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Orbital Interactions in Ethynylpyridines

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Received: September 22, 1997; In Final Form: November 11, 1997

He I and He II photoelectron spectra of several isomeric ethynyl- and diethynylpyridines have been measured. The spectra were analyzed with the aid of empirical arguments: relative band intensities and comparison with spectra of related compounds (ethynylbenzenes). AM1 calculations were also performed to confirm the assignment. We have deduced for the first time, solely on empirical grounds, the presence of orbital interactions between nitrogen lone pairs and in-plane π-orbitals of the ethynyl group. Relative Lewis basicities are predicted and rationalized.

Introduction

The study of electronic structure of pyridine and its derivatives by photoelectron spectroscopy (UPS) has been a subject of numerous previous reports and reviews.[1] The main considerations were the relative ordering of nitrogen lone pair (n) and ring π-orbitals (π_3, π_2) and the influence of substituents on the π-electronic structure of the aromatic ring.

π_3 π_2 π_1 n
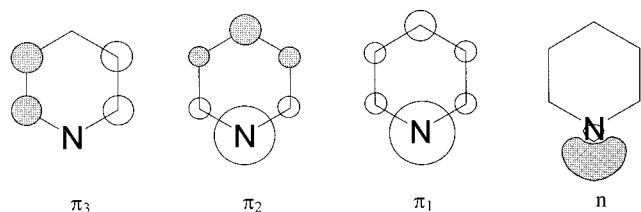
The assignment problem in pyridine was whether HOMO ionization corresponds to an n (a_1) or a π_3 (a_2) orbital. The overlap between the first two bands in the spectrum is so pronounced that even theoretical methods which go beyond Koopmans' approximation (OVGF, HAM/3) gave conflicting assignments.

The problem was finally settled by the work of Piancastelli et al.,[2] who demonstrated in their synchrotron radiation study that the order of ionic states in terms of increasing ionization energies is n < π_3 < π_2. The influence of substituents on the electronic structure is still being studied.[3,4] The results from previous studies can be summarized in two main conclusions: (i) The presence of substituents alters relative ordering of n and π ionic states and can be described in the language of orbital interactions and the composite-molecule model; (ii) The MO calculations are not a reliable guide to the assignment of ionic states.

Okubo et al.[4] have suggested, on the basis of perturbation MO theory applied to 2- and 4-ethynylpyridine, that a weak intramolecular n−π'_{cc} interaction takes place in the 2- but not in 4-ethynylpyridine.

π''_{cc} π'_{cc}
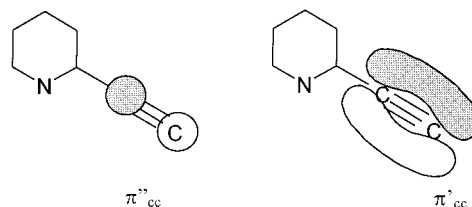
In 2-ethynylpyridine the n−π_2 energy difference is 0.95 eV, while in 4-ethynylpyridine it is 0.85 eV. This small (0.1 eV) difference was considered by Okubo et al.[4] as an indication of such interactions. We wish to present additional experimental evidence which will clarify not only the presence of n−π'_{cc} interactions but also the influence of the nitrogen atom on the substituted aromatic ring as a whole.

Experimental and Theoretical Methods

General. Melting points of diethynylpyridines were measured by a Büchi 530 melting point apparatus. Elemental analyses were performed on a Perkin-Elmer model 240c elemental analyzer. Mass spectra were recorded using a Micromass VG 7035E mass spectrometer at a source temperature of 200 °C and an ionizing voltage of 70V. NMR spectra were obtained on a Bruker ACF300 spectrometer using CDCl$_3$ as solvent and TMS as internal reference. IR spectra of all ethynylpyridines were measured on a Perkin Elmer 1600 IR spectrometer. UV spectra were recorded by a Hewlett Packard 8452A diode array spectrophotometer.

Synthesis. The synthetic route to ethynylpyridines is depicted in Scheme 1. The regioselective ethynyl cross-coupling procedures of Ames et al.[5] were used. Compounds **1a−1c** are known,[6−8] while the synthesis of **2a−2c** has not been reported. All compounds were characterized by 300-MHz NMR, FTIR, mass spectrometry, and elemental analyses.

Reagents and Conditions: HCCC(CH$_3$)$_2$OH/Et$_2$NH/Pd(Ph$_3$)$_2$-Cl$_2$(cat.)/CuI(cat.)/30 °C, then NaOH/PhCH$_3$/reflux.

