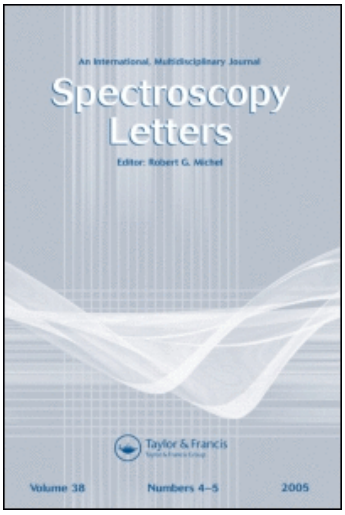

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Near UV Spectra of the Aniliniums: φCH$_2$CH$_2$X, φNH (CH$_2$X$_a$)CH$_2$X$_b$ and φNH (C$_2$H$_4$)$_2$X. Long Range Interactions Involving φ and X

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NEAR UV SPECTRA OF THE ANILINIUMS: $\phi NH_2^+CH_2X$, $\phi NH^+(CH_2X_a)CH_2X_b$ AND $\phi NH^+(C_2H_4)_2X$. LONG RANGE INTERACTIONS INVOLVING ϕ AND X.

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We have shown in preceding papers[1-3], in a study of some specific anilinium ions such as $\phi NH_{3-n}^+(CH_3)_n$, $\phi_2NH_2^+$ and ϕ_3NH^+, that varying the ammonium groups, or the medium, can lead to great changes in the intensity of the secondary transition of the chromophore[1-4] because of a σ,π coupling involving the substituent[1-10] and ϕ. In the present work we should like to extend our experiments to more complex ions - since apart our own works the UV spectroscopy of the aniliniums is almost unknown - to study the sensitivity of the chromophore to long range interactions with X through space or through the bonds of the substituents[11-16].

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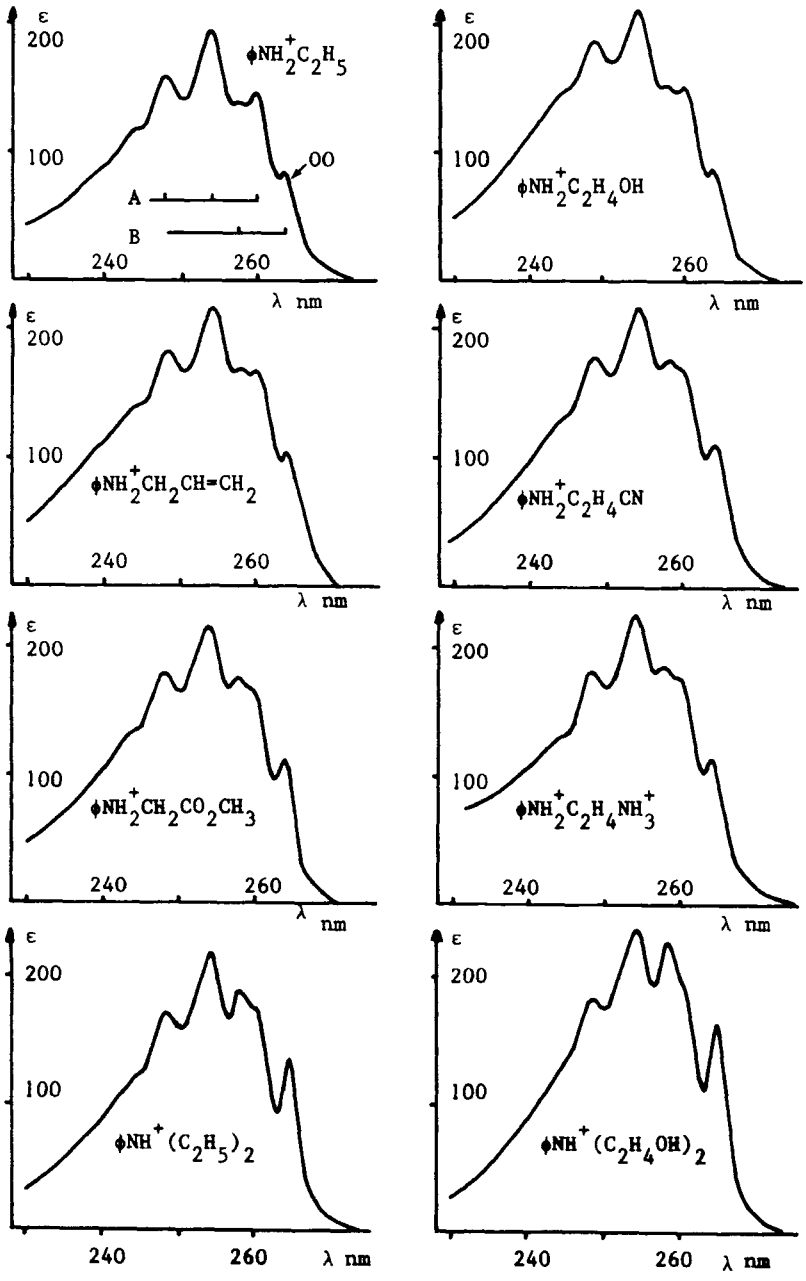

