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### The Dualistic Nature of -NH<sub>3</sub>, A weak $\pi$ -Donating, Strong $\sigma$ -Withdrawing Substituent. Effects on the Intensity of the UV Spectra of the Toluidinium Ions and Related Molecules

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THE DUALISTIC NATURE OF  $\text{-NH}_3^+$ , A WEAK  $\pi$ -DONATING,  
STRONG  $\sigma$ -WITHDRAWING SUBSTITUENT. EFFECTS ON THE  
INTENSITY OF THE UV SPECTRA OF THE TOLUIDINIUM IONS  
AND RELATED MOLECULES.

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Hyperconjugation is not restricted to alkyl groups<sup>(1-4)</sup> and ammoniums interact with  $\pi$  systems through  $\sigma$ - $\pi$  hyperconjugative coupling<sup>(5-9)</sup>. Their influence on the UV spectrum of the secondary transition of the benzene chromophore in anilinium ions has only been studied during the last years. Previously it was assumed without enough experimental support, that ammonium groups have no spectroscopic effects on a  $\pi$  chromophore (for example:<sup>(10,11)</sup>). In fact, although it is a strong  $\sigma$ -electronwithdrawing substituent, an ammonium group is a  $\pi$ -donating one<sup>(5-8)</sup>. Its  $\pi$ -donating ability - contrary to what is observed in the corresponding alkyl groups where N is replaced by C - increases whenever the number of  $\text{N}^+\text{-C}$

bonds increases, and  $-N(CH_3)_3^+$  could be as much  $\pi$ -donating as the  $-C(CH_3)_3$  group for pseudo-free molecules<sup>(5)</sup>.

Such a dualistic behaviour ( $\sigma$ -Withdrawing,  $\pi$ -donating) makes difficult to understand the spectroscopic effects of the ammonium groups in the anilinium type ions. There has been no proof until now that the ammonium group still displays a  $\pi$ -donating ability when there is another  $\pi$ -donating group linked to the benzene chromophore. Its spectroscopic influence could be changed.

In this paper we present a study on the effects of ammonium groups in toluidinium ions, using the CNDO and MNDO methods, together with the spectroscopy of the secondary transition of the benzene chromophore (towards 260 nm). The intensity of the secondary transition is linked to the distortion of the symmetry of the  $\pi$  system. When the symmetry is  $D_{6h}$  the transition is electronically forbidden as in benzene itself and there is only a weak progression called A. When the symmetry is distorted from  $D_{6h}$  towards another symmetry (such as  $C_{2v}$  for example), a new progression called B is observed, provided the secondary transition is allowed by the new symmetry. The bands of the progression B are lying between the bands of the progression A. The 00 band of the new progression is clearly visible on the long wavelength side of the spectrum. It has often been used to evaluate the intensity ( $\epsilon_{00}$ ) of the secondary transition<sup>(12-14)</sup>.

### CNDO AND MNDO CALCULATIONS

Preceding works have shown that the MNDO method compared to the CNDO and to the *ab initio* ones leads to a lower number of  $\pi$  electrons in aniliniums<sup>(8)</sup>. The CNDO method is more accurate for the study of these charged species, giving results nearer to those obtained by *ab initio* methods, and nearer to what could be deduced from experiment. As CNDO is more accurate for our present purpose we shall only discuss its results. Nevertheless we have checked that the MNDO method leads qualitatively to the same results.

For example, MNDO and CNDO show that in the toluidinium ions the two groups are still  $\pi$ -donating. In the orthotoluidinium ion the number of electrons given by the substituent to the  $\pi$  system is  $n = 0.0191$ . In the meta isomer  $n = 0.0238$ , and in the para one  $n = 0.0257$ . In the same conditions  $n = 0.0094$  for toluene and  $0.0043$  for the anilinium ion itself ( $\phi\text{NH}_3^+$ ). These results are quite surprising. Actually, when there are two  $\pi$ -donating substituents (such as two methyls or two OH for example) the number of  $\pi$  electrons given to  $\phi$  is often almost additive. Our calculations on toluidinium ions show that when the chromophore bears the two groups  $-\text{CH}_3$  and  $-\text{NH}_3^+$  there is no quenching of the global  $\pi$ -donating effect; on the contrary the effect is increased ( $n = 0.0257$  for the para isomer) compared to the sum of the two separate  $\pi$ -donating effects. That sum is  $0.0094 + 0.0043 = 0.0137$ .

