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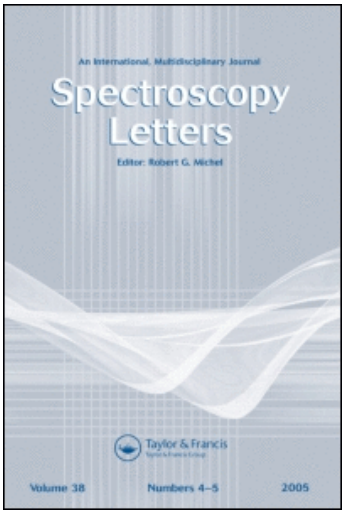

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Anilinium Ions: Relations Between pK, σ and Intensity of the UV Transition

Annick Darry-Henaut[a]; Bernard Vidal[b]
[a] Laboratoire de Spectroscopie de la Réactivité Chimique, UFR de Chimie, Université des Sciences et Techniques de Lille, Villeneuve d'Ascq Cédex, (France) [b] Université de La Réunion BP 5, Sainte Clotilde, La Réunion (France DOM)

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ANILINIUM IONS : RELATIONS BETWEEN pK, σ* AND INTENSITY OF THE UV TRANSITION

Annick DARRY-HENAUT
Laboratoire de Spectroscopie de la Réactivité Chimique,
UFR de Chimie, Université des Sciences et Techniques de
Lille. 59655 - Villeneuve d'Ascq Cédex (France)

Bernard VIDAL*
Université de La Réunion
BP 5, 97490 - Sainte Clotilde, La Réunion (France DOM)

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Spectroscopists have often assumed, based only on the UV spectrum of the anilinium ion (ϕNH_3^+), that ammonium groups cannot bring a "mesomeric" effect upon π systems. This assumption[1-3] which could be justified for the anilinium ion itself, whose OO band of the secondary transition (towards 260 nm) is very weak, has been unduly extended to all the ammonium groups. Actually, the interaction between a π system and $(NX_aX_bX_c)^+$ groups has been studied by several authors[4-8], and we have shown that contrary to what had been assumed by spectroscopists, such an interaction induces strong effects on the UV spectrum of the benzene chromophore[9-11]. Using the MNDO and the CNDO methods, we have studied the quantum factors which play a part in the long range interaction, between : an ω group X on the one hand, N on the other hand, and then ϕ, in $\phi NH_2^+CH_2X$, $\phi NH^+(CH_2X_a)CH_2X_b$ and $\phi NH^+(C_2H_4)_2X$.

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In this paper we present the relationship which may exist between the intensity of the secondary transition (measured at the 00 band of the progression B), and the pK of the molecule. Actually, the pK is a thermodynamic parameter characteristic of a great part of the behaviour of these acido-basic species. From a macroscopic point of view its significance is easier to grasp than the many paramaters to be taken into account when using quantum calculations[11]. We are going to compare such a parameter to the Taft σ^* constant.

EXPERIMENTAL RESULTS

Not all the pK values of the aniliniums studied in that work were known. We have had to measure several of them, limiting the complexity of the experimental determination to provide the accuracy necessary for our work. Two methods have been used: an electrochemical one, and a spectrophotometric one. They have been described previously[12]. The spectrophotometric method has been used because the electrochemical one was unreliable when the molecules studied were not soluble enough in water. Actually, in order to reach concentrations high enough for electrochemical determinations, we have sometimes had to use a medium containing up to 20% methanol. To check our results we have also measured the pK values already known in the literature for some molecules (Table I). We have also used empirical relationships for comparison[13-15].