2,5-Diethynylpyridine: Yield 55%; mp 88.5−90 °C; UV/vis (hexane) 218 (ϵ 138000), 262 (ϵ 250000), 268 (ϵ 240000), and 282 (ϵ 193000) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 3.31 (s, 1H), δ_H 3.25 (s, 1H), δ_H 7.43 (d, 1H, *J* = 8.08 Hz), δ_H 7.74 (q, 1H, *J* = 8.08 Hz, *J* = 2.13 Hz), δ_H 8.68 (d, 1H, *J* = 2.13

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J. Phys. Chem. A, Vol. 102, No. 6, 1998 **905**
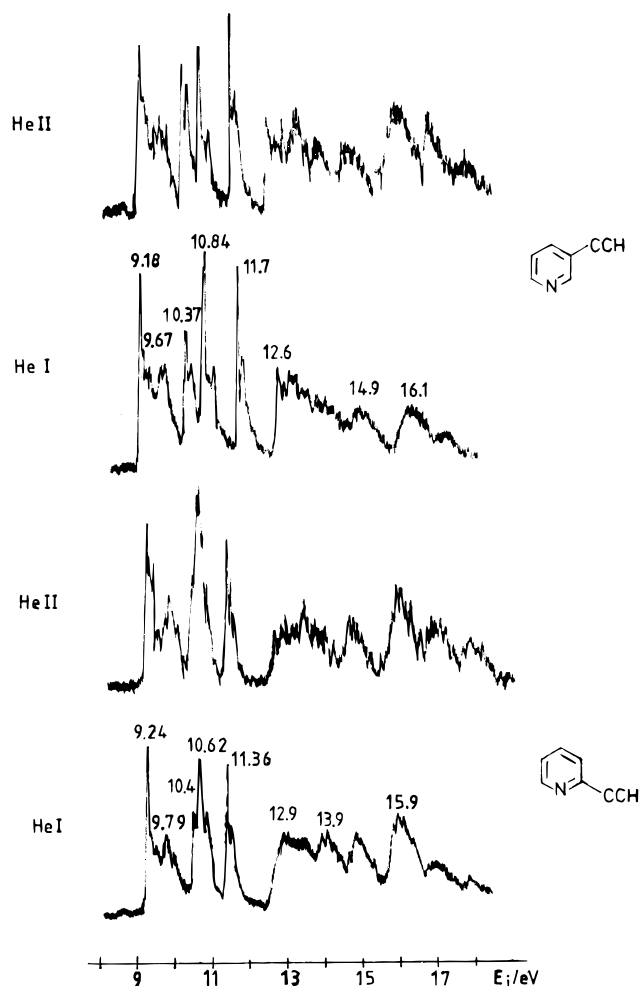
Figure 1. He I and He II UPS of 2- and 3-ethynylpyridine.

SCHEME 1. Synthesis of Ethynylpyridines

n=1
2-ethynylpyridine   (1a)
3-ethynylpyridine   (1b)
4-ethynylpyridine   (1c)

n=2
2,5-diethynylpyridine   (2a)
2,6-diethynylpyridine   (2b)
3,5-diethynylpyridine   (2c)
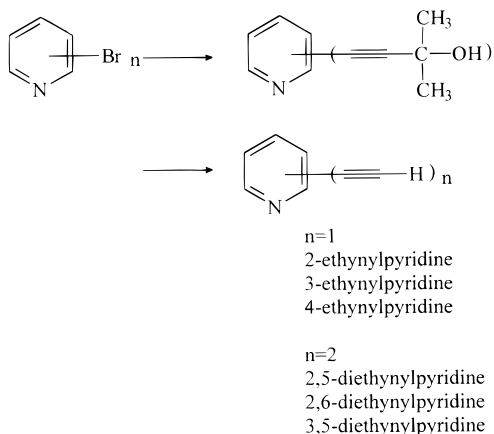
Hz) ppm; ^{13}C NMR (300 MHz, CDCl$_3$) δ_C 79.1, 80.0, 82.4, 119.0, 126.7, 139.1, 141.5, 152.9 ppm; IR (neat) 3236, 3075, 2104, 1550, 1415, 1323, 1150, 1026, 899, 737, 676, and 642 cm^{-1}; MS *m/z* 127 (100), 100 (59), 74 (70), 50 (68). Anal. Calcd for C$_9$H$_5$N: C, 85.02; H, 3.96. Found: C, 84.66; H, 4.28.