In the paratoluidinium ion the number of electrons given to the  $\pi$  system is almost twice the number which could have been expected. Such results show that there is a strong interaction between the two substituents. Although the number of  $\pi$  electrons is lower in the two other toluidinium ions, the interaction still exists.

The  $-\text{NH}_3^+$  group, being a  $\sigma$ -withdrawing substituent, increases the core attractions in the benzene nucleus. The  $\pi$ -electrons are more firmly attracted towards the  $\sigma$ -frame and the electrons of the pseudo- $\pi$  orbitals of  $-\text{CH}_3$  (orbitals built using the C-H bond orbitals) are more attracted towards the  $\pi$  system through the hyperconjugative  $\sigma$ - $\pi$  coupling. Actually the HOMO of  $-\text{NH}_3^+$  ( $-13.84$  eV) is lower than the HOMO of benzene ( $-9.46$  eV) and of toluene ( $-9.36$  eV). Thus, because of  $-\text{NH}_3^+$  in the toluidinium ions,  $-\text{CH}_3$  is linked to a group more  $\pi$  attracting than  $\phi$  alone. Although it is  $\pi$  donating,  $-\text{NH}_3^+$  seems to behave as a  $\pi$  attracting substituent since it induces  $-\text{CH}_3$  to give more electrons to the benzene chromophore.

The number of  $\pi$  electrons decreases when the two substituents come closer, in o-toluidinium specially. When  $-\text{CH}_3$  is near to  $-\text{NH}_3^+$ , that latter is more efficient to withdraw electrons from  $-\text{CH}_3$  through the  $\sigma$  bonds of the benzene chromophore; and the  $\sigma$  C-H

bonds of  $-\text{CH}_3$  are less able to be involved, as pseudo- $\pi$  hyper-conjugative orbitals, in a  $\pi$  donating exchange towards the  $\pi$  system. One could say that  $-\text{NH}_3^+$  "traps" the electrons of the  $-\text{CH}_3$  group in the  $\sigma$  skeleton, and the number of  $\pi$  electrons is all the less increased as  $-\text{CH}_3$  and  $-\text{NH}_3^+$  are nearer.

The two groups are  $\pi$  donors but they distort the  $\pi$  density quite differently. As it is well known  $-\text{CH}_3$  increases the electronic density in ortho and para positions, and our CNDO calculations mirror such a property (Figure 1). On the contrary  $-\text{NH}_3^+$  increases only - but strongly - the density on the site of substitution, and decreases the density on all the other sites. Thus  $-\text{NH}_3^+$  is not a classical  $\pi$ -donating substituent.

The  $\pi$  densities in the toluidinium ions can be understood on the qualitative basis of the coupled influences of  $-\text{NH}_3^+$  and  $-\text{CH}_3$ . In the para isomer the added influence of the two substituents, leads to a strong decrease of the  $\pi$  density at the site of substitution of  $-\text{CH}_3$  (since  $-\text{CH}_3$  tends to lower the density on its own site of substitution, and  $-\text{NH}_3^+$  in para to its own site). Furthermore,  $-\text{CH}_3$  causes an increase of the density in its ortho position, but this position is also the meta position to  $-\text{NH}_3^+$ , position where  $-\text{NH}_3^+$  induces a decrease. The two influences should be cancelled. Actually the density is near to 1 (Figure 2).

In the position meta to the  $-\text{CH}_3$  group, there should only be a small decrease of the  $\pi$  density, since the influences of  $-\text{CH}_3$  and  $-\text{NH}_3^+$ , are weak in that position.