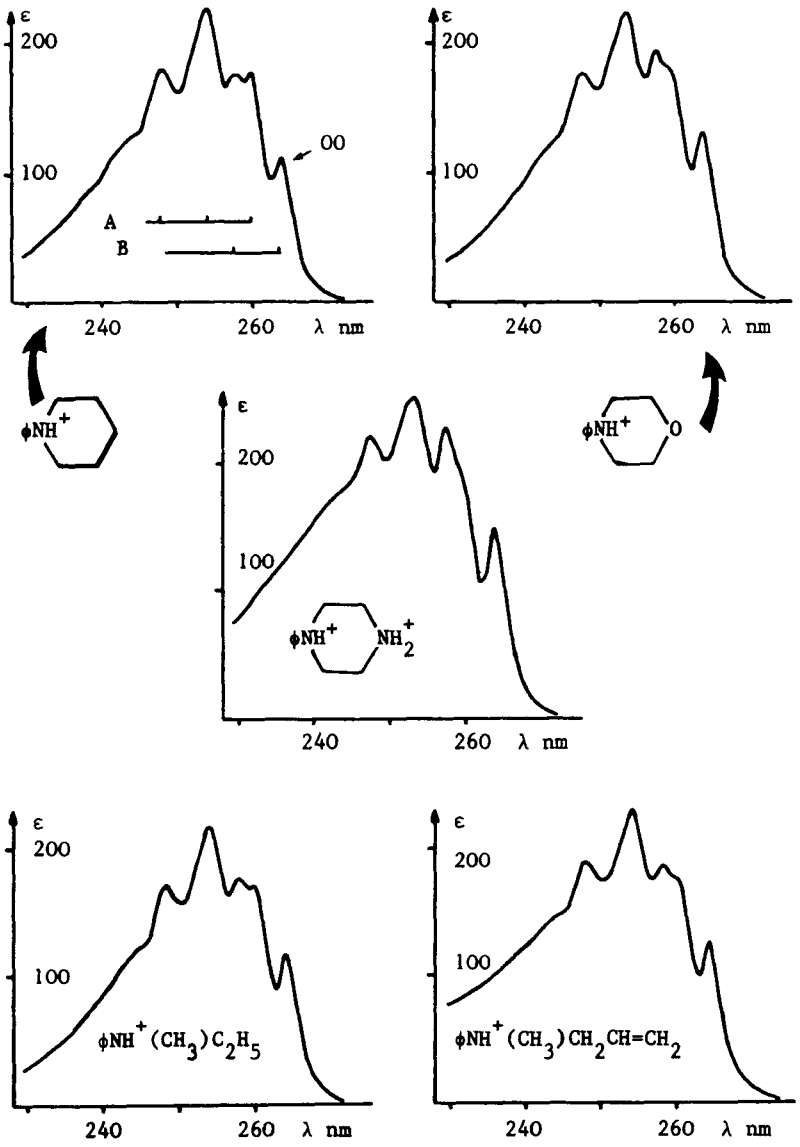

SPECTROSCOPIC RESULTS

When the symmetry of the benzene chromophore is D_{6h}, as in benzene itself, the secondary transition is electronically forbidden. A progression called A appears with a very low intensity. A substituent can distort the symmetry of the π system towards C_{2v} and the transition becomes more or less allowed according to the extent of the distorsion. Then a progression B, whose intensity is evaluated by the value ε_{oo} of its OO band, characteristic of the perturbation, is superposed upon the progression A[17-19].

The medium used in that work is HCl,H_2O pH=-0,5. In such a medium all the aniliniums studied are perfectly stable and no remaining intensity from their aniline form can be observed*. The table shows that the intensities seem to be scattered at random and, in the very first place, no simple explanation can be given. We have used the CNDO and MNDO methods to reach the basic parameters of the intensities of these aniliniums.

CNDO AND MNDO CALCULATIONS.

The MNDO method, in the present work, leads to a slightly π withdrawing effect for the substituents of ϕNH_3^+ and $\phi N(CH_3)_3^+$, which is contrary to experiments[4][7-10], to ab initio calculations[8,9], and to our own CNDO calculations (table). This latter method seems to be more reliable than MNDO for a study on the anilinium ions. Furthermore, it leads to a better correlation among the calculated values inside a given series. Therefore we shall mainly present the results obtained with that method, only briefly discussing our MNDO results.

The aniliniums are more complex species than alkylbenzene derivatives[17-20] since they bear a net ionic charge mainly located on the substituent. The field of that charge could induce a polarization of the π system. Furthermore, the ammonium groups, apart from their π-donating effects are, each one of them, strong σ-withdrawing groups (σ_I= 0.60 for $-NH_3^+$ and 0.73 for $-N(CH_3)_3^+$ [21]). They are able to modify the core potentials inside the σ frame of the chromophore, the σ densities, the σ charges ... and through these