2,6-Diethynylpyridine: Yield 45%; mp 70.5−71.5 °C; UV/vis (hexane) 218 (ϵ 146000), 262 (ϵ 255000), 268 (ϵ 249000), and 280 (ϵ 211000) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 3.15 (s, 2H), δ_H 7.44 (d, 2H, *J* = 7.65 Hz), δ_H 7.64 (t, 1H, *J* = 7.78 Hz) ppm, ^{13}C NMR (300 MHz, CDCl$_3$) δ_C 77.8, 82.1, 127.1, 136.5, 142.8 ppm; IR (neat) 3263, 3050, 2105, 1576, 1448, 1248,
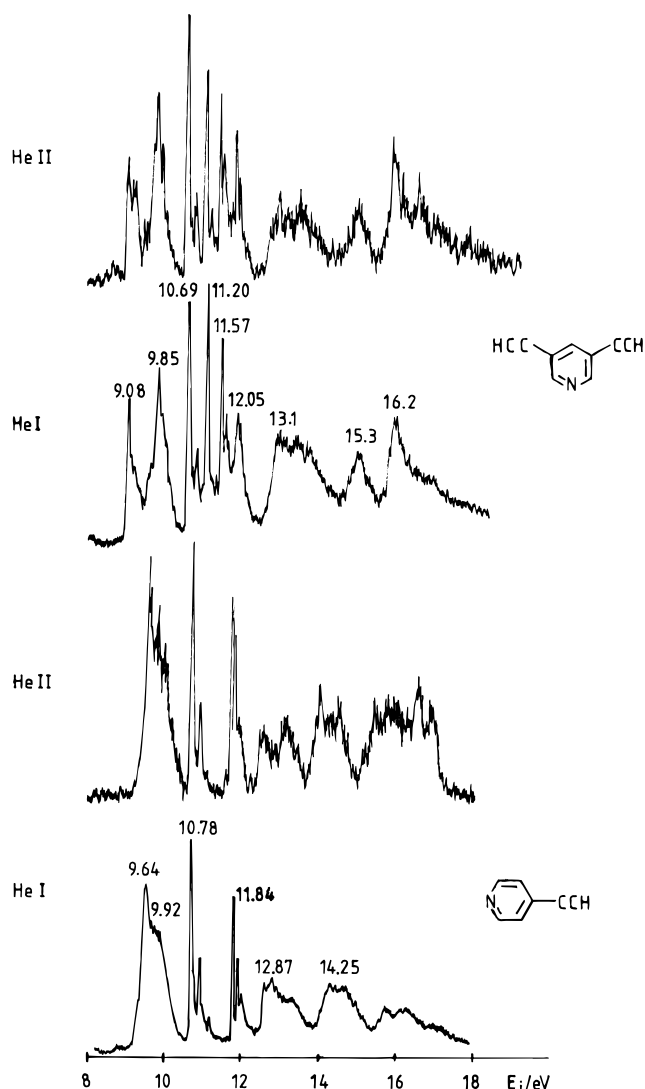

Figure 2. He I and He II UPS of 4- and 3,5-ethynylpyridine.

1198, 990, 814, 698, 668, and 627 cm^{-1}; MS *m/z* 127 (100), 100 (37), 74 (31), 50 (72). Anal. Calcd for C$_9$H$_5$N: C, 85.02; H, 3.96. Found: C, 84.75; H, 4.31.

3,5-Diethynylpyridine: Yield 54%; mp 77.5−78 °C; UV/vis (hexane) 200 (ϵ 20000), 206 (e 22000), 218 (e 148000), and 262 (ϵ 245000) nm; ^{1}H NMR (300 MHz, CDCl$_3$) δ_H 3.24 (s, 2H), δ_H 7.85 (t, 1H, *J* = 1.99 Hz), δ_H 8.65 (d, 2H, *J* = 1.97 Hz) ppm; ^{13}C NMR (300 MHz, CDCl$_3$) δ_C 79.4, 81.4, 119.0, 141.9, 152.0 ppm; IR (neat) 3236, 3050, 2104, 1655, 1560, 1415, 1150, 1026, 899, 737, 676, and 642 cm^{-1}; MS *m/z* 127 (100), 100 (56), 74 (62), 50 (63). Anal. Calcd for C$_9$H$_5$N: C, 85.02; H, 3.96. Found: C, 84.70; H, 4.28.

