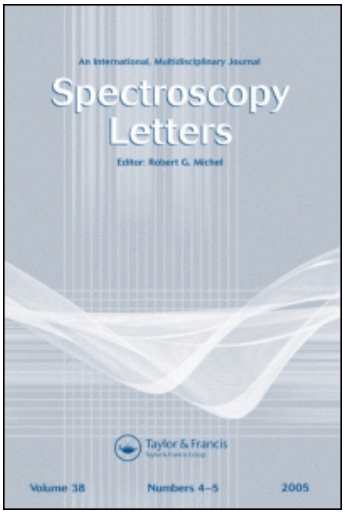


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# Interaction Vector. A New Concept to Approach the Intensity of the Secondary Transition of the Benzene Chromophore

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# INTERACTION VECTOR. A NEW CONCEPT TO APPROACH THE INTENSITY OF THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE.

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The new vector model (NVM), [1] designed for approaching the intensity of the secondary transition of the substituted benzene chromophore (towards 260 nm), has been based on MNDO calculations and on the SKLAR's vector model. [2-9] It leads to the simple relationship : $\varepsilon_{sm,c} = 4905$ (TS + V). Experimental intensity is given as $\varepsilon_{sm}$, the maximum of the smoothed absorption curve, as it has been defined by BALLESTER and RIERA [10] (the calculated value is : $\varepsilon_{sm,c}$). The vibrational component of intensity (V) is based, too, on their work. S is an increasing function of the number of substituents and of their ability to capture photons. It can be related to the UV cross section of the molecule, increasing when the UV cross section increases. T is the modulus of a vector related to the electronic transition moment. It is based on the distorsion of the $\pi$ electronic charges, from a pure $D_{6h}$ symmetry scheme. The MNDO method is used to calculate these charges. Thus, the modulus of the electronic transition moment being related to : $\mu = (TS)^{1/2}$, is the result of two complementary approaches.

The basic difference between the new vector model and the SKLAR's one lies in the fact that the interactions between the substituents are taken into account in the ground state of the transition by the MNDO calculations. On the contrary, the main weakness in the SKLAR's vector model - which is sometimes erroneous by 50 or 100% - is in assuming that the vectors, related to the substituents, and composing the transition moment vector, are additive, independently of possible interactions among the substituents. In the present work we should like to consider these interactions, in order to systematize the vector process, avoiding the step of the MNDO calculations.

## I - INTERACTION VECTORS

In the present work it has been choosen to take into account the substituent interactions by introducing interaction vectors – a new concept – in the vector scheme. Actually, we have been led to this model by our preceding work concerning the incidence of cyclization strain on intensity when a ring is fused to the benzene chromophore. [11] Such an incidence had been taken into account by calculating the vector scheme for the non cyclic corresponding molecule, and then adding a strain vector to the resulting vector of the two ortho substituents which are in the position of cyclization. It has been thought in the present work that, if it is possible to use a vector to take into account a strong ortho interaction (cyclization strain), it is possible to use vectors for small ortho, meta and para interactions. Experiment shows that the ortho interaction vector has to point in the direction bisecting the angle of the two vectors involved in the interaction, since the ortho interaction acts in the same direction as the two ortho substituents to induce a symmetry distorsion. The same happens for the meta interaction vector. It is the contrary for two para substituents, since in the SKLAR's model additivity leads to far too strong intensities (Figure 1).