The spectra have been recorded in $HCl-H_2O$ (pH = - 0.5). In such a medium all the aniliniums studied are stable, and the spectrum of their aniline form is not observed.

pK AND TAFT σ^* CONSTANTS

The pK values of the amines car be assesssed with some accuracy using empirical relationships. These relationships[13-15] are based on linear combinations of the Taft σ^*

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TABLE I

	ϕ-R R	ε_{oo} pH = -0.5	pK_a This work	pK_a literature
a	NH_3^+	60		4.60 [25]
b	$NH_2^+CH_3$	78		4.85 [25]
c	$NH^+(CH_3)_2$	104		5.06 [25]
d	$N^+(CH_3)_3$	170		
e	$NH_2^+CH_2CH_3$	84		5.25 [26]
f	$NH_2^+CH_2CH_2OH$	88	4.1$_5$ *	4.06 [27,28]
g	$NH_2^+CH_2CH{=}CH_2$	105	4.1 *	4.18 [27]
h	$NH_2^+CH_2CH_2CN$	110	2.3 *	
i	$NH_2^+CH_2CO_2CH_3$	112	2.2 *	2.08 [29]
j	$NH_2^+CH_2CH_2NH_3^+$	115	1.9 *	
r	NH_2^+-N-cyclohexyl	90	5.6	
s	$NH_2^+CH_2$	230	4.1 *	
k	$NH^+(CH_2CH_3)_2$	134		6.55 [25]
l	$NH^+(CH_2CH_2OH)_2$	160	4.1$_5$ *	4.07 [27]
m	NH^+<>CH_2 †	113	5.9 *	5.2(EtOH 50%) [32]
o	NH^+<>NH_2^+ †	150	1.2 *	
p	$NH^+(CH_3)CH_2CH_3$	119		5.98 [25]
q	$NH^+(CH_3)CH_2CH{=}CH_2$	126	5.0 *	
n	NH^+<>O †	130	3.1 *	3.20 [27]

The values of intensity and pk have been obtained in water

† the symbol <> stands for: $\begin{matrix} -CH_2-CH_2- \\ -CH_2-CH_2- \end{matrix}$

* This value has been obtained from a spectrophotometric experiment.

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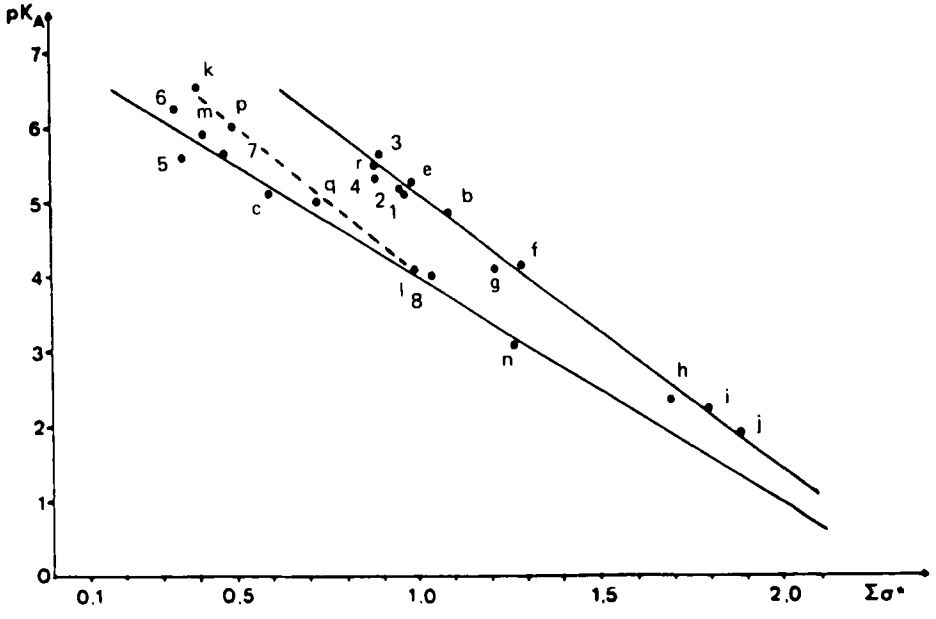

FIGURE 1

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values of the groups linked to the nitrogen atom : $pK=f(\Sigma_k \sigma_k^*)$, in which k stands for the different groups linked to N, including ϕ whenever there is an aromatic amine. The results of our calculations are given in figure 1. Some molecules not studied here from a spectroscopic point of view, have been taken into account in order to increase the accuracy of the curves. These molecules are labeled with numbers instead of letters. The corresponding pK values are given in table II. All the σ^* values used in our work are given in table III. Figure 1 shows that there is a good correlation between experimental data and empirical relationships. The data seem to lead to two distinct curves: one for the molecules where two CH_2 are linked to N, and another for the molecules where there is only one CH_2.

