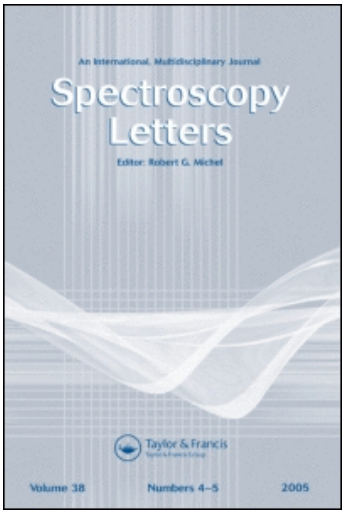

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INTENSITY OF THE 250 nm TRANSITION OF THE PYRIDINE CHROMOPHORE AND OF SOME METHYL DERIVATIVES

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Abstract. The intensity of the near UV transition of pyridine, pyrazine, and some of their methyl derivatives, is studied on the ground of the Interaction Vector Model (IVM), assuming that this transition is similar to the secondary one of the benzene chromophore.

The interaction vector model [1-6] (IVM) has been used to calculate the intensity of the secondary transition (255-260 nm) of the benzene chromophore of more than 80 molecules. Pyridine is interesting in the frame of the IVM, since it displays a chromophore with aromatic properties similar to the benzene ones. Nevertheless, the D_{6h} symmetry of the benzene molecule, which makes the secondary transition of that molecule forbidden, is destroyed in pyridine by the nitrogen atom. The 250 nm transition, corresponding to the secondary one in the benzene molecule, is slightly allowed, and its intensity is increased. Furthermore, pyridine displays a $n \rightarrow \pi^*$ transition owing to the fact that the nitrogen atom possess non bonding electrons (n). Using the Interaction Vector Model to calculate the intensity of the 250 nm transition in pyridine derivatives will allow to test to what extent the approach used in the IVM can be applied to non purely benzenic molecules.

I - THE BASIS OF THE IVM

Within the IVM [1,2] the SKLAR's [7] simple vector scheme approach is used with basis vectors $\mathbf{n}$ [1,2] (Figure 1) whose moduli n depend on the nature of the substituents. Several new concepts have been introduced, and they completly change the approach : the *interaction vector* (Fig. 1), which takes into account the interaction of two given substituents, the *strain vector* which takes into account the strain imposed by fused rings. This latter concept will be of no use here, since one will not study fused rings. A component related to a sort of *photonic cross section* has been introduced too (see S and σ underneath). Its value increases as much as

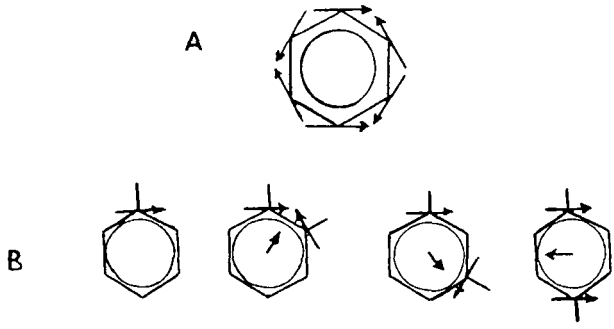

FIGURE 1. Direction of the basis vectors. A) The Sklar's basis virtual vectors pattern. B) The basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. All the directions are relative within a given molecule.

the substituents coupled to the π system enlarges this π system increasing its efficiency to capture photons.

A given interaction vector lies on the line bisecting the angle of the two basis vectors involved in the interaction. Their directions (Fig. 1) show that, as far as π donating substituents are concerned, the ortho substitution increases the transition moment more than an addition of the effects, and the para substitution less than addition.

A vibrational component [1,2,8] : V has been used to take into account the coupling of the vibrational motion with the electronic one. S and σ ($\sigma = S^{1/2}$) are functions of the number and of the nature of the substituents (n_C is the number of alkyl substituents, n_O the number of -OR ones) :

$$V = 0.0180 + 0.0390\,K + 0.0030\,(n_C + n_O) \quad ; \quad \text{if } n_O = 0 : K = 0 \text{ ; if } n_O \neq 0 : K = 1$$

$$S = [5n_O/(4{,}8 + 0.2\,n_O{}^2)] + n_C/(4{,}8 + 0.2\,n_C{}^{(2 + 0.5\,n_O)})$$

since : $S = hn_x/(4{,}8 + 0.2\,n_x{}^2)$, for a given substituent X. h is a constant depending on the nature of X.

