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THE ULTRAVIOLET AND PHOTOELECTRON SPECTRA OF SOME UNSATURATED FLUOROCARBON DERIVATIVES

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SUMMARY

The ultraviolet spectra and ionization potentials (by photoelectron spectroscopy) of some unsaturated amines, phosphines and stibines are reported.

INTRODUCTION

The ultraviolet spectra of vinyl arsines and phosphines show an absorption at ~2500 Å which has recently been assigned by Weiner and Pasternak[1] to an $n \rightarrow \pi^*$ or charge-transfer transition involving the lone pair on the Group V atom and antibonding π-orbitals on the vinyl group. A similar explanation had previously been put forward to account for the spectra of arylarsines[2]. We had also observed similar features in the spectra of unsaturated fluorocarbon derivatives of arsenic[3].

The present paper is concerned with a description of the UV spectra of some unsaturated amines, phosphines and stibines, most of which are fluorocarbon derivatives. We also describe some studies on the photoelectron (PE) spectra of these and related molecules which were made in an attempt to gain information about the energy levels involved in the UV transitions.

EXPERIMENTAL

Volatile compounds were manipulated using a vacuum system. Hexafluorobutyne-2 was purchased from Peninsular Chem. Research Inc. All other compounds were prepared by literature procedures.

The UV spectra were recorded on a Cary Model 14 spectrometer, and the maxima are accurate to ± 2 Å unless otherwise indicated. The PE spectra were obtained using either a spherical grid[4] or 180 degree hemispherical[5] energy analyzer, with a Fabritek 1024 channel memory for data averaging and storage. The photon source was helium I 584 Å radiation (21.22 eV) from a 2450 mcps microwave discharge[6].

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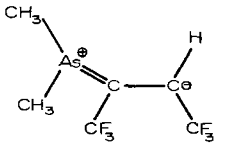
RESULTS AND DISCUSSION

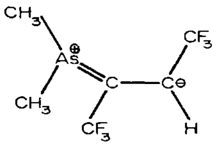
Ultraviolet spectra

The UV spectra of the compounds studied in this investigation are listed in Table 1. Most of the olefins have an absorption in the low energy region, as well as end absorption. The former are unlikely to be red-shifted olefin $\pi \rightarrow \pi^*$ transitions, and they can be assigned as either $n \rightarrow \pi^*$ or charge-transfer. It is significant that the silyl compound, which does not have a "lone pair", does not absorb in this region. No absorption is seen for tris-trifluorovinylarsine, presumably because the strongly electronegative fluorocarbon groups stabilize the lone pair electrons too much.

Weiner and Pasternak[1] found that the $n \rightarrow \pi^*$ band in their unsaturated hydrocarbons behaved as expected on changing solvent. Thus, the ground state was stabilized by more polar solvents and the band moved to higher energies. The fluorocarbon derivatives show the reverse trend, the band moving to lower energies with increasing solvent polarity. In the series $R_2EC(CF_3){=}C(CF_3)H$, the $n \rightarrow \pi^*$ band moves to the red as E changes from N to As to P. However, as may be seen from the data in Table 2, and the discussion below, the first ionization potential (IP) of these molecules (which is a measure of the "n" electron binding energy) is greatest for $E = As$. Thus, the energy of the transition, as pointed out by Weiner and Pasternak, is sensitive to factors other than the "lone-pair" energy. These would include the E–C bond length and the extent of delocalization of the n orbital and/or π orbital through pπ–pπ or dπ–pπ bonding.

The *cis*- and *trans*-isomers of $(CH_3)_2AsC(CF_3) = C(CF_3)H$ have significantly different UV spectra. In particular, the maximum of the *cis* compound is very much dependent upon the solvent and is approximately twice as intense as that of the *trans* compound. The intensity difference could be due to steric interactions in the excited states which can be represented by the following Valence Bond structures



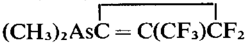


The diethyl analogue $(C_2H_5)_2AsC(CF_3) = C(CF_3)H$ (mainly *trans* isomer) absorbs at lower energies than the dimethyl compound. This is reflected in the first IP which is 0.4 eV less in the diethyl derivative. A similar energy shift is seen in the amine transitions.