Some points are worthy of notice when considering the other isomers. For example, in the meta toluidinium ion the  $\pi$  density at the site of substitution of  $-\text{NH}_3^+$  is weak compared to what happens in the ortho and the para isomers. Actually this site is meta to  $-\text{CH}_3$ , a site where  $-\text{CH}_3$  causes a decrease of density. On the contrary, as regards the ortho isomer, the site of substitution of  $-\text{NH}_3^+$  displays the greatest density observed in the three isomers. Actually, it is ortho to  $-\text{CH}_3$  and this is the site where  $-\text{CH}_3$  causes the greatest enhancement of density, increasing the density already increased by  $-\text{NH}_3^+$ .



FIGURE 1 :  $\pi$  densities in toluene and in the anilinium ion

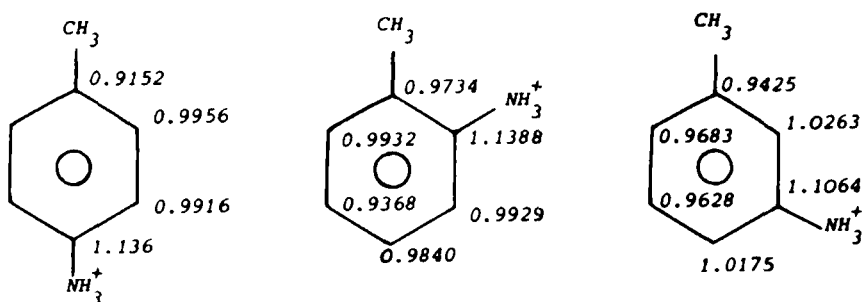


FIGURE 2 :  $\pi$  densities in the toluidinium ions

### INTENSITY OF THE SECONDARY TRANSITION

The spectra of the toluidinium ions are deeply puzzling when trying to understand them on the ground of two  $\pi$ -donating substituents. As these substituents introduce only small perturbations on the  $\pi$ -system of the benzene chromophore, the Sklar theorem<sup>(15)</sup> about the vector addition of the spectroscopic moments, should allow to calculate the intensities of the toluidinium ions, but it fails. This theorem which has been widely used, shows that whenever two  $\pi$ -donating substituents are in para the intensity should be much greater than what is observed for the ortho or the meta isomer. For example : toluene, o-xylene, m-xylene should have roughly the same intensity. Furthermore, p-xylene should display a higher intensity.

The experimental values are:  $\epsilon_{00} = 240, 210, 275$  and  $700$  (medium: hexane). That theorem holds fairly well when using  $\epsilon_{sm}$  (the maximum of the smoothed curve<sup>(16)</sup>) instead of  $\epsilon_{00}$ . With  $\epsilon_{sm}$  the incidence of the different vibrational structures (relative intensities of the vibrational bands; different widths) are minimized. In the present work,  $\epsilon_{00}$  is accurate enough to understand the evolution of intensity from one of the isomers to another. Nevertheless, to work on firmer basis, we shall use  $\epsilon_{sm}$  as well.

When considering the toluidinium ions, the main point to notice is the low intensity of the para isomer. As far as the ortho isomer is concerned  $\epsilon_{00} = 230$  and  $\epsilon_{sm} = 255$ ; for the meta one  $\epsilon_{00} = 295$  and  $\epsilon_{sm} = 285$ ; for the para one  $\epsilon_{00}$  is only  $225$  and  $\epsilon_{sm} = 240$  when it should be much higher than  $300$ . This result could be a mistake. Thus the series with  $-C_2H_5$  instead of  $-CH_3$  has also been studied. The intensities are  $\epsilon_{00} = 215, 255, 295$  and  $\epsilon_{sm} = 250, 270, 235$  as concerns the ortho, meta and para isomers respectively. The decrease concerning the para isomer still exists. The literature <sup>(17)</sup> gives similar results for the series with  $-CH_3$  and  $-NH^+(C_2H_5)_2$  for the ortho<sup>(17a)</sup> and para<sup>(17c)</sup> cases and  $-NH^+(CH_3)_2$  when the meta position is concerned<sup>(17b)</sup>. The fact that the ammonium group is not the same in the three compounds should not be too much disturbing since these data from the literature are only used to check roughly the evolution of intensity. The data are:  $\epsilon_{00} = 290$  then  $385$  and  $147$ . The decrease is quite strong when considering the para isomer: its intensity is much lower than what is observed for the ortho isomer. The same quenching of intensity is observed, strongly marked, in our present experiments, in the series of the dimethylated aniliniums when there is a methyle in para to  $-NH_3^+$ .