effects they can bring an influence upon the π system. Besides, the substituent causes a slight mixing of the σ and π levels favouring the interactions of the π system with the substituent.

A parameter designed for evaluating the perturbation in terms of distorsion of symmetry must take into account the characteristics of the π MOs since these orbitals , specially the two highest occupied ones, are those which are mainly implied in the transition. The π highest occupied one (π_h) contains a contribution of the AOs of the substituent (such a phenomenon can be described as an hyperconjugation since hyperconjugation is not restricted to groups with an α carbon atom[9][22-24]). On the contrary in the other π highest orbital the coupling with the substituent can be neglected. We have used π_h as a "test" orbital to evaluate the distorsion of symmetry by the changes of the coefficients $C_{i,a}$ of the AOs in that MO, taking the corresponding MO in the benzene molecule as a reference (coefficients $C_{i,b}$) : $F = \sum_i |C_{i,a} - C_{i,b}|$. Since there is no substituent in the benzene molecule the corresponding values are 0. The absolute values are used since two distorsions in different parts of the aniliniums have to be counted; they are distorsions and cannot cancel each other when they have opposite signs.

The figure I shows that,apart from the four species of the series I : $\phi NH^+_{3-n}(CH_3)_n$, there is a retrogression of the curves $\varepsilon_{oo} = f(F)$ when ε_{oo},the measure of the experimental distorsion of symmetry, increases. For the series II (species b,e,f,g,h,j), the series III (species c,k,l), IV (species c,m,n,o), V (species c,p,q), ε_{oo} cannot only depend on F.