The vectors **S** and **n** diplay the same direction. a is : $a = n^{1.5}\sigma^{0.5}$, and b : $b = n(n + \sigma)/2$. Then : $p = (a + kb)/(1 + k)$, with $k = d^6$, and : $d = |n - \sigma|$.

Intensity is given as ε_{sm}, the maximum of the smoothed absorption curve (BALLESTER and RIERA [8]) (the calculated value is : $\varepsilon_{sm,c}$). This approach minimizes the incidence of the vibrational fine structure on the measure of intensity. A general relationship has been obtained [1,2] :

$$\varepsilon_{sm,c} = 4905\,[1.025\,p + V]$$

In a preceding work (when π donating substituents are involved) it has been shown that empirical relationships could be used to approach n and V for a given substituent for monosubstituted molecules : [5]

$$n = -0.5204 + (0.27082 + 0.55801\,S)^{0.5}\ ;\ V = 0.03375\,S^2 + 0.00825\,S + 0.018$$

II - PYRIDINE AND SOME OF ITS METHYL DERIVATIVES

pyridine

The 250 nm transition of pyridine is composed of the secondary like transition superimposed to the $n \rightarrow \pi^*$ transition. It is necessary to work in non aqueous, non alcoholic solvents, to prevent the non bonding electrons of the nitrogen atom to be involved in hydrogen bonds. One has to use solvents as less solvating as possible. Otherwise, the intensity of the $n \rightarrow \pi^*$ transition would change, owing to the solvation state. This would change the correction to bring to the observed overall intensity to deduce the intensity of the secondary like transition. It would change the secondary like transition too, since solvating the non bonding electrons of the nitrogen atom would distort more strongly the symmetry of the π system. This would change the electronic properties of the nitrogen atom and then the intensity. Actually, intensities are much higher in alcohol or in water than in hexane. They are very sensitive to the medium, depending on the possibilities of solvating the non bonding electrons. Thus, the only data which can be used are those arising from non polar, non solvating hydrocarbon solvents. They are not numerous, but enough to test the use of the IVM on the pyridine chromophore.

When considering n (the modulus n of the basis vectors **n**), and σ (which is related to a sort of photonic cross section), n and σ should display the same values if the vector approach and the cross section one were perfectly equivalent. One knows that this is not the case, since the approximations used in the two fields are not the same. The IVM mixes the two approaches. Nevertheless, it is possible, in order to simplify, to assume that $n = \sigma$. The other empiric parameters will adapt to that condition. Knowing n this will fix S, since $S = \sigma^2$, and this will fix h in : $S_N = h n_N/(4{,}8 + 0.2\ n_N{}^2)$, where n_N is the number of nitrogen atoms in the ring.

The intensity of the $n \rightarrow \pi^*$ transition is difficult to measure, since it is superimposed to the secondary like one. Nevertheless, it can be roughly evaluated from the comparison of various spectra and litterature data. Its smoothed value should be : $\varepsilon_{sm,n\pi^*} = 375$, assuming that it does not change much from one methyl pyridine derivative to another. In hexane, the intensity of the 250 nm transition of pyridine is : $\varepsilon_{sm} = 1950$. Thus, the secondary like transition is : $\varepsilon_{sm,sec} = 1950 - 375 = 1575$. Knowing this value, one can calculate the modulus of the basis vector **n** for the nitrogen atom considered as a substituent, or at least as the origin of the perturbation imposed upon the π system : $n = 0.5300$. Then, since here : $n = \sigma$, this gives : $\sigma = 0.5300$ too. This leads to : $S = 0.2809$, thus to : $S_N = 1.4045 n_N/(4{,}8 + 0.2\ n_N{}^2)$. Owing to the fact that $n = \sigma \Rightarrow$

a = b = p = 0.2809. Furthermore, as there is no substituent outside the ring : V = 0.018 which is the value used for the benzene molecule, and :

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 0.2809 + 0.018] = 1500$$

Thus, the empiric determination of n giving the value : n = 0.5300, leads to 1500 + 375 = 1875 for the superimposed transitions, instead of 1950. One will use that value (n = 0.5300) as the modulus of the transition moment vector of the nitrogen perturbating site in pyridine.

