Intensity Behaviour of the Long Wavelength UV Transition of the Pyridine Chromophore Under Substitution in the Para Position to the Nitrogen Atom

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ABSTRACT

When pyridine is para substituted to the nitrogen atom, the intensity of the long wavelength electronic transition is strongly decreased compared to the ortho and meta derivatives. N belonging to the ring, plays the part of a donating center when a strong electron withdrawing substituent is in the para position, and the part of an attracting center when faced to a donating substituent. The local transition moment vector of N, is in both cases opposed to the vector of the substituent. Furthermore, the π HOMO is priviledged (instead of the two highest π MO in benzene), and this HOMO does not allow a strong interaction with the substituent in the para position.

EXPERIMENTAL

Intensity of Pyridine under Substitution

Substituting pyridine by : -CHO, -CO_2H, -CH_3, -$C(CH_3)_3$, -OCH_3, or NH_2, on the para position to the nitrogen atom, causes a decrease of the intensity of the low energy transition (250-260 nm in the pyridine molecule) compared to substituents in the ortho or meta positions (Table I). Such a surprising behaviour is only scarcely observed considering the benzene chromophore as a model.[1,2-9]

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TABLE 1

Molar extinction coefficients of pyridine derivatives ; medium : i : isooctane, w : water (w,pH), h : heptane, hx : hexane, d : dioxan, m : methanol

		ortho	meta	para
-CH3	$\Rightarrow \varepsilon_{max}$	2365 [13a] (i)	2240 [13b] (i)	1560 [13c] (i)
	ε_{corr}	2190	1865	1185
	ε_{max}	3560 [14](w)	3110 [14](w)	2090 [14] (w)
-Et	$\Rightarrow \varepsilon_{max}$	3690[14](w)	3210[14](w)	·2150[14](w)
-CMe3	$\Rightarrow \varepsilon_{max}$	3400[14](w)	3230[14](w)	2120[14](w)
-CHO	$\Rightarrow \varepsilon_{max}$	3750[15,11b](h)	3630[15](d)	2400[15](d)
-OCH3	$\Rightarrow \varepsilon_{max}$	3230[16a](w,7)	3960[16a](w,7)	2000[16a](w,9)
	ε_{max}	3650[15,11c](h)	3550[15] (m)	(2000)[15](w)
-NH2	$\Rightarrow \varepsilon_{max}$	4100[15] (hx)	4200[15](hx)	(980)[15](hx)
	ε_{max}	3800[14](hx)	3500[14](hx)	
	ε_{max}	3800[16b,17](w,9.5)	3000[16b,17](w,9)	2400[16b,17](w,12)
	(neutral amine species)			

Pyridine $\varepsilon_{max} = 2000^{11d}$(hx) ; $\varepsilon_{sm} = 1950$, ε_{sm}, corrected $= 1575$

Benzene and the Interaction Vector Model (IVM)

Owing to the D_{6h} symmetry of its π system, the intensity of the secondary transition of the benzene molecule is forbidden ($\lambda = 255\text{-}260$ nm ; $\varepsilon_{max} = 220$, medium hexane).[10] It can increase when perturbing the symmetry. The nature of the spectrum itself is changed when a strong π donating and a strong π withdrawing substituent destroy the D_{6h} symmetry. Nitrophenols[11a] display the next ε_{max} for the long wavelength transition in water: 3050 (ortho - $\lambda = 351$ nm), 1950 (meta - $\lambda = 333$ nm), and 9500 (para - $\lambda = 317$ nm).

