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Organophosphazenes. 24. Ultraviolet Photoelectron Spectra of Selected Alkenyl- and Alkynylfluorocyclotriphosphazenes[1]

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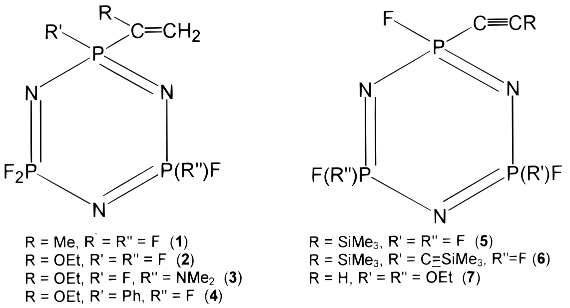
Introduction

The electronic structure of the cyclophosphazenes and their derivatives is a subject of continuing interest.[2,3] Although molecular orbital calculations at various levels have appeared,[4−10] experimental studies devoted to this problem are infrequent. The most extensive studies are interpretation of X-ray studies of solid-state structures.[2,11] Spectroscopic studies[2] have included UV−visible investigations[12] and several attempts to correlate NMR data with bonding models.[13,14] Surprisingly, few reports of determination of valence shell ionization energies, the most direct probe of electronic structure, have appeared.[15,16] In this paper, we report selected vertical ionization potentials of a series of alkenyl-and alkynylfluorocyclotriphosphazenes as determined by ultraviolet photoelectron spectroscopy (UPS), to probe the interaction between the cyclophosphazene and the unsaturated organic centers.

Experimental Section

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$ (Nippon Soda), was converted to $N_3P_5F_5CMe{=}CH_2$(**1**),[17] $N_3P_3F_5C(OEt){=}CH_2$ (**2**),[18] 2,4-$N_3P_3F_4$-[$C(OEt){=}CH_2$]NMe_2(**3**),[18] 2,2-$N_3P_3F_4$[$C(OEt){=}CH_2$]C_6H_5(**4**),[18] $N_3P_3F_5C{\equiv}CSiMe_3$ (**5**),[19] $N_3P_3F_4(C{\equiv}CSiMe_3)_2$ (**6**)[19] and $N_3P_3F_3(C{\equiv}CH)(OEt)_2$ (**7**)[19] by previously reported procedures. UPS data were obtained on a Perkin-Elmer PS-18 spectrometer using the He I resonance line (21.22 eV) as the excitation source. All data represent the average of three or more runs. Xenon was the internal calibrant.

Chart 1



Results and Discussion

The series of alkenylfluorocyclotriphosphazenes (**1**−**4**) with systematic variations in structure and the selected alkynlfluorocyclotriphosphazenes (**5**−**7**) employed in this study are shown in Chart 1. The ionization energy data for compounds **1**−**7** are summarized in Table 1. The assignments of the spectra are based on the composite molecule approach using the previously assigned spectrum of $N_3P_3F_6$[6,15] and those of the alkenyl and alkynyl substituents.[20] The results of an investigation of the photoelectron spectra of the series of phenylfluorocyclotriphosphazenes $N_3P_3F_{6-n}(C_6H_5)_n$ ($n = 1-4$)[16] provide a valuable guideline for assignment of the spectra and evaluation of the results. The out-of-plane π orbital ionization in $N_3P_3F_6$ is observed at 11.4 eV, and the in-plane π ionization, at 13.1 eV.[6,15] Replacement of the fluorine atoms by phenyl groups results in a decrease in the phosphazene ionization potentials.[16] On the basis of the variations in the phenylphosphazene ionization potentials and the fact that the substituents in this study are also π-electron-rich organic moieties, the I_1 set (Table 1) is assigned to the organic π system and the I_2 set to the in-plane phosphazene π ionization. Reversal of these assignments would require ionization potentials outside the range previously observed [20] for alkenes and structurally relevant alkynes. The I_3 set would be expected to contain contributions from the phosphazene in-plane π ionization and from the organic substituent.