The He I and He II UPS spectra were recorded on a UPG-200 Leybold-Heraeus spectrometer at a resolution of 16−20 meV (fwhm) in He I and 32−40 meV in He II excitation. Ar$^+$ ^{2}P$_{3/2}$ and ^{2}P$_{1/2}$ lines were used for calibration. AM1 calculations (full geometry optimization) were performed by a semiempirical AM1 method implemented in the HyperChem program package.[9]

Results and Discussion

The He I and He II photoelectron spectra of ethynylpyridines are shown in Figures 1−3. Their assignments can be achieved by comparison with the known spectra of pyridine and mono- and diethynylbenzenes[10] and by consideration of He I/He II

Figure 3. He I and He II UPS of 2,6- and 2,5-ethynylpyridine.

Figure 4. Energy level diagram (based on Koopmans' approximation).

relative band intensities. The correlation of energy levels for these molecules (Koopmans' approximation) is given in Figure 4. The assignment that follows from the correlation (Figure 4) is summarized in Table 1. AM1 results broadly support the empirical assignment except for a few bands whose ionization energies differ by <0.5 eV. In view of the unreliability of any assignments based on Koopmans' approximation at such close energy spacing, we have accepted empirical assignments as more reliable. The explicit values of canonical MO energies are also not given since they contribute no new information. Inspection of Figure 4 demonstrates that an "aza effect" is prominent in the ethynylpyridines, because the π-ionization energies increase

on going from the ethynylbenzene to the corresponding ethynylpyridine. However, the aza effect cannot be a purely inductive effect because different π levels are stabilized to different extents. The relative stabilization of each level depends on the electron distribution in the corresponding orbital; for example the π_2-orbital is stabilized more than π_3, which reflects the larger contribution of the energetically more stable N 2p orbital to π_2. The position of the ethynyl substituent also modifies the relative stabilization, as is evidenced by the different stabilizations of the π_2 in 2- and 4-ethynylpyridines. This is because substituents at different ring positions will interact (mix) in different ways with different ring π-orbitals

TABLE 1: Ionization Energies (E_i/eV),[a] Assignments, Vibrational Fine Structure, and $\pi_3-\pi''_{cc}$ Splitting for Ethynylpyridines (ΔE/eV). The Splitting in Parentheses Is the Reference Value in Ethynylbenzene

molecule	band	E_I	assignment	$\nu_{ion} \pm$ 80 cm^{-1}	ν_{mol}	ΔE/eV
2-et	X̃	9.24	$\pi_3-\pi''_{cc}$			4.2 (4.5)
	Ã	9.79	n			
	B̃	10.44	π_2			
	C̃	10.62	π'_{cc}	1610	1589	
	D̃	11.36	$\pi_3+\pi''_{cc}$	650	642	
3-et	X̃	9.18	$\pi_3-\pi''_{cc}$			5.0 (4.5)
	Ã	9.67	n			
	B̃	10.37	π_2	890	794	
	C̃	10.84	π'_{cc}	1940	2103	
	D̃	11.70	$\pi_3+\pi''_{cc}$	890	794	
4-et	X̃	9.64	$\pi_3-\pi''_{cc}$			
	Ã	(9.64)	n			
	B̃	(9.64)	π_2			
	C̃	10.78	π'_{cc}	1930	2095	
	D̃	11.84	$\pi_3 +\pi''_{cc}$	930	992	
2,6-et	X̃	9.04	$\pi''_{cc}-\pi_3-\pi''_{cc}$	1050	990	
	Ã	9.85	n			
	B̃	10.13	π_2			
	C̃	10.61	π'_{cc}	2020	2020	
	D̃	11.02	$\pi''_{cc}+\pi_3-\pi''_{cc}$	970	990	
	Ẽ	(11.02)	π'_{cc}			
	F̃	11.85	$\pi''_{cc}+\pi_3+\pi''_{cc}$	570	627	
3,5-et	X̃	9.08	$\pi''_{cc}-\pi_3-\pi''_{cc}$			
	Ã	9.85	n			
	B̃	(9.85)	π_2			
	C̃	10.69	$\pi''_{cc}-\pi_3+\pi''_{cc}$	1940	2104	
	D̃	11.20	π'_{cc}	1940	2104	
	Ẽ	11.57	π'_{cc}	890	899	
	F̃	12.05	$\pi''_{cc}+\pi_3+\pi''_{cc}$			
2,5-et	X̃	8.76	$\pi''_{cc}-\pi_3-\pi''_{cc}$			
	Ã	9.72	n			
	B̃	10.24	π_2			
	C̃	10.49	π'_{cc}			
	D̃	10.75	π'_{cc}			
	Ẽ	(10.75)	π''_{cc}			
	F̃	11.97	$\pi''_{cc}+\pi_3+\pi''_{cc}$	1190	1150	

[a] The ionization energies refer to unresolved bands. IUPAC notation is used to designate ionic states (X̃−F̃).