The retrogression in a given series comes from the decrease of f_s the part which in F is related to the substituent. That decrease means that the extension of the π system outside the ring decrease. Such a phenomenon is linked to an increase of the σ-withdrawing ability of the groups substituting the β carbon atom(ϕNC_β), since it causes an increase of the σ-withdrawing ability of the whole ammonium. When that latter effect becomes very strong the π electrons, owing to the interactions through the σ frame of the ring, are much more firmly bound to the nuclei of the ring - increa-

TABLE

n°	compound	ε_{oo}	π charge CNDO	π charge MNDO
a	ϕNH_3^+	60	- 0.0043	+ 0.0051
b	$\phi NH_2^+CH_3$	78	- 0.0135	+ 0.0021
c	$\phi NH^+(CH_3)_2$	104	- 0.0161	+ 0.0006
d	$\phi N^+(CH_3)_3$	170	- 0.0168	- 0.0003
e	$\phi NH_2^+CH_2CH_3$	84	- 0.0154	+ 0.0021
f	$\phi NH_2^+CH_2CH_2OH$	88	- 0.0148	+ 0.0027
g	$\phi NH_2^+CH_2CH{=}CH_2$	105	- 0.0158	+ 0.0014
h	$\phi NH_2^+CH_2CH_2CN$	110	- 0.0150	+ 0.0033
i	$\phi NH_2^+CH_2CO_2CH_3$	112	- 0.0151	+ 0.0035
j	$\phi NH_2^+CH_2CH_2NH_3^+$	115	- 0.0069	+ 0.0142
k	$\phi NH^+(CH_2CH_3)_2$	134	- 0.0191	- 0.0013
l	$\phi NH^+(CH_2CH_2OH)_2$	160	- 0.0183	+ 0.0016
m	$\phi NH^+CH_2CH_2CH_2CH_2\overline{CH_2}$	113	- 0.0191	- 0.0056
n	$\phi NH^+CH_2CH_2OCH_2\overline{CH_2}$	130	- 0.0185	+ 0.0012
o	$\phi NH^+CH_2CH_2NH_2^+CH_2\overline{CH_2}$	150	- 0.0107	+ 0.0114
p	$\phi NH^+(CH_3)\ CH_2CH_3$	119	- 0.0176	+ 0.0005
q	$\phi NH^+(CH_3)CH_2CH{=}CH_2$	126	- 0.0174	0.0000

ε_{oo} : Molar extinction coefficients of the OO band in H_2O,HCl pH=-0.5 ; π charge : Number of electrons given by the substituent to the chromophore (sign -) or withdrawn (sign +).

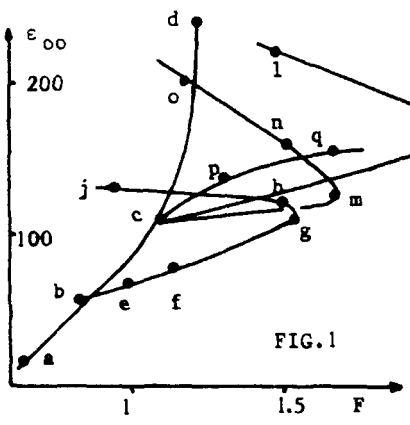

FIG.1

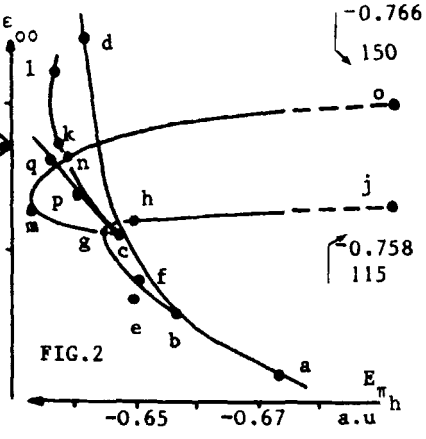

FIG.2

sing the ionization potentials (figure 2) - and the coupling of the p_π orbitals with the atomic orbitals of the substituent decreases. The intensity should decrease if there where no other possible interaction.

We have reported in figure 3 the values of the component E on the C_2 axis at the center of the chromophore, of the field coming from the distribution of the ionic charges on the substituent. There is also a retrogression of the curves. Contrary to what happens with F the field cannot explain the behaviour of the series I since when ε_{oo} increases the perturbation of the field decreases.