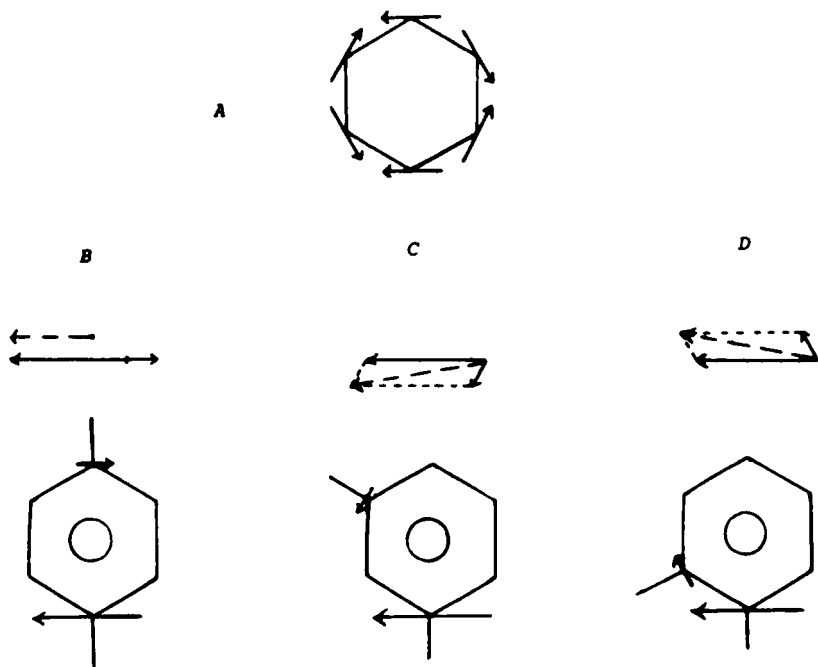
The origin of the above behaviour lies in the dualistic nature of  $-NH_3^+$  (it is a  $\sigma$ -withdrawing and a  $\pi$ -donating substituent). It has been shown in the beginning of our paper that, in the toluidinium ions - the  $-CH_3$  group is linked to a  $\pi$  system ( $-\phi NH_3^+$ ) which is more  $\pi$ -attracting than  $\phi$ , although  $-NH_3^+$  is a  $\pi$ -donating

group. The  $-\phi\text{NH}_3^+$  system is more  $\pi$ -attracting because its HOMO is lowered (the ionization potential is increased) under the  $\sigma$ -withdrawing action of  $-\text{NH}_3^+$  on the  $\sigma$  cores of the benzene ring. The  $\pi$  electrons are more attracted by the cores. As far as  $-\text{CH}_3$  is concerned, the  $\pi$  system becomes more electron attracting; for the  $\pi$  system,  $-\text{CH}_3$  becomes more electron donating. In other words, as far as the  $\pi$ -donating ability of the  $-\text{CH}_3$  group is concerned, the  $-\text{NH}_3^+$  group seems to be a  $\pi$ -withdrawing group (although it increases the electron density in the  $\pi_\phi$  system) because it induces the  $-\text{CH}_3$  group to give more electron to the  $\pi_\phi$  system. Thus, we observe in this work the first example of two  $\pi$ -donating substituents,  $-\text{CH}_3$  and  $-\text{NH}_3^+$  (the first one being a weak  $\pi$ -donating substituent, and the second one a very weak one), whose spectroscopic moments should point in opposite directions when considering them in the same situation. With such an assumption the vector addition (figure 3 gives three example to show how to proceed) leads to calculated values which mirror the observed intensities (Tables I and II).

The same is true in the series where the substituents are  $-\text{C}_2\text{H}_5$  and  $-\text{NH}_3^+$ . In this series the intensities are slightly lower than what is observed in the series with  $-\text{CH}_3$  and  $-\text{NH}_3^+$ . Actually,  $-\text{C}_2\text{H}_5$  displays a lower  $\pi$ -donating ability than  $-\text{CH}_3$ . This is observed when comparing toluene and ethylbenzene:  $\epsilon_{00} = 240$  as concerns toluene, and 215 as concerns ethylbenzene (medium : cyclohexane). In the latter molecule the symmetry is less distorted from  $D_{6h}$  by the hyperconjugative  $\sigma$ - $\pi$  coupling, and the transition is less allowed.