(see the Introduction). We also question whether ring−substituent interactions are stronger in ethynylbenzenes or ethynylpyridines. The best way to answer this question is to compare band intensities (photoionization cross sections) in the two classes of molecules, as was suggested previously.[11] However, no reported He II spectra of ethynylbenzenes exist. We shall then use measured differences of the ionization energies of π_3 and π''_{cc} levels (ΔE) to provide an estimate of ring−substituent interactions. The values shown in Table 1 suggest that the strength of interactions in ethynylbenzenes and ethynylpyridines is comparable.

The analysis for n−π'_{cc} interactions relies on variable photon energy measurements. The analysis of relative intensities assumes the Gelius model.[12] This model suggests that MO photoionization cross sections σ_i^{MO} can be expressed as

$$\sigma_i^{MO} = \sum_i P_{ij}\sigma_i^{AO}$$

where P_{ij} is the electron population of the ith AO. The atomic orbital photoionization cross sections σ_i^{AO} have been tabulated for all elements.[13] One can then estimate the MO character from the observed relative UPS band intensities and calculated atomic cross sections. The ratios of He II/He I cross sections for C 2p and N 2p ionizations are 0.307 and 0.449, respectively. These values suggest that the relative intensities of bands corresponding to ionizations from orbitals with N 2p character will decrease less (upon increasing photon energy) than of those with C 2p character. This fact provides a useful way of distinguishing orbital characters on an empirical basis, especially when MO calculations are unreliable because of the high density of states. Table 2 shows relative band intensities for bands that could be reliably deconvoluted.

The near degeneracy of n and π_3 levels in pyridine is lifted in ethynylpyridines. The distinction between π_3 and π_2 ionizations can be easily made by considering their orbital characters: the π_3-orbital has predominantly C 2p character, while the n-orbital has strong N 2p character. The analysis of relative ionization cross sections then leads to the conclusion that the band corresponding to the n-orbital ionization will increase in intensity compared to the π_3 band. This effect is clearly observed, and it leads to the conclusion that the HOMO ionization is always related to π_3.

In 2-ethynylpyridine the relative intensity of the B̃+C̃ band group (π_2, π'_{cc}) increases compared to the D̃ band (π''_{cc}). One may attribute the intensity change simply to the pronounced N 2p character of the π_2 ionization (B̃) which leads to an increase in B̃ band intensity. This increase then masks any changes of the C̃ band. The fact that this is not a correct explanation can be seen from consideration of the intensities in the 3- and 4-ethynylpyridines. The combined intensity of the B̃ (π_2) and C̃ (π'_{cc}) bands in 3-ethynylpyridine shows a relative decrease compared to D̃ (π''_{cc}), despite the fact that the B̃+C̃ group also contains the π_2 ionization. In the 4-ethynyl derivative, the B̃ band could not be resolved, but the intensities suggest that the C̃ band intensity decreases relative to D̃ on going from He I to He II. The final conclusion must be that the intensity of the B̃+C̃ group in 2-ethynylpyridine is enhanced by increases of both the B̃ and C̃ bands. How can this be possible if the C̃ band (π'_{cc}) does not have appreciable N 2p character? A plausible explanation lies in n−π'_{cc} (through-space) interaction which, for steric reasons, is possible in the 2-ethynyl derivative,

TABLE 2: Relative Band Intensities (Deduced from Band Areas). The Band Labels Are Given in Parentheses, Following the Intensity Values

	$h\nu$		intensities			
2-	He I	1.0(X̃)	0.78(Ã)	1.51(B̃+C̃)	0.86(D̃)	
	He II	1.0	0.71	1.52	0.73	
3-	He I	1.0(X̃)	1.00(Ã)	0.87(B̃)	1.27(C̃)	0.98(D̃)
	He II	1.0	0.74	0.87	0.79	0.96
4-	He I	1.0(X̃+Ã+B̃)	0.50(C̃)	0.33(D̃)		
	He II	1.0	0.55	0.44		
2,6-	He I	1.0(X̃)	1.80(Ã+B̃)	3.10(C̃+D̃+E)	0.92(F̃)	
	He II	1.0	1.86	3.13	0.99	
2,5-	He I	1.0(X̃)	0.92(Ã)	3.85(B̃+C̃+D̃+Ẽ)	1.07(F̃)	
	He II	1.0	0.80	4.42	1.0	
3,5-	He I	1.0(X̃)	2.02(Ã+B̃)	1.24(C̃)	1.34(D̃)	1.03(Ẽ)	1.0(F̃)
	He II	1.0	2.02	1.29	1.0	1.12	1.14

