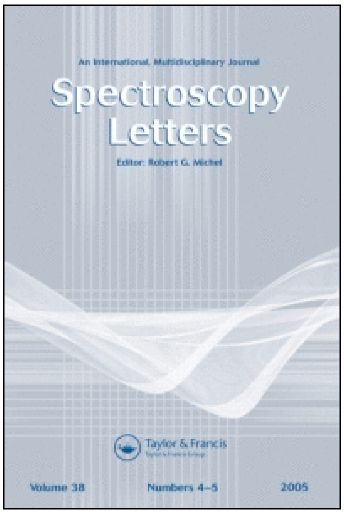

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INTENSITY OF THE SECONDARY TRANSITION OF SEVERAL ANILINIUMS IN AN ACID MEDIUM

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The UV spectrum of the secondary transition (towards 260 nm) of the anilinium ion (ϕNH_3^+) undergoes an increase of its intensity when the acidity of the medium increases at pH < 0 further than the complete protonation of the amine species. That phenomenon has been studied in a preceding work(1)(2), showing also that, contrary to the accepted opinions in UV spectroscopy(3)(4)(5), ammonium groups may interact by a "through space" coupling with the π_ϕ cloud. That coupling could be described as an hyperconjugative coupling since hyperconjugation can be extended to groups whose the central atom involved in the process is not a carbon atom (6-9). Furthermore , although some spectra which have never been studied are recorded in handbooks(10), except our preceding works the UV spectroscopy of aniliniums is almost unknown. However these ions are light and very simple species; they are "basic" molecules in organic chemistry. The lack of knowledge concerning them comes from the fact that they exist only in an acid medium and that their spectra are very sensitive to the acidity, as we have precedently shown for ϕNH_3^+. We extend in the present work our observations to the species $\phi NH_{3-n}^+(CH_3)_n$ where n is, in addition to 0 :1,2 or 3, and to $\phi_2NH_2^+$ and ϕ_3NH^+ whose spectra are completely unknown, in order to study the ampli-

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tude of the phenomenon and to find what are the factors governing its evolution from an anilinium to the other.

THE SECONDARY TRANSITION OF THE ANILINIUMS

The intensity of the secondary transition of the benzene chromophore increases in a very acid medium because the acid species can exert a perturbation on the electrons of the π_ϕ cloud. Such a perturbation, with that coming from the σ,π coupling which involves the chromophore and the bonds N-H or N-CH_3 of the substituent, distorts the symmetry of the π_ϕ cloud from D_{6h} - as it is in the benzene itself when the transition is forbidden - towards C_s, where all the transitions are allowed, so that the intensity increases(1-2).

The secondary transition of the aniliniums consists mainly of two progressions A and B (Figures). The progression A is observed, without B, with a low intensity, when the symmetry is D_{6h} and the transition forbidden. In addition to benzene itself, it is also the case of molecules in which the π-donating or π-withdrawing electronic effects of the substituent are non existent, or very small. The progression B, whose intensity is generally evaluated by the value ε_{00} of its 00 band, is superposed upon the progression A when the transition is allowed, and B is all the more intense as the transition is more allowed. In other words it is all the more intense as the π_ϕ cloud is coupled to orbitals outside of the ring. This mixing of orbitals distorts the symmetry towards C_{2v} where the transition is allowed(6)(11-16). So, the solvation effect on the π_ϕ cloud - for which we will use the notation $\overset{+}{H},\pi$ - can increase the intensity only because it exists already a σ,π coupling. Without the latter the $\overset{+}{H},\pi$ perturbation alone should distort the symmetry towards C_{6v} for which the transition is still forbidden. The C_s symmetry, being lower than a C_{2v} one, an increase of intensity is favoured.

Thus, logically, the efficiency of the solvation to increase the intensity should depend on the strength of the σ,π coupling already in action. The intensity should be all the more increased as it is already higher. On the contrary our present experiments show that the species which have the lowest intensities - that is to say those which have the lowest σ,π coupling - undergo the greatest increases. We should like to show that, in fact, this discrepancy is only apparent. The experiment can still be explained on the ground of the factors reviewed above; but other facts have to be taken into account: the perturbation induced by the medium on the intramolecular σ,π coupling and the possibilities of equilibrium of the molecular ion (which we will name sometimes: molecule) with the medium.