TABLE II

	φ-R, R:	pK_a		φ-R,R:	pK_a
1	NH-n-C_3H_7	5.10 [26]	5	N(n-C_3H_7)$_2$	5.60 [25]
2	NH-n-C_4H_9	5.17 [26]	6	N(n-C_4H_9)$_2$	5.21 [25]
3	NH-iso-C_3H_7	6.65 [26]	7	N(CH_3)n-C_3H_7	5.64 [26]
5	NH-cyclo-C_9H_{11}	5.30 [25]	8	N($CH_2\phi$)$_2$	4.00 [27]

TABLE III

substituent	σ*	substituent	σ*
H	+0.49 [19,21]	<>CH_2 †	-0.18 [21]
CH_3	0	<>O †	+0.67 [21]
CH_2CH_3	-0.1 [19,21]	<>NH_2^+ †	+1.40
CH_2CH_2OH	+0.2 [21]	cyclohexyl	-0.20 [19,21]
$CH_2CH_2NH_3^+$	+0.80	CH_2CO_2R	+0.71 [21]
$CH_2CH=CH_2$	+0.13 [21]	CH_2CH_2CN	+0.61
$CH_2\phi$	+0.22 [21]	ϕ	+0.60

† see table I for the meaning of <>

The σ* value concerning N-phenylethylenediamine (j) has been calculated from the value observed for CH_2-NH_3^+ (σ_I = 0.36), using the relationship[19-20]: $\sigma_I(X) = 0.45\sigma^*(CH_2X)$. The value obtained is 0.80. This value leads to pK=1.8 according to the curves of figure 1. In N-phenylpiperazine (o) there is a cyclic substituent. The corresponding σ* value has been calculated from the pK value of piperazine (pK_1=9.81, pK_2=5.55)[21] using the curve $pK=f(\Sigma_k\sigma_k^*)$ of the secondary aliphatic amines. The value is σ*=1.40. According to that calcula-

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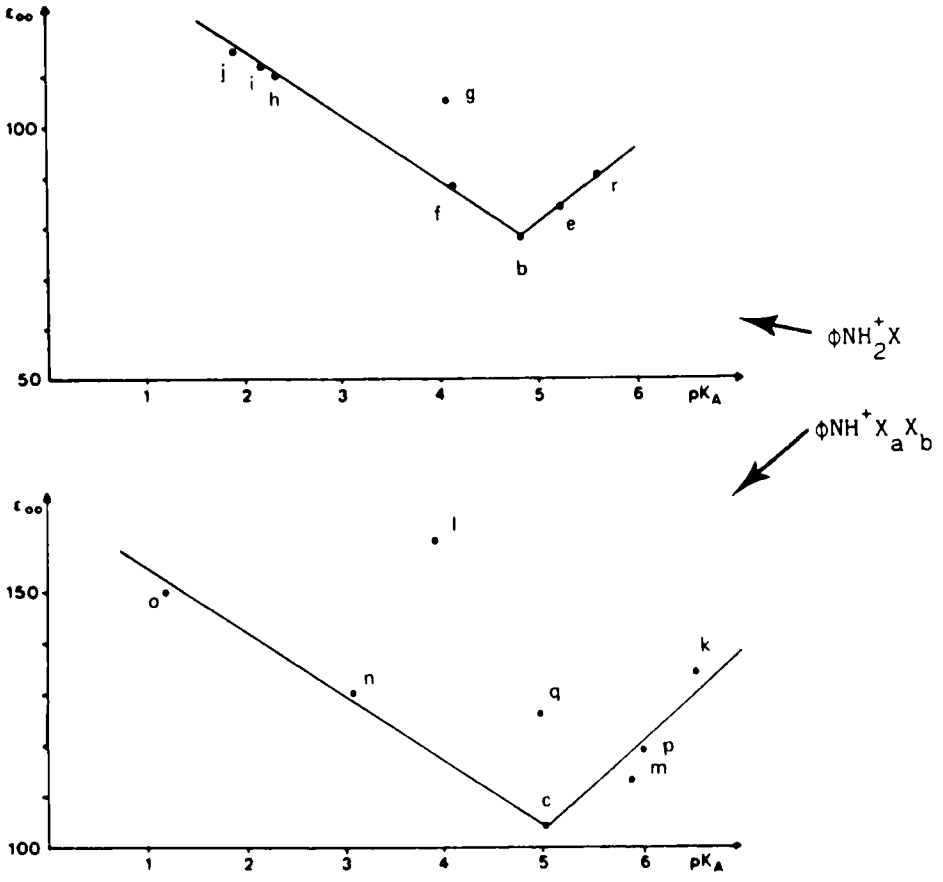