The I_1 value for **1** shows a significant stabilization of the $\pi_{C=C}$ orbital on going from $MeCH{=}CH_2$ (IP 10.01 eV),[21] which is accompanied by a corresponding destabilizing of the phosphazene ionization (I_2). The magnitude of the olefin stabilization shows that the very strong electron-withdrawing effect of the $N_3P_3F_5$ moiety noted in other systems[16,22,23] is equally manifested in alkenylphosphazenes. The next question is: how is the electronic effect of the phosphazene transmitted to the olefin? If significant delocalization from the olefin π system to the

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Table 1. Ionization Energies for Selected Organocyclotrifluorophosphazenes[a]

cyclophosphazene	I_1	I_2	I_3	I_4
$N_3P_3F_5CMe{=}CH_2$ (**1**)	10.53 ± 0.01	11.08 ± 0.02	12.08 ± 0.01	
$N_3P_3F_5C(OEt){=}CH_2$ (**2**)	9.70 ± 0.02	11.03 ± 0.02	12.32 ± 0.01	
2,4-$N_3P_3F_4[C(OEt){=}CH_2]NMe_2$ (**3**)	9.29 ± 0.01	10.44 ± 0.01	11.60 ± 0.01	
2,2-$N_3P_3F_4[C(OEt){=}CH_2]C_6H_5$ (**4**)	9.58 ± 0.03	10.49 ± 0.04	11.54 ± 0.02	12.24
$N_3P_3F_5C{\equiv}CSiMe_3$ (**5**)	10.57 ± 0.02	11.17 ± 0.03	11.79 ± 0.01	
$N_3P_3F_4(C{\equiv}CSiMe_3)_2$ (**6**)	10.54 ± 0.01	11.15 ± 0.01	11.79 ± 0.01	
$N_3P_3F_3(C{\equiv}CH)(OEt)_2$ (**7**)	10.21 ± 0.01	11.24 ± 0.01	11.66 ± 0.01	

[a] All values refer to vertical ionization potentials in eV.

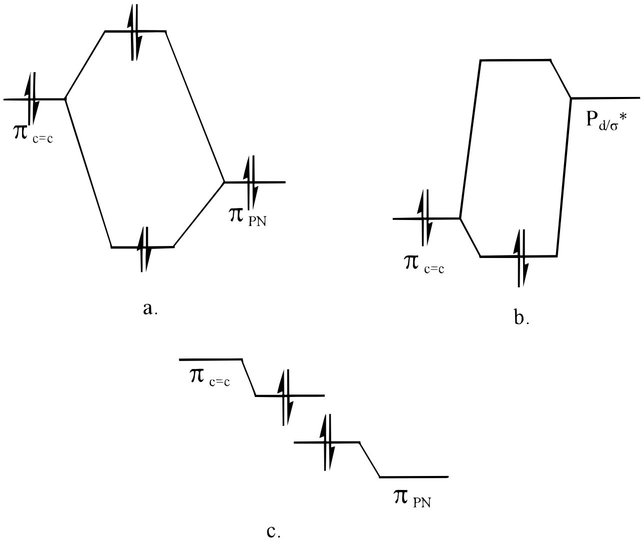

Figure 1. Possible electronic effects in alkenylphosphazenes.