The basis value n being established, it is possible to calculate the intensity of the monomethyl derivatives. The IVM has been built on the ground that substituents on the benzene ring interacts. Methyl substituents display interaction vectors whose moduli are small. Furthermore, here, nitrogen does not display an extension outside of the ring and this is not exactly a substituent. Thus, there should not be interaction vectors between N and $-CH_3$, or interaction vectors of very small values. So, one will not use interaction vectors.

4-methylpyridine

The relative direction of the basis vector of the methyl substituent, compared to the direction of the basis vector of the nitrogen atom, has to be fixed. In benzene derivatives, a basis vector arises from the local distorsion of the symmetry of the benzene chromophore on the atom (or around the atom) at the site of substitution. In the IVM the intensity of the secondary transition is mainly linked to the π HOMO. The third π orbital is too low in energy to be strongly involved in the transition. In a preceding paper the NVM (New Vector Model) [9] has shown that it is possible to use the distorsion of the densities in the two HOMOs to calculate the intensity of the secondary transition. Thus, we have only to look at the π densities in the two HOMOs near to the atomic center bearing the substituent. For example $-CH_3$ is a π donating substituent, and the density increases to 1.002 when adding the densities in the *p* atomic orbitals at the site of substitution and the two neighbouring centers. As concerns pyridine densities decrease to 0.784 at these three sites. Thus, the nitrogen atom distorts the densities at its position and near its position as a π attracting substituent would do. Its basis vector should display the same direction as the vector of an attracting substituent. That is to say a direction opposed to the direction of a π donating substituent in the same site. It has to be opposed, for example, to the direction of the basis vector of a methyl substituent. This allows to draw the vector schemes of figure 2.

First of all, the derivative with the methyl in the para position to the nitrogen shows that N and $-CH_3$ oppose their basis vectors. The length of the basis vector for a methyl has been established as being 0.0980 in preceding papers. [1-6] Thus : n = 0.5300 - 0.098 = 0.4320. Furthermore, using the above relationship to calculate S, one reminds that the contribution to S from the nitrogen atom is : 0.2809, and it is easy to calculate the contribution of the methyl : 0.2 (as it has been shown in preceding papers). [1-6] Thus : S = 0.4809, and σ = 0.6935.