FIGURE 2

tion the pK value of N-phenylpiperazine should be around 1. The experiment gives 1.2.

INTENSITY AND pK

The molar extinction coefficient ε_{00} of the 00 band of the secondary transition of the aniliniums ϕNH_2^+X, $\phi NH^+X_aX_b$, is

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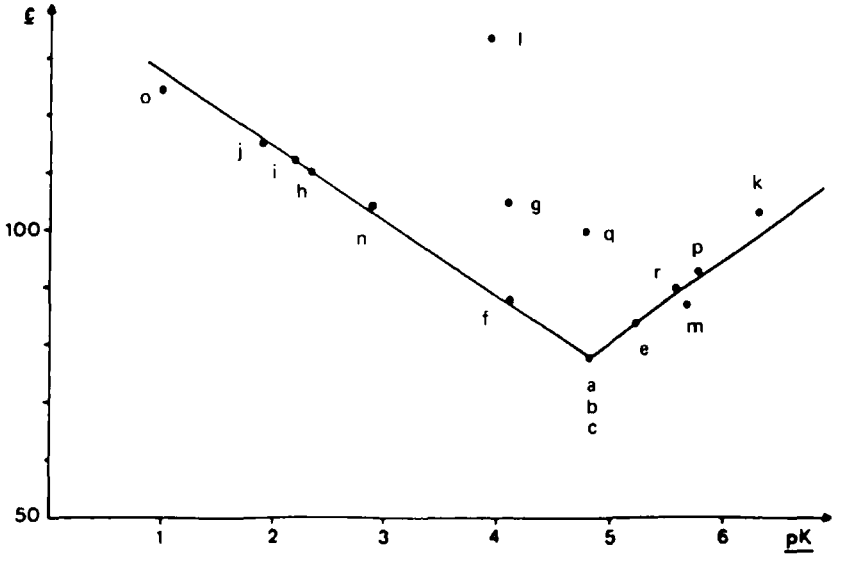

FIGURE 3

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a V shaped function of pK (figure 2), with the exception only of a few points. When using the parameters:

$$\underline{\varepsilon} = \varepsilon_{oo} - 26(n-1) \quad \text{and} \quad \underline{pK} = pK - 0.21(n-1)$$

only one curve is necessary to correlate all the points (fig.3); n is the number of CH_2 (or CH_3) linked to N. The data concerning $\phi N^+(CH_3)_3$ (d) have not been used to draw the curve since that molecular ion is not involved in a classical acido-basic equilibrium. The parameter n takes into account the σ-π coupling between π_ϕ and the $NH_2{}^+X$, or $NH^+X_aX_b$ group. That coupling depends on the number of substituents on N[9-11]. The CH_2 groups act as an hyperconjugative "bridge" through which a part of the σ electronic effects of the substituents linked to N is transmitted to the π_ϕ system. Every N-C bond adds 26 to the value of

ε_{oo} (when going from ϕNH_3^+ (a) to $\phi NH_2^+CH_3$ (b), then to $\phi NH^+(CH_3)_2$).

Whenever the number of methyls (or N-C bonds) increases n takes the increase of the pK value into account. Actually, whenever that number increases the π donating effect on N increases too. The non bonding electrons in the amine form are less attracted by the nitrogen nucleus: they become more basic, more able to be involved in a bond between N and a proton.