EXPERIMENTAL RESULTS

The aniliniums studied here, except for ϕNH_3^+, are slightly unstable in a very acid medium (H_2SO_4-98% ; pH ≃ -2,5). Thus the intensity of the secondary transition taken as a whole - that is to say without modification of the vibrationnal repartition of the intensity - decreases slightly with time. For the methylated species, the spectra of impurities - very broad - appear at higher wavelength than the secondary transition and do not overlap that latter. The incidence of such a problem on the measure of the intensities is lowered by preparing the solutions directly before recording the spectra. For $\phi_2NH_2^+$ and ϕ_3NH^+ in H_2SO_4-98% there is an overlap of the spectra of the impurities produced in the medium, with the secondary transition. Nevertheless the rate of formation of these impurities is low enough for $\phi_2NH_2^+$ to obtain the spectrum without further correction. On the contrary the spectrum of ϕ_3NH^+ needs to undergo a deconvolution since, mainly in H_2SO_4-98%, it is superimposed to another absortion whose intensity increases with time. The deconvolution is easy for the impurity has a very broad spectrum.

We shall point out that for the methylated aniliniums the increase of the system B in an acid medium is not restricted to H_2SO_4. It is observed in HCl too, where the instability is less pronounced. The increase of B compared to A is significantly observed until 3,5N of HCl is reached in the medium, without decrease of the total intensity of the transition with time. Thus, if there is a reaction with the medium, only an insignificant part of the aniliniums is involved. At acidity higher than 4,8 N in HCl the solutions becomes slightly coloured, showing that some sort of complex, or carbocation ... could be produced.

We have choosen to present ou results obtained in H_2SO_4. In that medium higher acidities can be reached, allowing a greater amplitude to the phenomenon. Furthermore ϕ_3NH^+ is produced only in H_2SO_4. For that molecule the medium needs to be more acid than H_2SO_4 55-60% since its pK is very low (pK=0 $^{(17)}$).

We have had to take into account the evolution with time to calculate the intensities when the aniliniums are in the very acid medium. The correction has been evaluated by comparing the spectra with other spectra of the secondary transition showing the same relative intensities in the vibrationnal structure. The correction is easy to evaluate for $\phi N^+(CH_3)_3$ since the relative intensities of A and B do not change when going from a medium H_2SO_4-5% to a medium H_2SO_4-98%. A modification in the intensity of the transition should appear as a modification of B compared to A. Thus, the intensity in the two mediums are nearly the same. We have had to correct the intensity of that trimethylated anilinium in H_2SO_4-98% by increasing its value of 5%. The correction has been 7% for $\phi NH_2^+CH_3$ and $\phi NH^+(CH_3)_2$ respectively.

In the aromatic derivatives the intensity of the system B, which is characteristic of the perturbation brought upon the symmetry of π_ϕ, is generally measured at the 00 band. That band appearing on the longwavelength side of the transition is the most clearly distinguishible band of the system. To measure its intensity, and the increase of its intensity with the increasing acidity, we have taken into account the overlap with the system A. When going from 5% to 98%-H_2SO_4 the intensity is multiplied by :

	8,0	2,8	1,5	≈1,0
for :	ϕNH_3^+	$\phi NH_2^+CH_3$	$\phi NH^+(CH_3)_2$	$\phi N^+(CH_3)_3$

We shall point out that the change for the trimethylated species is very low, but not absolutely non existent. We see that although our precision could be questionned about some per cent on the intensities of the spectra, the changes from an anilinium to the other, for the increase of the 00 band, are significative since the lowest one goes from 1,5 to 1.

ORIGINS OF THE CHANGES IN THE INCREASE OF THE INTENSITY IN AN ACID MEDIUM.

The increase in a given acidity of the intensity, when the number of $-CH_3$ linked to the nitrogen atom increases, has been precedently explained(1-2).