When alkyl substituents are linked to the nitrogen atom ( $-\text{NHR}_2^+$  for example) the ammonium group becomes a stronger  $\sigma$ -withdrawing group<sup>(18)</sup>, and a stronger  $\pi$ -donating one<sup>(5)</sup>. All the electronic effects, as well as their differences, should be enhanced. The modulus of the spectroscopic moment vector (transition moment vector) should be greater than the corresponding modulus used for the  $-\text{NH}_3^+$  group. Actually, the intensities of the ortho and meta isomer are enhanced compared to the corresponding toluidiniums. For





**FIGURE 3** : A) Vector addition of spectroscopic moments showing how change the directions of the components of identical substituents. B) Vector addition of two para substituents displaying opposite electronic effects (with different amplitudes) on the  $\pi$  system. C) the same for meta substituents. D) the same for orthosubstituents.

the para isomer the two vectors lie on the same axis and they point towards opposite directions. As the modulus of the spectroscopic moment vector concerning the  $-\text{NHR}_2^+$  group is greater than the modulus concerning  $-\text{NH}_3^+$ , but still smaller than the modulus concerning  $-\text{CH}_3$ , the modulus of the resulting vector for the para isomer with  $-\text{CH}_3$  and  $-\text{NHR}_2^+$  is smaller than what is observed for the corresponding para toluidinium ( $-\text{CH}_3, -\text{NH}_3^+$ ).

One can see from the vector addition theorem, that the ortho and meta isomers must have the same intensities in a given series. When using  $\epsilon_{00}$  they are different, although the difference does not

TABLE I

ions	$\epsilon_{00}$	$\epsilon_{sm}$ exp.	$\epsilon_{sm}$ calc.
o-toluidinium	230	255	275
m-toluidinium	295	285	275
p-toluidinium	225	240	230
o-ethylanilinium	215	250	255
m-ethylanilinium	255	270	255
p-ethylanilinium	195	235	220
2,3-dimethylanilinium	285	275	290
2,6-dimethylanilinium	365	365	290
2,5-dimethylanilinium	630	575	525
2,4-dimethylanilinium	225	250	245

Medium HCl+H<sub>2</sub>O (pH=1.5)TABLE II

ions	$\epsilon_{sm}$ exp.	refer.	$\epsilon_{sm}$ calc.
2-methyl-NNdiethylanilinium	370	(17a)	345
3-methyl-NNdimethylanilinium	360	(17b)	345
4-methyl-NNdiethylanilinium	250	(17c)	260
2,5-dimethyl-NNdiethylanilinium	790	(17d)	605
2-methyl-Nmethylanilinium	290	(17e)	305
3-methyl-Nmethylanilinium	310	(17f)	305
2,6-dimethyl-NNmethylanilinium	1000	(17g)	375
2,4,6-trimethylanilinium	500	(17h)	190

Medium: HCl+CH<sub>3</sub>OH

violate too strongly the theorem. In fact the same observation can be made when comparing o-xylene and m-xylene. When using  $\epsilon_{sm}$ , which is the maximum of the smoothed curve<sup>(16)</sup>, that discrepancy disappears showing that it is mainly a problem linked to the vibrational fine structure and to the width of the vibrational progressions inside the electronic transition. Nevertheless, it should be kept in mind that interaction between two substituents is difficult to evaluate and it can perturb the vector additivity. An example is given when considering the 2,6-dimethylanilinium ion: the calculated value is lower than the experimental one (table I). The steric strain, and the electronic distortions, have not been completely taken into account in this work, since we have used the same geometry for the three moieties ( $\phi$ ,  $-\text{CH}_3$ ,  $-\text{NH}_3^+$ ) all along the calculations. Because of the possible intramolecular interactions, such a model, which is the basis of the vector addition theorem, is certainly not accurate enough when three substituents are on three adjacent sites. Furthermore, the interactions with the medium can be different for two different ammoniums when their pK are different.