The V shape of the curve results from the dependency of the pK values on the electron donating or withdrawing powers of the substituents linked to N. The intensity of the 00 band depends on the perturbation distorting the D_{6h} symmetry of the chromophore - a symmetry for which the transition is electronically forbidden - towards a C_{2v} symmetry - for which the transition is allowed. The intensity of the 00 band increases as the distorsion, the perturbation, the electronic effects imposed upon the chromophore, increase. In other words, intensity can increase from what is observed in a free benzene molecule, when the substituent on ϕ is electron donating as well as when it is electron withdrawing. The increase is dependent on the absolute value of the perturbation[22,23].

In each series the parent compound ($\phi NH_2^+CH_3$ and $\phi NH^+(CH_3)_2$) is the lowest point of the curve. Considering the chromophore reaching as far as the N-H and N-C bonds, whenever the σ electron donating effects of the substituents linked to N increase the pK value increases; ε_{oo} increases too since the σ donating effects are transfered to π_ϕ (through the hyperconjugative coupling of the N-H and N-C bonds) and distorts the D_{6h} symmetry. Thus, the σ donating substituents are on the right part of the curve. When the σ electron withdrawing power of the substituents increases, the symmetry is distorted: intensity increases, but the pK value decreases because the non bonding electrons are less free and less basic. Thus, the aniliniums

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whose N is bearing a σ electron attracting substituent are on the left branch of the curve. For example, on the left branch : N-phenylpiperazine (o), and then $\phi NH_2^+CH_2CH_2NH_3^+$, display the highest ε and the lowest values of pK since they bear strong electron withdrawing substituents (NH_2^+ and NH_3^+).

Three points are outside the curve. Actually, the pK takes into account the characteristics of the couple: aniline/anilinium; on the contrary in the spectroscopic study we use a medium where only the acid form (the anilinium ion) can exist. Furthermore, solvation can induce, or quench[10], a distorsion of π_ϕ or an interaction through space between substituent and chromophore. The incidence of these effects could be weak on pK and strong on intensity. In other words, when considering the aniliniums, pK and intensity depend on some common factors but intensity does not depend on pK. These factors are the electronic effects induced by the substituents linked to N. Thus we could have better correlation if we should use the Taft σ* constants of the substituents to explain intensities.

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INTENSITY AND TAFT σ* CONSTANTS

ε_{oo} is a V shaped function of $x = \Sigma_{k'}\sigma_{k'}^*$ which is the sum of the σ* values of the different substituents linked to N, with the exception of φ since that group is the same for the whole series. When considering the series I (ϕNH_2^+Y, molecules b,e,f,g,h,i,j,r) one can see that g is still out of the curve as it was when pK was used instead of x. Thus, such a behaviour is not linked to a characteristic feature of pK. Among all the phenomena which could be put forward to explain that observation, one of them is a long range interaction involving the two unsaturated parts of the molecule, or an interaction N ⇔=; but for lack of data we cannot confirm such an assumption. Series II is composed of molecules where two CH_2 are linked to the nitrogen atom (molecules c,k,l,p and q). Series III is composed

of the parent compound c and of the molecules with a cyclic substituent linked to the nitrogen atom by two bonds (m,n,o).

As regards the species with a cyclic substituent, the curve is flatter than the corresponding one (II) with two distinct substituents. Actually, the electronic effects of the donating or attracting group in position 4 in the heterocycle are less efficient in increasing intensity, than two groups whose electronic effects are induced through two chains. The higher in absolute value the two slopes of a V shaped curve, the higher the increase of intensity for a given variation of x. The same can be said also concerning the efficiency of the substituents on the aniline nitrogen. For the same reason as above, the curve I for the species with one CH_2 on N is flatter than the curve II corresponding to species with two CH_2 on N.