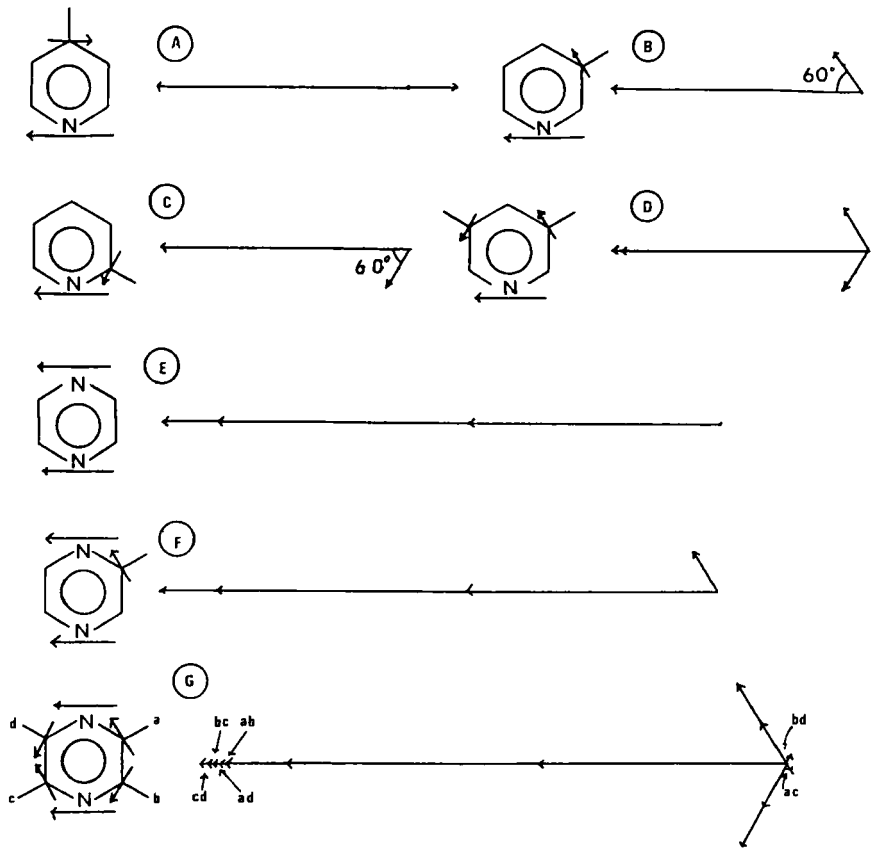

Figure 2. A) 4-methylpyridine. Left part : directions of the basis vectors are shown on the pyridine ring. Lengthes are only indicative. Right part : the vector addition with lengthes proportional to the moduli. B) 3-methylpyridine. C) 2-methylpyridine. D) 3,5-dimethylpyridine (as equivalent to 3,5-dibutylpyridine). The short vector is the interaction vector between the two meta methyls (length : 0.06). E) pyrazine. The left vector is the interaction vector between the two nitrogen atoms. Its length is 0.12. F) 2-methylpyrazine. G) 2,3,5,6-tetramethylpyrazine. The couples of small letters stand for the interaction vectors between the methyl substituents in the corresponding positions : ab stands for the interaction vector between the methyl a and the methyl b. Owing to preceding works : interaction vectors between ortho methyls or meta methyls are 0.06 long, and in the direction of the resultant of the basis vectors of the two involved methyls. The para interaction vectors point in the direction opposed to the resultant of the two para vectors. their length is : 0.012. Here, interaction vectors have little effect because they are far shorter than the lengthes of the basis vectors of the nitrogen atoms.[1-6]

a = 0.2364 = b = p. As there is a methyl on the chromophore, the vibrational component to intensity is : V = 0.021, thus :

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 0.2364 + 0.021] = 1292$$

As n→ π^* is $\varepsilon_{sm,n\pi^*}$ = 375. The calculated intensity will be :

$$1292 + 375 = \mathbf{1667}$$

Experiment gives **1560** (determined from : [10a]). The difference is Δ = + 6.7 %. This is quite satisfactory, since it is within ±10%. Thus, the main reason for the decrease of intensity, when substituting by a methyl the chromophore in para position to the nitrogen atom, lies in the fact that the methyl group is a π donating substituent, when the nitrogen atom displays, on the π HOMO densities, the same effects as a π attracting substituent. This arises although the total π density increases strongly on the nitrogen, when it should decrease if there was a π attracting substituent on its site. The increase of the total density arises because it includes the lowest π orbital which is not much involved in the secondary like transition. Only the HOMOs are of importance.

Thus, considering the toluene molecule, when a methyl is added in the para position to the already existing methyl (giving 1,4-dimethylbenzene), intensity increases strongly from ε_{sm} = 192 to 425 (121%) (these values and those given underneath for methyl and hydroxy substituted benzene chromophores have been given in our preceding work : [1]). When a methyl is added in the same para position in phenol, (1-hydroxy-4-methylbenzene) intensity increases from ε_{sm} = 1450 to 1900 (31%). The intensity increases strongly for the dimethyl derivative because the length of the basis vector is doubled (0.098·2), and because the interaction vector is short (0.012 ; for two methyl substituents, in para positions, it is opposed to the direction of the basis vectors). σ is the same for all the dimethyl substituted chromophores, since it is related to their number. Intensity increases less when considering the phenol molecule (1-hydroxy-4-methylbenzene) because the methyl adds a short vector (0.098) to a much longer one (0.390), and it does not change much σ (1 ⇒ 1.095) causing a smaller relative change. For the pyridine derivative, it decreases because the effects of the pyridine nitrogen atom and the methyl, in the para position, oppose owing to their relative effects on the π system. It is the first time that the phenomenon is explained on such a simple basis.