The Sklar's vector model of intensity [1] has been superseded by the *Interaction Vector Model* [2-9] (IVM). In the IVM, as in the Sklar's approach, a basis vector **n** [2,3] is
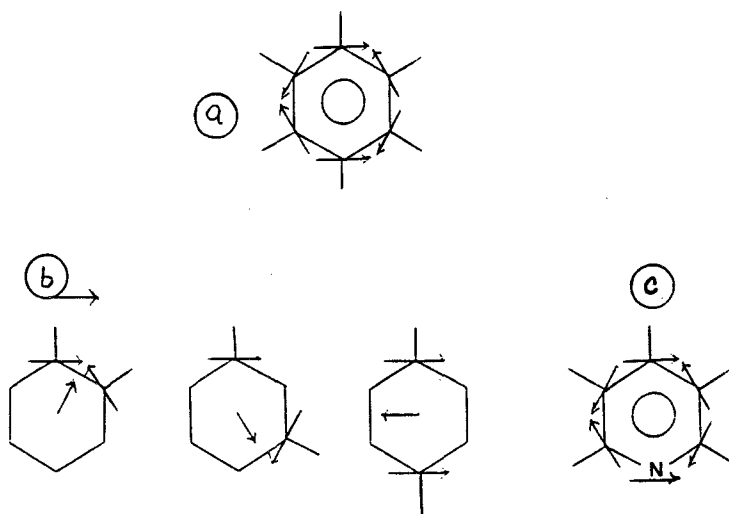
FIG. 1. a) The old Sklar's vector scheme for the benzene chromophore. A substituent on a given position, " activates " the corresponding basis vector, making it effective and contributing to the transition moment vector of the secondary transition. It is as much long as the substituent is efficient to perturb the π_ϕ system. b) The direction of the interaction vectors concerning the ortho, meta and para substituents, are shown in the center of the benzene ring. c) The vector scheme for the pyridine ring for substituents which could be able to display the same effects as the nitrogen atom.

ascribed to each position of substitution (Figure 1). New concepts are used : *interaction vectors*; *strain vectors*, S (UV cross section) which increases, as much as, the substituents enlarges the π system, a vibrational contribution V. The molar extinction coefficients of the maximum of the smoothed graph (ε_{sm}) are used [12]. Here, IVM cannot be used on a large scale since one lacks experiments, in a given solvent, necessary for parametrizing. A part of the problem lies in solvent effects. Working on a qualitative basis, we use only **n**, comparing ε_{max} instead of ε_{sm}.

Intensity of Pyridine Derivatives

The nitrogen atom forbids the D_{6h} symmetry. Thus, the transition of the secondary like transition is slightly allowed ($^1B_1 \Leftarrow ^1A_1$, C_{2v}). Intensity increases to ε_{251nm} = 2000 (medium: hexane). N belonging to the ring, does not display the same effects on the

π electrons as an external substituent would do. The observed low value of intensity for para substitution is surprising. It is inconsistent that π withdrawing and π donating substituents display the same intensity effect on the pyridine π system already polarized by N.

Considering N as a π electron attracting center [its π density is 1.1538 (MNDO calculations)], the basis transition moment vector of N and that of a π withdrawing substituent in the para position to N should point in the same direction; intensity should increase. On the contrary, the basis vector of a π donating substituent should point in the opposed direction (or at least should display a strongly different behaviour). Intensity should decrease if the interaction is weak. If the interaction would be strong it should polarize strongly the π system, and intensity should very strongly increase. Actually, when in para positions of a benzene ring, two substituents X (π donating), and Y (π withdrawing), display a strong conjugation through the ring ($^{+\delta}X{=}\phi{=}Y^{-\delta}$), changing the nature of the chromophore intensities, and a charge transfer transition arises (Note: N being part of the ring, one cannot observe the same interaction with pyridine). Nevertheless, when pyridine is substituted by -OH, -SH, -NHR, -CHR$_2$ etc. a tautomeric form can exist, an H atom can be exchanged between the substituent and N. This is the reason why OCH$_3$, -CHO can be studied here, and not -OH or -CO$_2$H : H$^+$ can fix on N inducing complex equilibria. This could happen too for -NH$_2$ [16c]. In fact, hexane limits the tautomeric ionic structures. The exchange in water has been studied by Mason[17] who has shown that basic conditions allow one to obtain the neutral species, without tautomerism. CMe$_3$ is used here to check the results concerning the methyl (no H transfer to N).