An interaction vector modulus depends on the nature of the substituents. We deal in that work only with $\pi$ donating substituents, such as $-CH_3$, -OH (or $-OCH_3$, considering -OH and $-OCH_3$ as the same chemical function) since our main concern is the spectroscopy of natural products, although interactions involving the substituents around the benzene ring is an important field of research (ex : [12]). As far as their absolute value is concerned, interactions vectors are longer for -OR than for $-CH_3$, since -OR is a much more $\pi$ perturbating substituent. The lengthes of hetero interaction vectors (-OR interacting with $-CH_3$) are taken as a kind of average of the two corresponding homo interactions. As the moduli of homo interactions are far greater for -OR than for $-CH_3$, using the arithmetical mean should lead to values which would be very near to half the value used for -OR. Using the geometrical mean would take into account too much of the lowest value. So, first of all, the following iterative process was used till consistency was achieved. Taking $n_o$ and $n_c$ as the moduli for a given homo interaction between respectively two -OR ($n_o$) and two $-CH_3$ ($n_c$) substituents, the geometrical mean : $x = (n_o \cdot n_c)^{1/2}$, and the arithmetical one : $y = (n_o + n_c)/2$ have been calculated, then carrying out the geometrical and the arithmetical mean with x and y, and starting again with the results till the consistency was achieved. It has been obtained : 0.047, 0.021, 0.073 for the moduli of the ortho, meta and para hetero interactions. Results are good. They are far better than what can be obtained from a simple Sklar treatment. Nevertheless, we tried to improve these results starting from the above hetero parameters trying to narrow the gap between calculation and experiment on a purely empirical basis. The following moduli have been obtained : 0.0520, 0.0240, 0.0630 for hetero ortho, meta, and para interactions. The results of these calculations are given in table I.

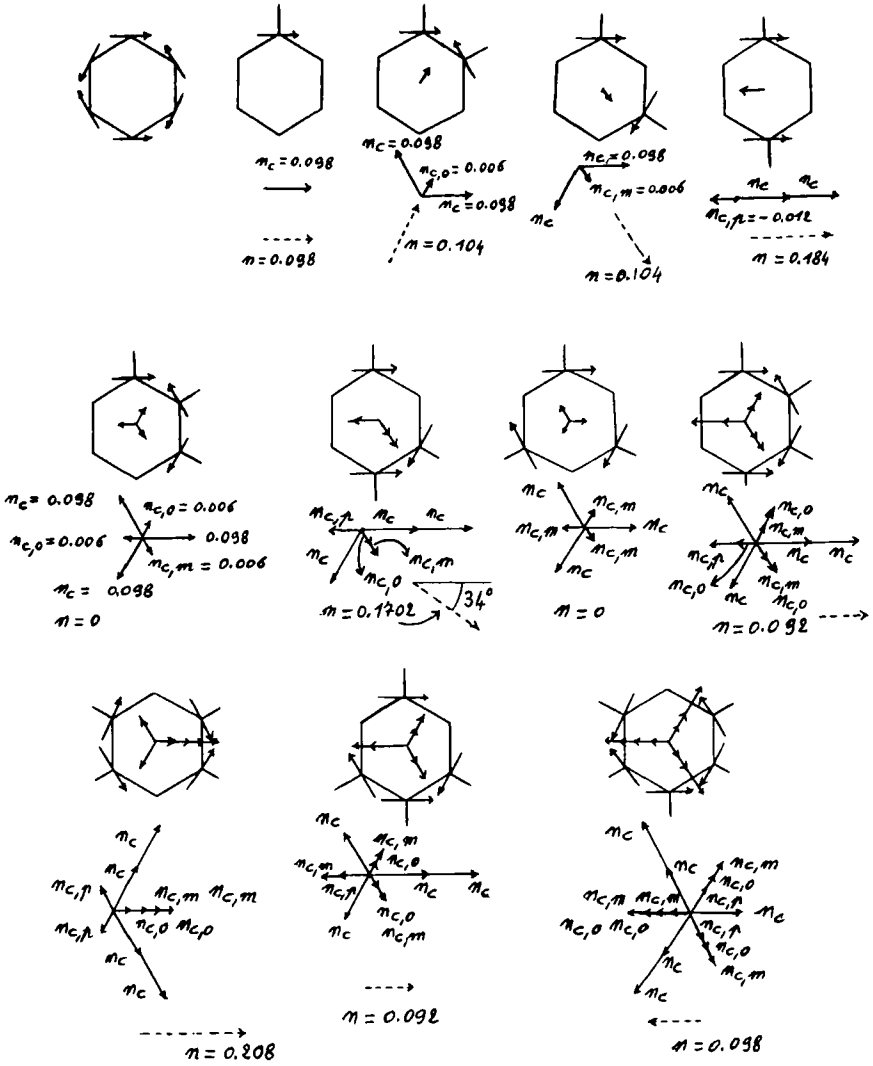


**Figure 1**. Vectors used to calculate n for methylbenzenes. The first drawing shows the basis vector pattern. The interaction vectors are drawn at the center of the benzene ring. For the sake of clarity these vectors have been drawn at an increased scale compared to the basis vectors. Under each drawing there is the complete vector scheme. The dotted vector correspond to n. (The π system of the benzene chromophore has not been drawn).