2-ethynylpyridine
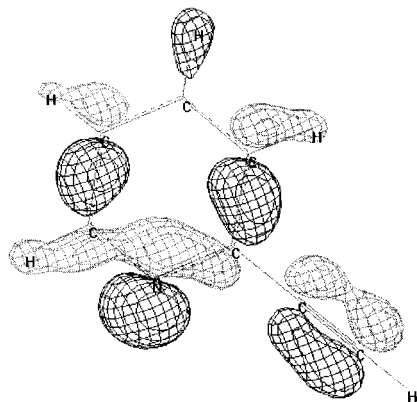
2,6-ethynylpyridine
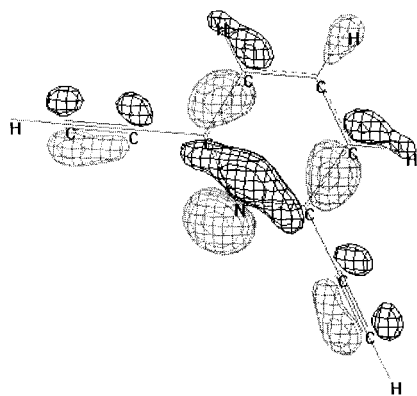
Figure 5. Some MOs in 2- and 2,6-ethynylpyridine which show $n-\pi'_{cc}$ mixing (interaction).

but not in 3- and 4-ethynylpyridine. The $n-\pi'_{cc}$ interaction introduces some N 2p character into π'_{cc} and the intensity variations of $\tilde{C}$ and $\tilde{D}$ will be reversed on going from the 2- to the 3- and 4-ethynyl derivatives. Deductions about $n-\pi'_{cc}$ interactions in the spectra of 2,6-ethynylpyridine and 3,5-ethynylpyridine can be made simultaneously. In the 2,6-derivative only minor differences occur between the intensities of the π''_{cc} and π'_{cc} ionizations, while in the 3,5-derivative differences of He I/He II intensities can be easily observed.

A tentative rationalization assumes that $n-\pi'_{cc}$ interactions are only possible in the 2,6- and not in the 3,5-derivative, implying an increase of N 2p character of the π'_{cc} orbitals in 2,6-ethynylpyridine and a reduction of differences between the orbital characters of π'_{cc} and π''_{cc}. In the 3,5-derivative there are no through-space interactions and the π'_{cc} and π''_{cc} orbitals retain their distinct compositions, a fact reflected in the band intensity changes.

Finally, 3,5-ethynylpyridine can be considered an intermediate case with a single $n-\pi'_{cc}$ interaction. However, band overlap precludes a detailed analysis.

Conclusion

The order of ionic states in pyridine ($n < \pi < \pi$) is different from ethynylpyridines, where HOMO ionization corresponds to π-orbital ionization. Since Koopmans' (and even non-Koopmans') approaches failed for pyridine, we have based our analysis on He I/He II band intensities rather than MO calculations. The latter were used only for a qualitative description of electron distributions in ionic states.

We have provided experimental evidence for intramolecular $n-\pi'_{cc}$ interactions. The interactions are reflected in orbital mixing in 2- and 2,6-derivatives, as shown in Figure 5. Our results are also useful in predicting gas-phase (Lewis) basicities. The basicity among monoethynylpyridines should follow the sequence 4 > 3 > 2. The order for diethynylpyridines should be 2,5 > 3,5 > 2,6. In fact, in the absence of UPS data, the basicity can be used as an indicator of such interactions.

The UPS study of 2-halopyridines[3a] could provide an answer to the possible occurrence of similar interactions with a halogen substituent. Unfortunately, band overlap and inferior resolution in the He II spectra make the answer merely suggestive.

It appears that the intensity of the n band is not enhanced significantly on going from He I to He II. This could be due to an admixture of halogen np character, because it is well-established that Cl, Br, and I np^{-1} ionization cross sections decrease very significantly upon increasing the photon energy.

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