The $n \rightarrow \pi^*$ transition involving the non-bonding electrons of N superimposes to the secondary like one. It is roughly : $\varepsilon_{sm} = 375$, for non protonating solvents. This value has been assumed constant for the all pyridines studied. In order to prevent solvation effects, spectra in aprotic non-polar solvents should be used. Owing to their scarcity in literature, data in various medium have been used. Actually, it is possible to find data in protonating solvents assuming similar effects on the lone pair for several states of substitution of a given substituent. The intensity of the para derivative is generally lower than the intensity of the ortho and the meta derivatives.

In hexane the intensity of the 250 nm transition of pyridine is : $\varepsilon_{sm} = 1950$. Thus, the secondary-like transition, corrected from the overlaping $n \rightarrow \pi^*$ one, displays the next value : 1950 - 375 = 1575.

INTENSITY OF THE SECONDARY-LIKE TRANSITION IN SOME MONOSUBSTITUTED PYRIDINES
The Picolines Series (-CH3 or -CMe3 substituents)

In isooctane : ε_{max} = 2365 (ortho derivative), and : 2365 - 375 = 1990 for the secondary-like transition alone. The meta derivative displays : ε_{max} = 2240, ie : 2240 - 375 = 1865, and the para derivative : ε_{max} = 1560, i.e., 1560 - 375 = 1185. When going from the pyridine molecule to the ortho derivative intensity increases. There is a substituent effect on the vibrational part of the transition (V) which tends to slightly increase intensity [11]. Hyperconjugation extends the π system and S increases slightly. Furthermore, if N is a π attracting center (it accumulates π electrons), and CH3, a π electron donating substituent, addition of their basis vectors (n) increases the transition moment vector. For the meta substitution, the length of the resulting vector does not change much compared to the ortho substituted case.

The main fact is the strong intensity decrease when a -CH3 is in the para position : ε_{max} = 1185. Within the IVM, and the Sklar's approach, the two basis vectors, one for the N position and one for CH3, should point in opposing directions because N is electron attracting (its π density is 1.1538), and -CH3 is electron donating.

Using -CMe3 : ε_{max} = 3400, 3230, 2120 (water) shows that the low intensity for the para substitution is not caused by a tautomeric exchange involving H. Intensities are higher than for the methyl series because water solvates N, distorting the D_{6h} symmetry.

Other Derivatives

As concerns COH in the para position, if N is considered as an attracting center, COH, being electron withdrawing, one should observe an increase of intensity when it is in the para position to N, since the basis vectors should point in the same direction. In fact, N, being electron attracting inside the π system of the chromophore, is electron rich. Faced to a strong electron attracting substituent, such as -COH, it could be able to give a part of its electron excess. This would lead, owing to the IVM, to an intensity increase for substitution in the ortho or meta positions and a decrease for the substituent in the para position.
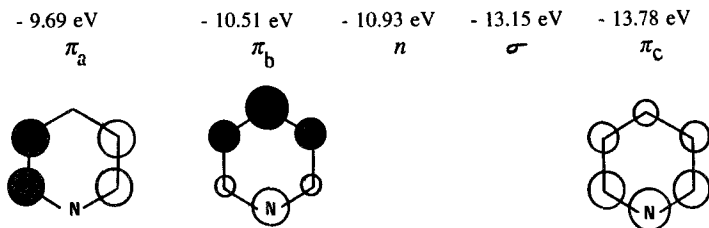
When the substituent is π donating, that is to say electron rich (-CH3, -OCH3...), N could play the part of an attracting center. This would also lead to a strong decrease of intensity, for a substituent in the para position to N (basis vectors pointing in opposed