## TABLE I : CALCULATIONS AND DATA

o stands for -OR, c for $-CH_3$; $c_i$ for another alkyl, or alkyl like substituent identified at the end. Medium for phenols or anisole derivatives : methanol. Medium for hydrocarbons : hexane or another non hydroxylic non polar solvent. The $\varepsilon_{sm}$ experimental values are those which have been measured by [10] on API spectra. All the other values have been measured on literature spectra.[1] $\Delta$ is the relative difference between experimental and calculated value, using the experimental value as the reference. When the experiment is known for the -OH and the $-OCH_3$ derivative the two values are given one ($-OCH_3$) below the other (-OH) in the column $\varepsilon_{sm}$, then $\Delta$ is calculated using the average of the two experimental values. p is : $p = (n^{1.5}\sigma^{0.5} + d^6\, n(n + \sigma)/2\,)/(1+ d^6\,)$. Thus : $\varepsilon_{sm,c} = 4905\ (1.025\ p + q + V)$

Positions on the benzene ring :
1 2 3 4 5 6

| | | | | | $\varepsilon_{sm,c}$ (calc.) | $\varepsilon_{sm}$ (exper.) | $\Delta$ |
|---|---|---|---|---|---|---|---|
| benzene | (a) | n = 0 | σ = 0 | q = 0.006 | **118** | **110** | + 7.3 |
| | | a = 0 | b = 0 | V = 0.018 | | | |
| | | d = 0 | p = 0 | | | | |
| | | $\varepsilon_{sm,c} = (0 + 0.006 + 0.018)\ 4905$ | | | | | |
| c | (b) | n = 0.0980 | σ = 0.4472 | q = 0 | **206** | **192** | + 7.3 |
| | | a = 0.02052 | b = 0.02671 | V = 0.021 | | | |
| | | d = 0.3492 | p = 0.02053 | | | | |
| | | $\varepsilon_{sm,c} = (0.02053 \cdot 1.025 + 0 + 0.021)\ 4905$ | | | | | |
| c c | (c) | n = 0.1040 | σ = 0.5976 | q = 0 | **249** | **234** | + 6.4 |
| | | a = 0.02593 | b = 0.03648 | V = 0.024 | | | |
| | | d = 0.4936 | p = 0.02608 | | | | |
| | | $\varepsilon_{sm,c} = (0.02608 \cdot 1.025 + 0 + 0.024)\ 4905$ | | | | | |
| c . c | (d) | n = 0.1040 | σ = 0.5976 | q = 0 | **249** | **234** | + 6.4 |
| | | a = 0.02593 | b = 0.03648 | V = 0.024 | | | |
| | | d = 0.4936 | p = 0.02608 | | | | |
| | | $\varepsilon_{sm,c} = (0.02608 \cdot 1.025 + 0 + 0.024)\ 4905$ | | | | | |
| c . . c | (e) | n = 0.1840 | σ = 0.5976 | q = 0 | **425** | **425** | 0.0 |
| | | a = 0.06101 | b = 0.07191 | V = 0.024 | | | |
| | | d = 0.4136 | p = 0.06106 | | | | |
| | | $\varepsilon_{sm,c} = (0.06106 \cdot 1.025 + 0 + 0.024)\ 4905$ | | | | | |
| c c c | (f) | n = 0 | σ = 0.6742 | q = 0.006 | **162** | **170** | - 4.7 |
| | | a = 0 | b = 0 | V = 0.027 | | | |
| | | d = 0.6742 | p = 0 | | | | |
| | | $\varepsilon_{sm,c} = (0 + 0.006 + 0.027)\ 4905$ | | | | | |
| c . c c | (g) | n = 0.1702 | σ = 0.6742 | q = 0 | **423** | **440** | - 3.9 |
| | | a = 0.05765 | b = 0.07186 | V = 0.027 | | | |
| | | d = 0.5040 | p = 0.05788 | | | | |
| | | $\varepsilon_{sm,c} = (0.05788 \cdot 1.025 + 0 + 0.027)\ 4905$ | | | | | |