$\epsilon_{sm}$  is the sum of  $\epsilon_v$  and  $\epsilon_a$ .  $\epsilon_a$  is the square of the modulus of the resultant of the spectroscopic moments of all the auxochromes substituting the benzene chromophore.  $\epsilon_v$  is a vibrational contribution<sup>(16)</sup> whose value has been calculated in our work using the formula :

$$\epsilon_v = 180 + 25 n$$

$n$  being the number of alkyl substituents linked to the nitrogen atom. When  $-\text{NH}_3^+$  is concerned  $n = 0$  and  $\epsilon_v = 180$ . This value is near to what has been calculated by Ballester and Riera <sup>(16)</sup> (170 for two alkyl auxochromes; 175 for three etc...). Considering the accuracy of such calculations, the same formula has been used throughout our work for all the molecules, whatever the number of auxochromes is.

The moduli used for the  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$  spectroscopic moments proceed from those obtained by Ballester and Riera in their experiments on alkylbenzenes<sup>(16)</sup>. Nevertheless, as the intensities of

the spectra used by these authors are systematically too low, the transition moments should be 10% higher. We have used 8.8 for  $-\text{CH}_3$ , 7.8 for  $-\text{C}_2\text{H}_5$ , instead of 8.0 and 7.0. When using these values the best one for  $-\text{NH}_3^+$  is 1.7 and the formula taking all the molecules into account is:

$$\mu_{(\text{NRR}'\text{H})} = 1.7 + 0.75 n$$

Our results have been dissociated in two parts : in table I our calculations corresponding to our own experiments; in table II our calculations corresponding to experimental data of the literature (as concerns these latter data we have had to correct some of them from overlap with spectra of impurities). They support our above assumption about the intensity of 2,6-dimethylanilinium (table I) whose value is certainly increased by interactions among the substituents. Actually, the experimental intensity is much higher everytime that three auxochromes are on three adjacent sites (2,6-dimethyl-NNmethylanilinium and 2,4,6-trimethylanilinium).

The most important result is not the calculation of the various parameters used in that work, nor the good agreement observed when comparing experiments and calculations, but the fact that our spectroscopic results can be explained only on the basis that the spectroscopic moments for the alkyl groups on the one hand and the ammonium groups on the other, should point towards opposite directions (when they are on a given site), although all of them are  $\pi$ -donating substituents.

### SOLVATION EFFECTS

We did not try to compare the intensities of the secondary transition of the ammoniums studied in our work to the intensities of the corresponding alkylbenzenes, since the medium used is quite different : HCl + water for the ammoniums, and non polar solvents or weakly solvating mediums (such as hexane, methanol) for the alkylbenzenes. Furthermore, the ammoniums are acido-basic species and display a specific behaviour in the medium.

In preceding works<sup>(7,19)</sup>, it has been shown that the interaction of the  $\pi$  system of the aniliniums with the acid species of the medium is possible at low pH. The effects begin to be observed at pH below 0.5. Such an interaction should lead to a sort of loose complex, with enhanced intensity because of a greater distortion of the symmetry of the  $\pi$  system. It has been shown also that sometimes, on the contrary, such a solvation effect can quench the hyperconjugative coupling and can cause a decrease of the intensity. In order to obtain the spectrum of a given ammonium, and to prevent possible distortions imposed by solvation effects, or by stronger interactions with the medium, the spectra at various pH have been recorded (about twenty to thirty measurements) to draw the curve  $\epsilon = f(\text{pH})$ . With such curves we have been able to locate the range of pH where the "free" ammoniums can exist, spectroscopically free of the amine forms and with a minimum of complexing interaction. That range roughly extends from pH=1 to pH=2. Some of the ammoniums can exist at lower pH, without having their intensities changed because of an increasing interaction with the medium, or at higher pH without pollution by the spectrum of the amine form. Thus the spectra which have been studied have been recorded between pH=1 and pH=2 when there is a plateau in the curve  $\epsilon = f(\text{pH})$ .

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