Our calculations show that when the attracting ability of the group X in ω of the substituent increases it polarizes the substituent. It increases the electronic density around ω, favouring the appearance of a negative charge (or a decrease of the positive charge) and, consequently, the appearance of a greater positive charge on the other parts of the substituent nearer to the chromophore, owing to the polarization induced in the σ frame. Being nearer to the chromophore, the increased positive charges induce an increased field polarizing the π cloud. The effect of that field cannot be cancelled by the increased field of the negative charges near to the ω part (or the decrease of the positive charge in that part) because these latter charges are located farther from the chromophore.

The polarization of the substituent, the polarization of the π cloud, which parallels the preceding one, with an increasing electronic density in the p_π orbital of the carbon which in the chromophore is linked to N (although the overall number of π electrons decreases) are linked not only by the field, but also through the σ frame of the chromophore itself. Actually, when the attracting power of the group in the ω part is strong, it increases the σ withdrawing effect that the whole substituent is able to bring upon the frame of the chromophore.

The calculation of the field is a way, among others, to evaluate the incidence of the substituent on the π cloud. We could

have choosen also, for example, the direct calculation of the distorsion C of the charges in the chromophore (fig.4 ; C is the difference of densities in the p_π orbital of the carbon linked to N and in the p_π orbital of its neighbour in the chromophore).

Although ε_{oo} is not linked only to E, C or F, a combination of these parameters : $P = E^{3/2}.F$ or $P' = C^{3/2}.F$ leads to a good correlation for several series, particularly for the series II (species b, e,f,g,h,j) (fig.5 and fig.6). One sees that for the weakest perturbations - the lowest values of ε_{oo} - the intensity increases as F increases in a given series, that is to say when the extension of the π system on the substituent increases, and that can be linked to an increase of the volume of the substituent, an increase of the number of AOs able to couple with the π system. For the highest perturbations, for the highest values of ε_{oo}, when the σ attracting power of the substituent linked to N increases,E, or C, becomes the key parameter. The distorsion of symmetry comes from a greater polarization of the substituent, which causes a greater polarization of the π cloud inside the chromophore. That phenomenon arises because of the field, and because of the influences on the π system of the substituent through the σ frame of the chromophore. Thus, in a given series other than I, the distorsion of the D_{6h} symmetry towards C_{2v} goes for the lowest values of ε_{oo} from an extension of the π system outside the ring - which is mainly a through space interaction of π_ϕ with the AOs of the substituent - to a distorsion of the π system inside the chromophore itself for the highest values of ε_{oo}. That latter case could be described partly, because of the rôle of the field in the process, as a through space interaction, but also, because of the interaction directly through the σ frame, as an interaction through an "extended system" [25-28].

The series I is a specific one since the number of methyles substituting the nitrogen atom increases one at a time all along the series. On the contrary in each one of the other series there is always the same number of sustituents on the nitrogen atom. Our calculations for that series show that the evolution of the dis-