3-methylpyridine

When the methyl is in the meta position the two basis vectors display a 60° angle. The vector addition is given in figure 2. The modulus of the resulting vector is : n = 0.5680. S is the same as above since it depends only on the number and on the nature of the substituents, and σ too : σ = 0.6935. Thus : $a = 0.5680^{1.5} \cdot 0.6935^{0.5} = 0.3565$. As $d^6 = (0.6935\text{-}0.5680)^6 = 4 \cdot 10^{-6}$ it is devoided of interest to calculate b. This leads to p = a : p = 0.3565. Thus :

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 0.3565 + 0.021] = 1895$$

The transition towards 250 nm should be 1895 + 375 = **2270** when experiment is **2240**. The difference is only Δ = + 1.5%.

A methyl, when in the meta position to the nitrogen atom in pyridine increases strongly the intensity of the secondary like transition by 20 %. Considering what happens when introducing in the meta position a methyl in the toluene molecule, intensity increases by 20 %, from 192 to 234. When, in phenol, the methyl is added in the meta position to the -OH, intensity is almost kept constant. It increases only by 3 %, from 1450 to 1500, which is not very significant. When considering 1,3-dimethylbenzene compared to toluene, a slight increase of n arises from the interaction vector, but the main part of the increase arises from σ which goes from 0.447 to 0.598. Considering the phenol molecule with a methyl in the meta position (1-hydroxy-3-methylbenzene), the addition of the two basis vectors leads to a decrease of n, although the interaction vector is greater in that case. Actually one adds a short basis vector (0.098 for methyl) to a much longer one (0.39 for -OH) when their directions display a 120° angle. Paralleling that decrease of n, there is a small increase of σ, since the methyl adds, in that case, only a small contribution. The net effect of the changes in n and σ is a very small increase of intensity. Thus, the same substituent : a methyl, when in the meta position to the perturbating group leads to very different effects on intensity owing the nature of that group. Furthermore, when intensity seems unchanged, its value originates in fact from different grounds.

2-methylpyridine

Owing to the fact that there is no interaction between N and the methyl substituent (or a negligible one), the vector addition leads to the same value as that obtained for 3-methylpyridine since the angle between the basis vectors of the two substituents is the same (Figure 2). Thus : $(\varepsilon_{sm,c})_{sec}$ = 1895, and : 1895 + 375 = **2240** for the superimposed UV transition, when experiment gives **2365**. The difference is only Δ = - 4.9%. Although weak and satifactory, this difference is higher than above for the meta derivative. The calculation gives a value lower than experiment. This means that, perhaps, the interaction in the ortho position between N and $-CH_3$ is not completely negligible, as it is when the nitrogen atom and $-CH_3$ are meta or para.

The same behaviour happens for the ortho dimethyl substituted benzene (1,2-dimethylbenzene) : intensity is the same as the meta one, since the interaction vectors are the same in the both cases. As concerns the phenol molecule with a methyl substituent in ortho to the -OH group (1-hydroxy-2-methylbenzene), intensity increases from 1450, considering phenol, or 1500, considering the meta methyl substituted phenol (1-hydroxy-3-methylbenzene), to 1650 for the ortho substituted molecule. This increase arises, because there is an important interaction vector in the ortho position between -OH and $-CH_3$ (0.052).