directions). In pyridine the a density on the nitrogen atom is 1.154. The π electron density on N for the methyl substituted derivative in the para position is : 1.151. This is not very conclusive concerning the methyl. It is necessary to use a group displaying a stronger effect, such as a methoxy one. In this latter case, the a density on the nitrogen atom is 1.185 for the methoxy substituent in para to the nitrogen atom (the same when using an OH substituent). N plays the part of a aattracting center. When using -COH, the π nitrogen density decreases to 1.128. The nitrogen atom appears as a donating towards - COH. Thus, whatever the substituent in the para position is (-OCH3 or -COH), provided that the substituent is strongly a donating, **or** strongly a attracting, the nitrogen atom tends to behave in a way contrary to the nature of that substituent : increasing its own a electron density ; and playing the part of an electron attracting center, when the substituent is a π donating one (-OCH3), and decreasing its own a electron density (electron donating center) when the substituent is a a electron withdrawing one (-COH).

The aelectrons which are taken into account on N, " belong " to the whole π MOs, whatever their potential is, whatever the ability they display to be involved in a transfer, whatever their importance in the electronic transition. It has been shown that the New Vector Model NVM), using MNDO calculations [18] grounded on the two highest a occupied orbitals degenerate in benzene and almost degenerate in the studied benzene derivatives leads to satisfactory results.

In pyridine, N removes the degeneracy. The two HOMOs are no more equivalent. N lies on a node of π_a, and on an amplitude extreme of π_b. The gap between the two highest occupied molecular orbitals π_a and π_b in pyridine is 0.82 eV (MNDO), a high value. π_a and π_b cannot play the same part contrary to what they do in the benzene molecule. π_a, being the true HOMO, should display the most important part in the intensity calculation. In π_a, N being on a node, the second node lies in para to N (Figure **2**). Thus, a substituent in para to N, being on a node of π_a, cannot couple strongly with π_a, and cannot perturb efficiently the electronic density, thus the symmetry ; and intensity is weak.

The two above explanations, grounded on IVM and NVM, are not contradictory. When the substituent is in the ortho or the meta position to N, π_a and π_b can be involved in the interaction (π_a is the most important). The substituent distorts the amplitudes of π_a and π_b and the distribution of their a densities. Within the IVM, that distorsion of π

- 9.69 eV   - 10.51 eV   - 10.93 eV   - 13.15 eV   - 13.78 eV

π_a π_b n σ π_c

FIG. 2. The highest π occupied molecular orbitals in pyridine. The nitrogen atom lies on a node in π_a. Two non π MOs lie between π_b and π_c.

densities is taken into account by vectors whose lengths and directions are empirically determined using reference molecules. Neither is considered identifying what precisely in the π system is distorted compared to the D_{6h} π system of benzene, nor what in the distorsion of the amplitudes is responsible for the intensity changes. Only interested in the direction to give empirically to the different **n**, and by the consideration that the interaction is acting as a π donating or a π withdrawing one. Actually, when saying that a substituent displays a π donating effect, this effect is related to the whole population of the π system, whatever the molecular orbitals involved. When considering the problem from a spectroscopic point of view, and the intensity of the secondary like transition only, the third π_c orbital (in the free benzene chromophore) is neglected. Thus, within the IVM, the donating or withdrawing effect, taken into account, is the effect imposed on π_a and π_b. When considering the para position, the electronic effect on π_a is much weaker than the effect on π_b. Mainly the interaction with π_b is important for intensity. When saying that a given substituent is π donating or π withdrawing, as concerns the IVM, that means that it is the π_b orbital which is mainly distorted. Electronic effects should increase or decrease densities in that MO.

The IVM mirrors the overall phenomenon. The NVM tries to distinguish among the orbitals involved.

CONCLUSION

N, in the pyridine ring, plays the part of a donating center when a strong electron withdrawing substituent is in the para position, and the part of an attracting center when

faced to a donating one. The local transition moment vector ascribed to N, is in both cases opposed to the vector of the substituent. This decreases the resultant vector, and the intensity for a para substitution to N. The π HOMO has to be priviledged in pyridine, and this MO does not allow a strong interaction with the substituent in para position to N.

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