The acetylene derivatives of the Group V elements also show a low energy transition which is absent in the silicon analogue, and which in the case of tripropynylarsine exhibits a red shift on changing to a more polar solvent. This band is probably an $n \rightarrow \pi^*$ transition. All the alkynyl derivatives show a higher energy band which is probably due to a $\pi \rightarrow \pi^*$ transition.

TABLE 1

ULTRAVIOLET MAXIMA OF UNSATURATED FLUOROCARBONS

Compound	Low energy absorption			Higher energy absorption	
	Solvent[a]	λ_{max} (Å)	ε_{max}	λ_{max} (Å)	ε_{max}
$CF_3C{\equiv}CCF_3$	gas	2410[b]			
$(CH_3)_2NC(CF_3)=C(CF_3)H$	gas	2475	—		
	N	2510	9440	2100	2000
	E[f,g]	2540	6350	2160	1970
	E[f]	2550	10000	2150	2000
	M[f]	2560	10120	2125	1800
$(C_2H_5)_2NC(CF_3)=C(CF_3)H$	E	2585	5535	e	e
	M	2608	5735	e	e
trans-$(C_2H_5)_2PC(CF_3)=C(CF_3)H$	N	2881	662	c	c
	E[b,h]	2861	660	c	c
	M[b,h]	2885	552	c	c
cis-$(CH_3)_3SiC(CF_3)=C(CF_3)H$	E	—	—	c	c
 $(CH_3)_2AsC=C(CF_3)CF_2$	E	2506	4500	d	d
	M	2518	4950	d	d
$As(CF=CF_2)_3$	gas	—	—	b	b
$(CH_3)_3SiC{\equiv}CCF_3$	gas	—	—	2025 ± 10	—
$CH_3As(C{\equiv}CCF_3)_2$	gas	2350[i]	—	2140[i]	—
	M[i]	2350	850	2150	4500 ± 450
trans-$(CH_3)_2AsC(CF_3)=C(CF_3)H$	N	2610 ± 2	1520 ± 20	c	c
	E	2614 ± 1	1335 ± 55	c	c
	M	2614 ± 1	1370 ± 40	c	c
	C	2627 ± 3	1345 ± 35	c	c
cis-$(CH_3)_2AsC(CF_3)=C(CF_3)H$	N	2585 ± 1	2700 ± 100	c	c
	E	2612	2705	c	c
	M	2662	2730	c	c
	C	2630	2764	c	c
$(C_2H_5)_2AsC(CF_3)=C(CF_3)H$	gas	2608	—	c	c
(90% *trans*)	E	2962	1000 ± 70	c	c
	M	2698	1062	c	c
$P(C{\equiv}CCH_3)_3$	N[d]	2460[i]	1400	2200[i]	1650
$As(C{\equiv}CCH_3)_3$	N[d]	2345[i]	3520	2199[i]	3610
	M	2355[i]	—	2190[i]	—
$Sb(C{\equiv}CCH_3)_3$	N	2432	9100	2290	9100

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[a] Solvent is the solvent used, where M is MeOH, E is Et_2O, N is n-heptane, and C is CH_2Cl_2. "gas" refers to a gas phase spectrum.

[b] ±15 Å.

[c] A strong end absorption at $\leqslant$ 2000 Å.

[d] A medium strength end absorption at $\simeq$ 2000 Å.

[e] A weak end absorption at $\simeq$ 2000 Å.

[f] No end absorption at $\simeq$ 2000 Å.

[g] Exposed to air.

[h] Very broad.

[i] Peaks overlap so error is *ca.* ±15 Å.

Ionization potentials

The IP values determined in this investigation by photoelectron spectroscopy are listed in Table 2. The quoted IP values are designated AIP or VIP (adiabatic or vertical). Where PE bands overlap, only the VIP values are estimated.