3,5-dibutylpyridine

Intensity is : ε_{max} = 3010 [11] in cyclohexane, and : ε_{sm} = 2960. The alkyl substituents are butyl ones instead of methyl ones. Nevertheless, it

is possible, as it has already been done, to calculate $\varepsilon_{sm,c}$ for the methyl derivative, since the main part of the intensity arises from the nitrogen atom. The difference between the methyl and the butyl derivative should be small. The vector addition is given in figure 2. The resultant displays the same length : 0.098, as one of the two components, since their angle is 120°. The basis vectors addition of the two alkyl substituents displays the same direction as the basis vector of the nitrogen atom. Their effects should increase intensity compared to pyridine. This is to be compared to the derivative where an alkyl substituent is in the para position, that is to say between the two positions occupied by the tertiobutyl substituents. Substitution in the para position decreases intensity.

An interaction vector between the two alkyl groups has to be taken into account, as it is done for two methyls (0.006). Thus n = 0.5300 + 0.0980 + 0.0060 = 0.6340. As above the contribution of the nitrogen atom to S is 0.2809, and the contribution is 0.3571 for the two methyls, since there is no -OR group: S = 0.2809 + 0.3571 = 0.638, σ = 0.7987. Thus : a = 0.4512 and b = 0.4542, $d^6 = 2 \cdot 10^{-5}$. This leads to : p = a = 0.4512. As there are two methyls : V = 0.024.

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 0.4512 + 0.024] = 2386$$

Taking into account the superimposed $n \rightarrow \pi^*$ transition gives : 2386 + 375 = **2760**. Experiment leads to : **2960**. Δ = - 6.8%. This is satisfactory.

pyrazine

That molecule displays two nitrogen atoms in para positions. Their basis vectors are in the same direction : n = 0.5300·2 = 1.0600. As there are two nitrogen atoms : S = 0.5016, and : σ = 0.7082. Thus : a = 0.9184. p = a, since d^6 is very small. $(\varepsilon_{sm,c})_{sec}$ = 4905[1.025·0.9184 + 0.018] = 4706. Experiment in hexane gives : ε_{max} = 6000, [12] This gives : ε_{sm} = 5700. Contrary to what happens for the above molecules, there is no overlap with the two $n \rightarrow \pi^*$ transitions [these $n \rightarrow \pi^*$ transitions interact and they display a new pattern of transitions]. The secondary like transition and the $n \rightarrow \pi^*$ transition are distinct. There is a great discrepancy between experiment and calculation. Actually, it is known that the non bonding orbitals on the nitrogen atoms couple. That should change the core potentials at the nitrogen sites, and modify the π system. Thus, one has to take into account such a change by using an empiric interaction vector between the two nitrogen atoms. In order to have a good fit experiment-calculation, the interaction vector has to point in the same direction as the two basis vectors of the nitrogens, and it has to display the value : **0.1200**. This leads to : n = 1.18, a = 1.0787, b = 1.114, d^6 = 0.02, p = 1.0794. $(\varepsilon_{sm,c})_{sec}$ = 5515. Using the spectrum of pyrazine, the value obtained for the interaction vector allows to calculate the intensities of several methyl substituted molecules.

2-methylpyrazine

The vector addition is given in figure 2. n = 1.2143, S = 0.5016 + 0.2 = 0.7016, σ = 0.8376, a = 1.2246, d^6 = 0.003, b = 1.2458, p = 1.2247 :

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 1.2247 + 0.021] = \mathbf{6260}$$

experiment (from : [10b]) gives : **6115** (medium isoöctane). $\Delta = +2.4\%$.

Introducing a methyl group in ortho to one of the nitrogen atoms (2-methylpyrazine), increases the intensity by 7.3%. When doing the same in the para dimethyl benzene derivative (1,4-dimethylbenzene), intensity is increased only by 3.5%. Considering the 1,4-dihydroxy-benzene molecule the increase is 12%.

As concerns the compound which displays three methyls (1,2,4-trimethylbenzene), the 3.5 % increase arises from σ (the third substituent displays almost the same efficiency as each one of the two already existing methyls, in increasing the photonic cross section) : 0.5976 $\Rightarrow$ 0.6742. The increase of intensity cannot arise from n, since n decreases (0.1840 $\Rightarrow$ 0.1702) because the basis vector of the third methyl displays a 120° angle with the basis vectors of the para methyls. The third methyl introduces new interaction vectors whose directions are such that they tend to increase n, but interaction between methyls is weak.