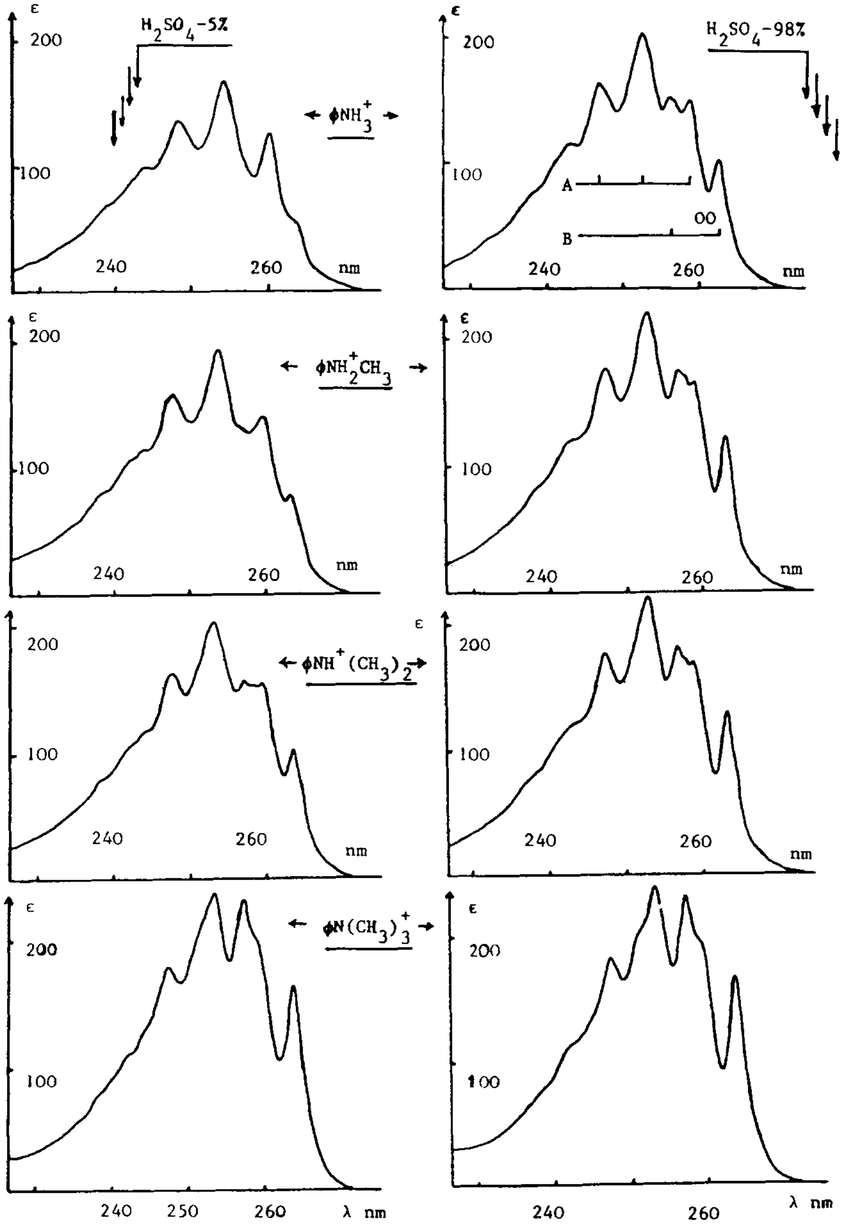
The distribution of the positive charge on the ions influences the formation of the solvation shell. Nevertheless it is difficult to think that its changes from a species to an other species could be sufficient to prevent an association of the medium with π_ϕ. Nevertheless,to check that point we have calculated by means of the MNDO method the effective charge on the carbon atoms of the ring. First of all, the charge is negative. Such a result support our preceding assumption of an association of the positive acid species with the aromatic ring.. The major part of the charge is located on the atom linked to N and decreases slightly when the number of methyles increases : -0,1671 ; -0,1530 ; -0,1407 ; -0,1253. The carbon located in the para position bears a positive charge : +0,0244 ; +0,0181 ; +0,0133 ; +0,0091. The decrease of the negative charge on the carbon linked to N is weak and cannot cause the quenching of the association with the acid species. Furthermore, in fact, we have to take the whole charge on the ring into consideration to evaluate the attracting effects involving that ring and the acid species. That charge is almost a constant when the number of methyles increases : -0,2228 ; -0,2264 ; -0,2278 ; -0,2275. Thus the association with the medium can exist for all the species.

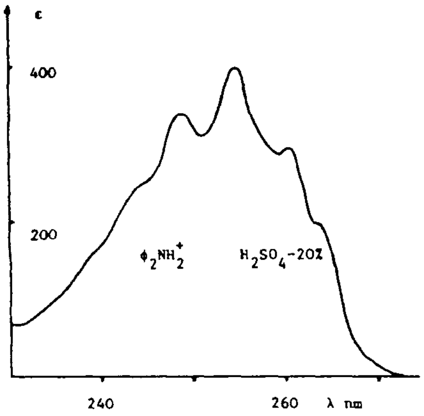
Two factors can be put forward to explain the decrease of the efficiency of the sulfuric medium when the number of $-CH_3$ increases.