TABLE 2

IONIZATION POTENTIALS OF SOME ADDUCTS AND PRECURSORS (eV)*

$(CH_3)_2NH$ 8.07 (8.96); 11.70 (12.73); (13.32); (13.88); (15.09); (16.69).
$(C_2H_5)_2PH$ 8.69 (9.64); (11.52); (12.13); (13.34); (14.12); (15.54); (16.78); (18.82).
$(CH_3)_2AsH$ 8.55 (9.12); 10.23 (11.12); (11.71); 12.68 (13.71); (14.71); (17.8).
cis-$(CH_3)_2AsC(CF_3)=C(CF_3)H$ 8.61 (9.42); 10.31 (10.96); (11.98); 12.77 (13.70); (14.96); (15.60); (16.72).
trans- 8.71 (9.47); (10.59) (11.04); (12.0); 13.10 (14.0); (15.0); (15.7); (17.09).
$(C_2H_5)_2AsC(CF_3)=C(CF_3)H$ 8.44 (9.00); 9.85 (10.44); (11.55); (12.68); (13.58); (14.2); (14.94); (15.72); (17.0).
$(CH_3)_2NC(CF_3)=C(CF_3)H$ 8.22 (8.78); 10.79 (11.42); 12.43 (12.92); (13.4); (14.48); (15.76); (16.98).
cis-$(CH_3)_3SiC(CF_3)=C(CF_3)H$ 9.86 (10.91); (11.74); 12.53 (13.68); (14.79); (15.89); (16.99).
$CF_3C\equiv CCF_3$ 12.31 (12.83); 14.88 (15.48); (15.7); (16.42); (17.49).
$CF_3C\equiv CH$ 11.83 (12.12); 13.76; 14.67 (15.22); (15.62); (15.96); 17.13; 18.07; (18.28).

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* AIP values; VIP values in parentheses.

The first IP of dimethylarsine has previously been determined as 9.0 ± 0.1 eV (standard deviation) by electron impact[7]. It is believed that this IP is associated with the removal of a non-bonding "lone-pair" electron from the arsenic atom. Our photoelectron VIP of 9.12 eV (AIP = 8.58 eV) is considerably more accurate. As is often the case, the electron impact IP lies between the adiabatic and vertical values. The AIP for dimethylarsine is lower than that of arsine (10.06 eV)[8], presumably because of the electron-donating ability of the methyl groups and the change in hybridization at the arsenic which results in the lone pair having more "p" character. One of the two inner AIP values of dimethylarsine at 11.12 and 11.71 eV may be associated with ionization from the As–H bond, since the corresponding AIP in arsine occurs at 11.9 eV[8].

When dimethylarsine reacts with hexafluorobutyne-2 to give the adducts *cis*- and *trans*-$(CH_3)_2AsC(CF_3)=C(CF_3)H$, the PE spectra of the products are very similar to a combination of the spectra of the two reactants. (The spectrum of the butyne is described below). There are, however, a number of differences between the spectra of the isomeric products. The VIP values of the *cis* isomer are mostly a few tenths of a volt less than those of the *trans*, and the *trans* isomer has a strong band peaking at 19.16 eV while the *cis* has only a slight inflection at 18.8 eV. The first AIP values of the adducts are greater than that of dimethylarsine (8.58 eV). This is probably due to the influence of the highly electronegative fluorocarbon group on the arsenic "lone pair". If the second VIP in the adducts at ~11.0 eV is assigned to removal of a π-electron, then the VIP at 11.12 eV in dimethylarsine is probably the one associated with the As–H bond. This assignment would allow the VIP of 11.71 eV in dimethylarsine (which would be associated with the $(CH_3)_2As$ moiety) to appear in the adducts at ~12.0 eV.

The first AIP of ethylene (10.48 eV) has been assigned to the removal of a π-bonding electron[5,10,11]. The adiabatic first IP values of some olefins are listed in Table 3. It can be seen that, rather surprisingly, the AIP of tetrafluoroethylene is less than of ethylene. Halogen-substitution on the fluoro-olefin has much the same effect as on the hydrocarbon, resulting in a lowering of the IP value. The extent of lowering increases as the atomic number of the halogen increases. This indicates that delocalization of positive charge stabilizes the ion. On the other hand, the inductive effect of the trifluoromethyl group results in an increase in IP of both parent olefins. Thus, the IP of the π-bonding electron in the adduct

$$(CH_3)_2AsC(CF_3)=C(CF_3)H$$

would be expected to be greater than that of ethylene by about 0.6 eV (~0.3 eV per CF_3 group). On this basis, the assignment of the VIP of 11.12 eV to removal of a π-bonding electron is not unreasonable, especially since the $(CH_3)_2As$ fragment would be expected to decrease the value slightly.