phosphazene π system occurs, then the requisite orbital mixing would lead to a raising of energy (lower I_1) of the olefin ionization and a lowering of energy (higher I_2) of the phosphazene ionization (Figure 1a). The fact that the opposite (higher I_1, lower I_2) situation is observed demonstrates the lack of significant interaction between the organic and inorganic π systems. This observation is consistent with the predicted nodes in the phosphazene π system at the phosphorus centers.[2,7−10] Stabilization of the olefin π ionization could occur by two different mechanisms: delocalization of olefin π electrons into phosphorus d or σ^* acceptor orbitals (Figure 1b) or a σ polarization of $\pi_{C=C}$ by the strongly electron-withdrawing phosphazene (Figure 1c). While earlier NMR studies have been interpreted in terms of π delocalization to the phosphazene in a series of fluorophenyl derivatives,[24] the π delocalization model is inconsistent with the results of other studies. The phosphazene electron-withdrawing effect in the phenylphosphazenes has been unamibiguously shown by previous UPS studies to be dominated by a σ polarization mechanism.[16] Alfrey−Price parameters derived from reactivity ratios in copolymerization reactions of cyclophosphazenes containing olefinic substitutents show no evidence for significant olefin delocalization.[25] Thus the most reasonable model for the observed electron-withdrawing effect is one primarily involving transmission through the σ system. Increased insight into the phosphazene−alkene interaction is provided by the UPS data for **2**. The decrease in olefin ionization energy on going from **1** to **2** (0.83 eV) is equivalent to the change on going from $MeCH{=}CH_2$ to $EtOCH{=}CH_2$ (9.15 eV).[26] In each case, the well-established strong electron-donating effect of the ethoxy unit[18] is equally transmitted to the olefin. If there were significant donation into phosphorus d or σ^* acceptor orbitals, one might expect an increased interaction in the more $\pi_{C=C}$ electron-rich species (**2**). The equivalence of the change in ionization energy between the free olefins and the phosphazene derivatives shows that this is not the case. In contrast to the olefin ionizations, the phosphazene ionizations are almost equal in **1** and **2**. The fact that, despite a major increase in olefin π electron density on going from **1** to **2**, no change occurs in the weakly bonded phosphazene π orbital clearly demonstrates the absence of any interactions between the organic and inorganic π components of the molecules in question. The disubstituted species **3** and **4** allow for examination of substituent effect transmission in the cyclophosphazene series. The $\pi_{C=C}$ ionization is more strongly perturbed (relative to **2**) in **4** than in **3**. The stronger electron-donating effect of the dimethylamino group relative to the phenyl group [27] dominates the electronic effects in these compounds even though it (the dimethylamino group) is on a distant phosphorus atom, while the phenyl group is on the same atom as the ethoxyvinyl substituent. The phosphazene ionizations (I_2) are equivalent in **3** and **4**. The destabilization of I_2 in **3** and **4** relative to **1** and **2** is consistent with changes observed in the phenylfluorophosphazenes.[16] The equivalence of I_2 in **3** and **4** suggests that substituent effects on the phosphazene ring are not manifested in the phosphazene $\pi_{C=C}$ system; consequently electronic effects are transmitted through the phosphazene σ bond system.

The UPS data for the alkynylphosphazenes **5**−**7** show limited variation and hence are less informative than those of the alkenylphosphazenes. The stabilization of the $\pi_{C\equiv C}$ (I_1) ionization on going from $HC{\equiv}CSiMe_3$ (10.2 eV)[28] to **5** (and the related species **6** and **7**) is significantly less than that observed for the alkenylphosphazenes. This observation is consistent with the higher orbital electronegativity of an sp carbon of the alkyne vs the sp^2 carbon of the alkene. In the alkynylphosphazenes (**5**−**7**), the electron-withdrawing ability of the organic function is greater than that of the alkenylphosphazenes (**1**−**4**), and thus more effectively counter balances the electron withdrawing effects of the phosphazene. Consequently, the σ polarization of the exocyclic organic function by the phosphazene is less significant in the alkynylphosphazenes. If, on the other hand, the organic moiety functioned as a π donor, the electron donation would be accentuated in the alkynylphosphosphazenes. Since this is contrary to the observations, the σ polarization model is favored. The decreased difference between the fluoro and organo group electronegativities leads to a similar decrease in the modulation of the phosphazene π (I_2) ionization energies as is also noted.

In summary, the UPS data for selected organofluorocyclotriphosphazenes have been consistently interpreted in terms of a model in which phosphazene substituent effects are exclusively transmitted through polarization of the endo- and exocyclic σ bonds.

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