If the solvation can introduce a perturbation on the symmetry of the π_ϕ cloud, in other words if the electrons of that cloud are involved in some sort of bonding with the medium, that solvation can also certainly operate upon the electrons involved in the σ,π

coupling which links through space the substituent and the chromophore. Previous results [(13)] suggest that the vulnerability of these electrons - and the vulnerability of the coupling - towards the acid species must increase when the number of N-H bonds decreases. As a matter of fact we have shown that the N-H bonds, because they are short and because the bonding electrons are near to N, have little efficiency to generate a coupling with π_ϕ. So the σ,π coupling is weak in ϕNH_3^+ and involves electronic exchanges near to the σ frame of the molecule. In $\phi \overset{+}{N}H_2CH_3$ the efficiency of the σ,π coupling increases, owing to the fact that the N-CH_3 bond is longer than the N-H one, and that the bonding electrons are held farther from N, so the overlap involving the σ orbitals of the substituent and π_ϕ is greater. Yet this σ,π coupling involves electronic exchanges farther from the σ frame than for ϕNH_3^+ and so it is more sensitive to the perturbations of the medium. Several phenomena can occur when the acidity is increased : The solvation H^+,π of π_ϕ leads to an increase of ε_{oo} (the molar extinction coefficient of the 00 band), since with the σ,π coupling that perturbation distorts the symmetry towards C_s. At the same time the solvation can quench the σ,π coupling which allows the solvation on π_ϕ to have a spectroscopic efficiency. This latter phenomenon leads the intensity to decrease because on the one hand the σ,π perturbation decreases, on the other hand that perturbation decreasing, the solvation is less efficient to distort the symmetry towards C_s. Thus the increase of intensity by solvation involving the acid species of the medium should be weaker for $\phi \overset{+}{N}H_2CH_3$ than for ϕNH_3^+. The same holds true when another $-CH_3$ is introduced. The sensitivity to the medium of the σ,π coupling is increased, the quenching also and the increase of intensity is less and less apparent when going through the series ϕNH_3^+, $\phi \overset{+}{N}H_2CH_3$, $\phi \overset{+}{N}H_2(CH_3)_2$, $\phi N^+(CH_3)_3$.

Paralleling the above hypothesis we must point out that the number of hydrogen atoms potentially acid is reduced all along the series. The highest is the number of hydrogen atoms linked to N, able to be involved in an acido-basic equilibrium with the solvent, the best the species will be solvated and the best it will be


ε
200
100
H_2SO_4-5%
H_2SO_4-98%
← ϕNH_3^+ →
A
B
00
240
260
nm
← $\phi NH_2^+CH_3$ →
← $\phi NH^+(CH_3)_2$ →
← $\phi N(CH_3)_3^+$ →
240
250
260
λ nm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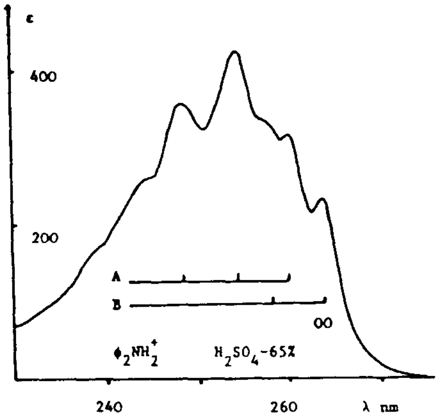
400
200
Φ2NH2+
H2SO4-20%
240
260
λ nm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200
A
B
00
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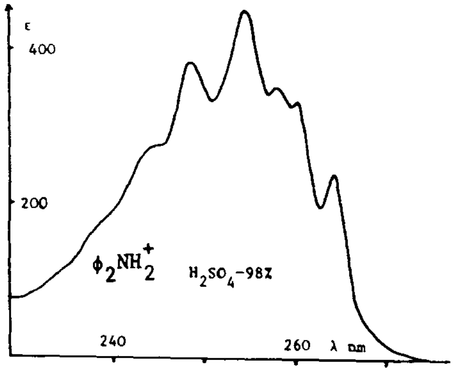
240
260
λ nm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400
200
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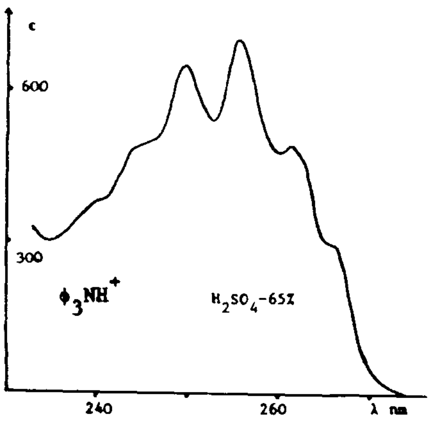
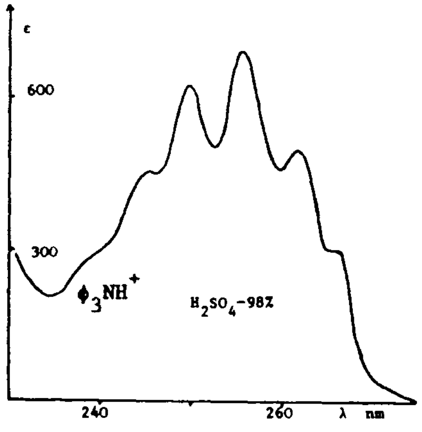
H2SO4-98%
240
260
λ nm