TABLE 3

THE FIRST IONIZATION POTENTIALS OF VARIOUS ETHYLENES (AIP VALUES)

Ethylene	IP value (eV)	Fluoroethylene	IP value (eV)
$H_2C=CH_2$	10.56[a]	$CF_2=CF_2$	10.32
	10.48[b]		10.12[c]
$CH_2=CHCl$	10.06[a]	$CF_2=CFCl$	9.82
	9.99[c]		
$CH_2=CHBr$	9.80[b]	$CF_2=CFBr$	9.67
$CH_2=CCl_2$	9.83[a]	$CF_2=CCl_2$	9.62
	9.79[c]		
$CCl_2=CCl_2$	9.40[a]		
$CH_2=CHCF_3$	10.9[c]	$CF_2=CFCF_3$	10.62

[a] From Ref. 15.
[b] From Ref. 16.
[c] From Ref. 17.

The fact that the outer IP values of the *cis*- and *trans*-arsine adducts are so similar supports the conclusion that the differences in their UV spectra arise because of excited state differences. Furthermore, the adduct of diethylarsine with hexafluorobutyne-2 has its IP values at lower energies than those of the dimethylarsine adducts. This accounts partly for the lower energy of the $n \rightarrow \pi^*$ transition of this compound. This significant difference is also seen in the first AIP values of the parent arsines (8.92 and 8.57 eV respectively). A similar effect is seen in the electron impact IP values of dimethylamine (8.93 eV) and diethylamine (8.44 eV)[12].

The IP values of dimethylamine as determined in this investigation (Table 2) are in satisfactory agreement with the results of a recent investigation[9]. The VIP at 15.09 eV in dimethylamine may be due to the removal of an electron from the N–H bond, since the corresponding IP in ammonia occurs at 15.5 eV[13].

The adduct of dimethylamine and hexafluorobutyne-2 has its first AIP at 8.78 eV, which is lower than that of the parent amine. This is unexpected, and is difficult to rationalize in view of the opposite effect found for the dimethylarsine adduct. Furthermore, if the UV transitions described above were purely $n \rightarrow \pi^*$, the energy of the transition should correlate moderately well with the first IP of the compound. As pointed out above, the transition in the amine adduct occurs at higher energy than the arsine yet the first IP of the amine adduct is lower. The second IP of the amine adduct at 11.42 eV is probably associated with the loss of a π-bonding electron.

The IP values of the adduct formed between trimethylsilane and hexafluorobutyne-2 are also listed in Table 2. The most striking feature of the PE spectrum is its general similarity to the spectra of the amine and arsine adducts, apart from the absence of an IP at lower energies (<10 eV) which could be assigned to loss of a "lone-pair" electron. The first IP of the silane adduct at 10.91 eV is probably due to loss of an electron from the π-bond.

The first VIP of hexafluorobutyne-2 at 12.83 eV is probably associated with the removal of a π-electron. Substitution of trifluoromethyl groups into acetylene causes a progressive increase in the first IP. The inductive effect of the trifluoromethyl groups is evidently dominant. Vibrational structure on the butyne first band can be assigned to ν(C≡C) (2129 ± 40 cm^{-1}) and to ν(C–F) (1073 ± 40 cm^{-1}). These frequencies in the molecular ground state are 2300 and 1248 cm^{-1} respectively[14]. This suggests that there is considerable delocalization of the π-electrons over the whole molecule. Vibrational structure on the 17.49 eV band can be assigned to ν(C–F) (1266 ± 50 cm^{-1}) and ν(C–C) (733 ± 50 cm^{-1}), the corresponding frequencies in the neutral being 1245 and 771 cm^{-1} respectively. The electron is probably lost from a C–C bonding orbital. On this basis, the group of IP values in the butyne in the region 15–17 eV is probably associated with C–F bonding and F non-bonding orbitals. However, the central PE band of the group at 15.7 eV exhibits vibrational structure (990 ± 50 cm^{-1}), which does not appear to correspond with a band in the infrared spectrum[14].

The first IP of 3,3,3-trifluoropropyne (12.12 eV) is a little below that of hexafluorobutyne-2. This PE band shows structure corresponding to ν(C≡C) (2016 ± 40 cm^{-1}) and ν(C–F) (1081 ± 40 cm^{-1}), these frequencies in the neutral being 2165 and 1254 cm^{-1} respectively.

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