Research.

Registry No. $P_3N_3F_5C_6H_5$, 2713-48-6; *trans*-2,4-$P_3N_3F_4(C_6H_5)_2$, 22341-00-0; *cis*-2,4-$P_3N_3F_4(C_6H_5)_2$, 21079-47-0; 2,2-$P_3N_3F_4(C_6H_5)_2$, 18274-73-2; 2,2,4,4-$P_3N_3F_2(C_6H_5)_4$, 21050-24-8; $P_3N_3F_5C_6H_4N(CH_3)_2$, 53968-86-8.

---

(25) Distefano, C.; Pignataro S.; Szepes, L.; Borassay, J. *J. Organomet. Chem.* **1976**, *104*, 173.