As concerns the phenol molecule (1,4-dihydroxy-3-methylbenzene), intensity increase arises mainly from σ too (1.3363 $\Rightarrow$ 1.4092). Actually, the basis vector of the methyl displays, as above, a 120° angle with the basis vectors of the -OH groups, decreasing their contribution. Of course, the interaction vectors involving methyls and -OH are far more important than those involving methyls, and they point in a direction which favours the increase of n. This increases only slightly n (0.6000 $\Rightarrow$ 0.6080).

In the 2-methylpyrazine molecule, the methyl substituent increases intensity; since it increases σ (0.6000 $\Rightarrow$ 0.6080), but, contrary to the two preceding molecules, the increase of n is very important : it goes from 1.060 to 1.214. This is possible because the angle between the basis vector of the methyl group and the basis vectors of the -OH groups is 60° (when it is 120° for the two preceding molecules). Actually, the nitrogen atom plays the part of a π attracting group as far as the intensity of the secondary like transition is concerned.

Thus, in the first molecule with the three methyls, the increase of intensity arises from σ, and n tends to decrease intensity. In the phenol molecule the increase arises from σ and the change in n has little influence. In the methyl pyrazine molecule increase arises from σ and from n. One sees that the similarity of the effects of the same substituent in the same position in several molecules (an increase of intensity), could lead to think that the same factor is responsible for that effect. This is not the case.

2,3,5,6-tetramethylpyrazine

The vector addition is given in figure 2. n = 1.388, S = 0.5016 + 0.5 = 1.0016, σ = 1.0008. a = 1.636, d^6 = 0.003, b = 1.658, p = 1.636 :

$$(\varepsilon_{sm,c})_{sec} = 4905\ [1.025 \cdot 1.636 + 0.030] = \mathbf{8372}$$

experiment (measure from : [10c]) leads to : **7850** (medium : isoöctane) ($\Delta = +6.6\%$). This value is corrected from the overlap with the $n \rightarrow \pi^*$

transition which lies towards 290-297 nm. Without correction the smoothed intensity is : 8595.

Compared to pyrazine (ε_{sm} = 5700), intensity is very much increased. Actually, σ increases from 0.7082 to 1.0008, since the four methyls increase the photonic cross section, and n from 1.180 to 1.388.

Considering the 1,4-dimethylbenzene molecule, intensity is : ε_{sm} = 425. It decreases to 260 when introducing four methyls in the vacant sites, obtaining hexamethylbenzene (one could say too that the D_{6h} symmetry is restaured and the transition becomes more tightly forbidden). One does not possess the spectrum of the 1,4-dihydroxy-2,3,5,6-tetramethylbenzene corresponding phenol molecule, but one can compare the 1-hydroxy-4-methylbenzene molecule and the pentamethylphenol one. In the first one, intensity is : 1900. It decreases to 1200 in the second one. Introducing four methyls in pyrazine increases strongly intensity. Introducing four methyls in the same sites in the two other molecules decreases drastically intensity.

As the contribution of σ to intensity is an increasing one when the number of methyls increases, the difference of behaviour is linked to the relative directions of the basis vectors of N, OH or $-CH_3$. These difference lies in the fact that, in the pyrazine derivative (Figure 2), the direction of the resultant vector contribution of the four methyls, and the direction of the vector contribution of the two nitrogen atoms are the same. They add and the methyl groups increase intensity. In the two other molecules the resultant of the vector contribution of the four methyls opposes to the resultant of the para substituents, decreasing intensity.

This work will not be concerned by other pyridine like derivatives with two or more nitrogen atoms. Actually, the geometries of the rings are strongly distorted, destroying the similarity with the benzene chromophore. Thus, studying them would need a strong parametrization, involving the spectra in non polar solvents of more methyl derivatives than is available.

CONCLUSION

Using the similarity of the two chromophores : pyridine and benzene, the intensities of the secondary like transition of pyridine derivatives are calculated by the IVM. This model is also used with pyrazine compounds. It explains, for the first time on a very simple ground, the changes of intensity when modifying the substitution pattern.

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