If curves I and III were translated that would roughly superimpose them. The similarity of the cyclic substituent $-NH^+(CH_2CH_2)_2X$ electronic effects on ϕ with the $-NH_2^+(CH_2)_2X$ ones is only fortuitous. Just as is fortuitous the fact that when drawing $\varepsilon = f(\underline{pK})$, all the points of series I and series III seem to belong to the same curve since the pK values depend on the σ^* values. When using x instead of pK the molecules with a cyclic substituent constitute a distinct series, and so do the molecules k,p,c,q,l also. Thus, if the molecules q and l are not correlated with the others in figure 2 and 3 when considering the curve $\varepsilon = f(\underline{pK})$, we must assume that they constitute with p and k a distinct series. Such a series should appear as a V shaped curve. The angle between the two branches should be more accute than the angle observed in the main curve, mirroring what occurs in figure 4. Two facts prevent to observe that curve as a distinct curve in figure 2 and 3. First of all, p and k seem to be correlated to the right branch of the main curve: they do not appear as deserving a specific treatment with q and l. Secondly the series k,p,q,l seems to have no parent molecule:

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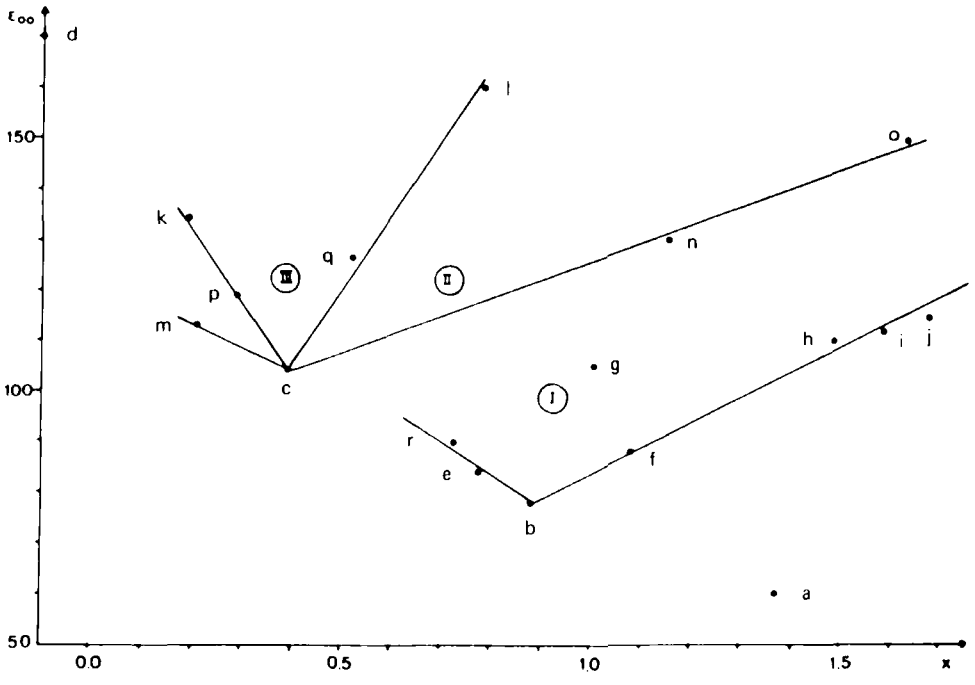

FIGURE 4: I) ΦNH_2^+X II) $\Phi NH^+ <> X$ III) $\Phi NH^+X_aX_b$

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the curve of the series is shifted away from c, which should have been the lowest point of the curve. The pK values of k,p,q,l are shifted from their theoretical values when considering $\Sigma\sigma^*$, since the correlation of ε_{oo} with $x = \Sigma\sigma^*$ is good when the σ^* are only taken into account (figure 4). Thus, these four species seem to display a specific behaviour as far as their acido-basic properties and/or their solvation properties are concerned. Their pK values are increased compared to what is observed for the other aniliniums. In other words, the intensities of l and q in figures 2 and 3 are not anomalous, but the whole series is specific regarding the pK. This is supported by

the curves in figure 1 : the two points, k and p, are poorly correlated to the lower curve. In fact, it is easy to see that they do constitute a series with q and l (the doted curve) , and the curve of that series is far from c, their parent molecule.