ε
600
300
Φ3NH+
H2SO4-65%
240
260
λ nm


ε
600
300
Φ3NH+
H2SO4-98%
240
260
λ nm

able to undergo the $\overset{+}{H},\pi$ effect. So ε_{00} will increase. Nevertheless, although the acid hydrogens could play a part, the intensity is slightly modified in $\phi N(CH_3)_3^+$ where there is none. Furthermore there is no increase of the intensity for ϕ_3NH^+ where there is an hydrogen linked to N. Thus the number of H although it could favour the interaction $\overset{+}{H},\pi$ is not the main factor. Its effects depend also on the series of aniliniums involved.

The increase of intensity in the series ϕNH_3^+, $\phi_2NH_2^+$, ϕ_3NH^+ (ϕ_4N^+ does not exist) cannot be measured between 5% and 98%-H_2SO_4 since under 65% the species ϕ_3NH^+ is not easily observed. We have measured the intensities between 65% and 98%-H_2SO_4. The increase is 2,38 for ϕNH_3^+, 1,08 for $\phi_2NH_2^+$ and $\simeq$1,0 for ϕ_3NH^+. That observation parallels qualitatively the precedent one on the N-methylated aniliniums and deserves the same explanation. But on the contrary of the methylated series, where there is an increase of intensity when adding more substituent on N, we obtain $(\varepsilon_{00})_{1\phi}$= 65, 115, 100 for ϕNH_3^+, $\phi_2NH_2^+$ and ϕ_3NH^+ in H_2SO_4-65% , with a decrease when a third substituent is added on N. That observation could be linked to the fact that the increase of intensity in this series is less than in the methylated one (taking into account the lowest range of acidity possible) as we shall see hereunder.

In the amine forms the "non-bonding" electrons on N, are all the more included in the π systems as there are more phenyl chromophores. The pK decreases : pK=4,65$^{(18)}$for ϕNH_3^+ , 0,85$^{(17)}$for $\phi_2NH_2^+$ and 0 $^{(17)}$ for ϕ_3NH^+, since, because of their increasing π character , the "non-bonding" electrons are more firmly bound. Thus to obtain the aniliniums the acid medium has to strongly interact with the π systems to which these electrons belong. The increased solvation could prevent the π electrons to couple with the substituents. The σ,π coupling being weakened when the number of ϕ increases, $\phi_2NH_2^+$ and ϕ_3NH^+ should have lower intensities than their homologues bearing one or two CH_3 instead of one or two extra phenyl groups. Thus for these molecules with several ϕ there is not only the quenching appearing when the number of N-C bonds increases as in the methylated aniliniums, but there is also the quenching coming from the increase of the number of π systems. the increase of intensity in an acid medium will be weaker for them since the σ,π coupling which is necessary to observe the spectroscopic incidence of the solvation is weakened. We see that the solvation which, by interacting with π_ϕ, can increase the intensity because there is a σ,π coupling involving π_ϕ and the substituent, can also, when it is strong enough quench that coupling and prevent the increase of intensity.

CONCLUSION

The UV spectroscopy of the aniliniums is very much dependent of the medium. The solvation $\overset{+}{H},\pi$ increases the intensity of the secondary transition because, with the σ,π coupling,it distorts the symmetry of the π_ϕ cloud towards C_s. It should lead to an increase all the more important as the σ,π coupling is stronger. In fact two phenomena can restrict that increase. On the one hand the decreasing number of hydrogen atoms on the nitrogen weakens the interaction of the aniliniums with the medium. On the other hand the quenching of the σ,π coupling by solvation when the number of methyles increases - since the σ,π coupling becomes more and more vulnerable to the acid species - changes the symmetry. Furthermore the acidity, when there is an increasing number of phenyl groups linked to N can also quench all intramolecular interaction.

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