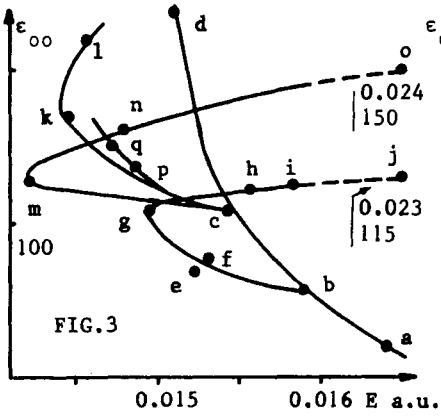

FIG.3

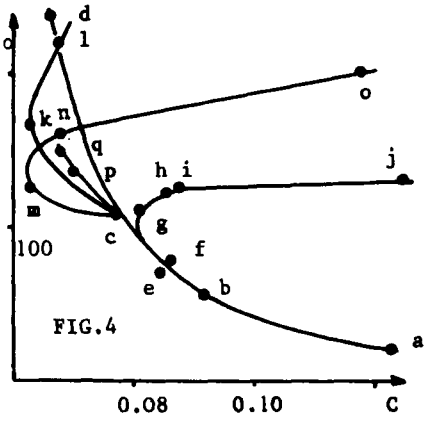

FIG.4

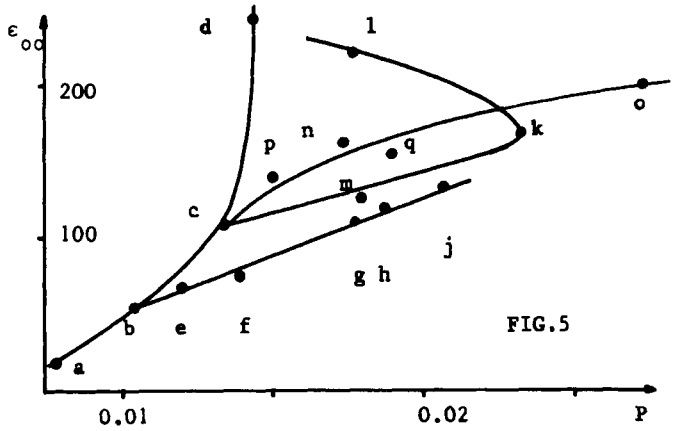

FIG.5

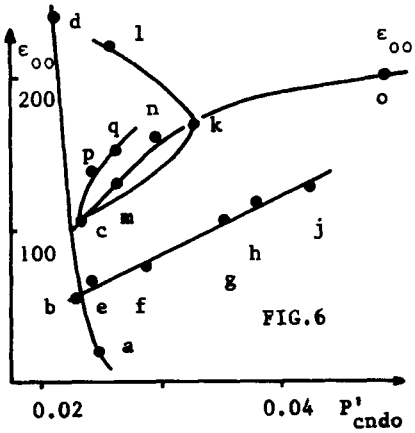

FIG.6

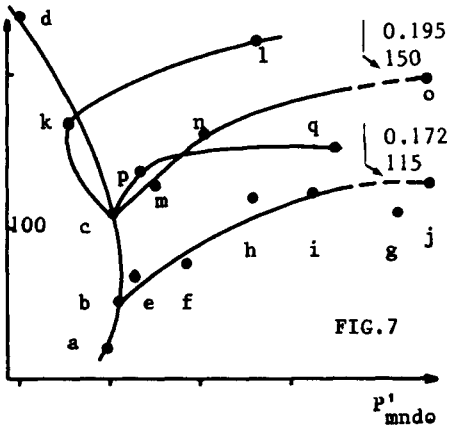

FIG.7

torsion of symmetry does not come from the polarization, the distorsion of the π system inside the ring of the chromophore, or from the connected field effect, since ε_{oo}, the actual measure of the perturbation, increases when these effects decrease. The increase of ε_{oo} in that series has to be linked to the extension of π_ϕ on the substituent. That result agrees with our preceding work[2] on the hyperconjugative coupling in such aniliniums, between π_ϕ and the bond orbitals N-C or N-H. A better coupling between π_ϕ and the bond orbitals means a better extension of the π system on the substituent. Furthermore, in that preceding work, we had emphasized the coupling of the N-C bonds with π_ϕ in the series I. Actually the present calculations show for that series that the coefficients related to the $1s_H$ orbitals of the hydrogen atoms linked to N, only play a small part in F when considering the contribution of the other orbitals. For example, in $\phi NH_2^+CH_3$ the contribution to F of each one of the hydrogen atoms linked to N is 0.067 when the carbon atom of the methyle contributes for 0.251, the group of the hydrogen atoms of the methyle for 0.113, and N for 0.193. Thus, contrary to what happens in the alkylbenzenes, although the coupling scheme is very similar, where the C_α- H bonds mainly contribute to the hyperconjugation, in the aniliniums the hyperconjugation mainly involves the $(N\text{-}C)^{+\delta}$ bonds.