CONCLUSION

The above results show that using the pK of the anilinium ions to correlate the intensities of their secondary transitions, can be misleading. Actually, the pK depends on the electronic effects of the groups linked to the nitrogen atom; these effects play a part in the value of intensity. But it depends also on several other factors which are not involved in intensity. The parameter x, based on the $\Sigma\sigma^*$ of the groups linked to N, constitutes a firmer basis to explain the spectroscopic properties of the aniliniums. Paralleling what occurs for the toluene derivatives it shows that their intensity is a V shaped function of the electronic effects.

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REFERENCES

1) H.SUZUKI, "Electronic Absorption Spectra of Organic Molecules. An Application to Molecular Orbital Theory.", Academic Press, New York, 1967, p.222

2) H.H.JAFFE, M.ORCHIN, "Theory and Applications of Ultraviolet Spectroscopy.", J.Wiley, New York, 1962, p.25

3) D.M.BISHOP, D.P.CRAIG, Mol.Phys. **6**,139(1963), and references

4) W.F.REYNOLDS, T.A.MODRO, P.G.MEZEY, J.C.S.Perkin II, **8**,1066(1977).

5) A.RICCI, F.BERNARDINI, R.DANIELI, D.MACCIANTELLI, J.H.RIDD, Tetrahedron **34**,193(1978)

6) A.R.KATRITZKY, R.D.TOPSOM, Angew.Chem.Int.Ed. **9**,87(1979)

7) P.J.Q.ENGLISH, A.R.KATRITZKY, T.T.TIDWELL, R.D.TOPSOM, J.Amer.Chem.Soc. **90**,1767(1968) and references

8) W.ADCOCK, J.ALSTE, S.Q.A.RIZVI,M.AURANGZEB, J.Amer.Chem.Soc. **98**,1701(1976)

9) A.DARRY-HENAUT, B.VIDAL, Spectrosc.Letters **17**,463(1984)
10) A.DARRY-HENAUT, B.VIDAL, Spectrosc.Letters **19**,265(1986)
11) A.DARRY-HENAUT, B.VIDAL, C.CERF Spectrosc.Letters **19**,1099 (1986)
12) A.DARRY-HENAUT, Thèse, Lille, 1987, p.61
13) F.E.CONDON, J.Amer.Chem.Soc. **87**,4485(1965)
14) G.J.BIJLOO, R.F.REKKER, Quant.Struct.-Act.Relat.Pharmacol. **2**,66(1983)
15) G.J.BIJLOO, R.F.REKKER, Quant.Struct.-Act.Relat.Pharmacol. **3**,111(1984)
16) D.COURTOIS, B.VIDAL, J.Chim.Phys. **80**,559(1983)
17) D.COURTOIS, B.VIDAL, Spectrochimica Acta **40A**,441(1984)
18) M.CHARTON, J.Org.Chem. **29**,1222(1964)
19) L.S.LEWITT, Z.Naturforsch **34b**,81(1979)
20) H.S.WIDING, L.S.LEWITT, Z.Naturforsch **34b**,321(1979)
21) H.K.HALL, J.Amer.Chem.Soc. **79**,5441(1957)
22) G.BASTAERT, B.VIDAL, J.BROCARD, Spectrochimica Acta **35A**,1043(1979)
23) B.VIDAL, Spectrochimica Acta **38A**,367(1982)
24) D.DENIS-COURTOIS, B.VIDAL, Spectrochimica Acta **39A**,735(1983)
25) S.PATAI, "The Chemistry of the Amino Group.", Interscience Publishers, London, 1968, p.188
26) P.DEMARIA, A.FINI, F.M.HALL, Gazz.Chim.Ital. **113**,69(1983)
27) E.FOLKERS, O.RUNQUIST, J.Org.Chem. **29**,830(1964)
28) R.MIQUEL, A.LATTES, P.MARAVAL, Bull.Soc.Chim.Fr. 303(1962)
29) A.BRISON, N.R.DAVIES, E.P.SERJEANT, J.Amer.Chem.Soc. **85**,1933(1963)
30) M.D.ROZEBOOM, K.N.HOUK, S.SEARLES, S.E.SEYEDREZAI, J.Amer.Chem.Soc. **104**,3448(1982)

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