With the MNDO method the π molecular orbital which couples strongly with the substituent is just under the highest π occupied one. That method sometimes leads to correlations, inside a given series, which are not so good as in CNDO. The main point of the comparison lies in the fact that with MNDO F increases as ε_{oo} increases. Thus it does not appear to be necessary to involve a field effect, or the polarization of the π system inside the ring. Nevertheless that polarization still exists and evolves as it evolves in CNDO. The figure 7 where the curves $\varepsilon_{oo} = f(C^{3/2}\cdot F)$ are given as an example, shows that, deeply, there is no contradiction with the evolution obtained in figure 6 with the CNDO method. Furthermore, when considering in F the parts f_s and f_ϕ, the calculations show that for strong σ withdrawing substituents the distorsion of sym-

metry comes mainly from the orbitals inside the aromatic ring, paralleling what comes from the CNDO calculations. Thus the two methods lead rougly to the same picture of the phenomena.

When using the MNDO method, only taking into account F, the series III (species c,k,l) evolves as the other ones do : ε_{oo} increases with F. Thus, F being the key parameter in that method, the behaviour of the series III is normal. The retrogression of the curve $\varepsilon_{oo}=f(F)$ could be too much pronounced in CNDO and the behaviour of that series as concerns its curve $\varepsilon_{oo} = f(E^{3/2}.F)$ could be an artefact of the method. Furthermore, the evolution of the curve $\varepsilon_{oo} = f(C^{3/2}.F)$ in one of the methods is exactly the opposite of what is obtained with the other. It is the reason why we have not discussed above the corresponding CNDO results. Besides, the species m which is poorly correlated in CNDO, is on the curve of its series with the MNDO method. On the contrary, with that latter method the species g is out of the place where it should be.

Not too much attention should be paid to these irrelevant behaviours, which are artefacts of the semi-empirical methods used, to concentrate on the overall picture of the phenomena which are basically the same.

GEOMETRIC MODEL

Within the benzene moiety all bond angles were assumed 120° and the bond lengths calculated for ϕNH_3^+ have been used unchanged for the other aniliniums (d_{12}=1.411 Å, d_{23}=1.403 Å, d_{34}=1.413 Å). Within the substituent, tetrahedral angles of 109,5° where used when the connectivity is 4. To obtain the conformations of lower energies we have optimized, in the series I, the bond lengths of the substituent (ϕ-N : 1.476 Å, N-CH_3 : 1.513 Å and N-H : 1.025 Å) and the dihedral angles involving the rotation of the substituent. For anilinium itself two conformations have the same energies : when a N-H bond is in a plane orthogonal to ϕ and when it is in the plane of ϕ. We have used that latter conformation. For the trimethylated species the conformation when a N-CH_3 bond is in the plane of ϕ has a slightly lower energy and it has been used in our calculations.

In $\phi NH_2^+CH_3$ the N-CH_3 bond mainly lies in a plane orthogonal to the chromophore. In $\phi NH^+(CH_3)_2$ the conformation with the N-H bond in the plane of the chromophore has the lowest energy. The conformation of the parent compound of a series has been used for the other species of that series. For the other parts of the substituents we have used standard parameters[29] and staggered conformations for bonds connecting atoms with tetrahedral angles. In the species g, i and q the plane of the double bond is parrallel to the chromophore the energy being lower for that conformation. In the species m,n,o we have used a chair shaped structure.

CONCLUSION

The intensity of the secondary transition of the aniliniums, for a given σ,π coupling scheme (a given number of substituents on N) increases, for the weakest perturbing substituents, when these substituents are able to allow a greater extension of the π system outside the aromatic ring. The D_{6h} symmetry is distorted towards C_{2v} and the transition is less forbidden. On the contrary when the substituent strongly interacts with the chromophore, the distorsion of the densities of the π_ϕ cloud mainly arises inside the aromatic ring.

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* The spectra of the species $\phi NH_{3-n}^{+}(CH_3)_n$ do not appear in that work since they have already been published[3] (medium H_2SO_4,H_2O near to the medium used in that work)

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