**TABLE I Continued**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| c . c . c | (h) | n = 0 | σ = 0.6742 | q = 0.006 | **162** | **170** | - 4.7 |
| | | a = 0 | b = 0 | V = 0.027 | | | |
| | | d = 0.6742 | p = 0 | | | | |
| | | $\varepsilon_{sm,c}$ = (0 + 0.006 + 0.027) 4905 | | | | | |
| c c c c | (i) | n = 0.0920 | σ = 0.7071 | q = 0 | **269** | **265** | + 1.5 |
| | | a = 0.02347 | b = 0.03676 | V = 0.030 | | | |
| | | d = 0.6151 | p = 0.02415 | | | | |
| | | $\varepsilon_{sm,c}$ = (0.02415·1.025 + 0 + 0.030) 4905 | | | | | |
| c c . c c | (j) | n = 0.2080 | σ = 0.7071 | q = 0 | **549** | **615** | -10.7 |
| | | a = 0.07977 | b = 0.09517 | V = 0.027 | | | |
| | | d = 0.4991 | p = 0.08000 | | | | |
| | | $\varepsilon_{sm,c}$ = (0.08000·1.025 + 0 + 0.030) 4905 | | | | | |
| c . c c c | (k) | n = 0.0920 | σ = 0.7071 | q = 0 | **269** | **250** | + 7.6 |
| | | a = 0.02347 | b = 0.03676 | V = 0.030 | | | |
| | | d = 0.6151 | p = 0.02415 | | | | |
| | | $\varepsilon_{sm,c}$ = (0.02415·1.025 + 0 + 0.030) 4905 | | | | | |
| c c c c c | (l) | n = 0.0980 | σ = 0.7143 | q = 0 | **296** | **260** | +13.8 |
| | | a = 0.02593 | b = 0.03980 | V = 0.033 | | | |
| | | d = 0.6163 | p = 0.02665 | | | | |
| | | $\varepsilon_{sm,c}$ = (0.02665·1.025 + 0 + 0.033) 4905 | | | | | |
| Experimental value from Ballester [10] (measured on the API spectra [13]). Our own measure on the same spectrum is 265. The spectrum of Sadtler [14] leads to 300. | | | | | | | |
| c c c c c c | (m) | n = 0 | σ = 0.7071 | q = 0.006 | **206** | **225** | - 8.4 |
| | | a = 0 | b = 0 | V = 0.036 | | | |
| | | d =0.7071 | p = 0 | | | | |
| | | $\varepsilon_{sm,c}$ = (0 + 0.006 + 0.036) 4905 | | | | | |
| o | (1) | n = 0.3900 | σ = 1 | q = 0 | **1526** | **1450** | +3.5 |
| | | a = 0.2436 | b = 0.2711 | V = 0.060 | | **1500** | |
| | | d = 0.6100 | p = 0.2449 | | | | |
| | | $\varepsilon_{sm,c}$ = (0.2449·1.025 + 0 + 0.060) 4905 | | | | | |
| o o | (2) | n = 0.5230 | σ = 1.3363 | q = 0 | **2562** | **2550** | +0.5 |
| | | a = 0.4372 | b = 0.4862 | V = 0.063 | | **2550** | |
| | | d = 0.8133 | p = 0.4482 | | | | |
| o . o | (3) | n = 0.4350 | σ = 1.3363 | q = 0 | **2071** | **2000** | +3.6 |
| | | a = 0.3317 | b = 0.3853 | V = 0.063 | | **2000** | |
| | | d = 0.9013 | p = 0.3504 | | | | |
| o . . o | (4) | n = 0.6000 | σ = 1.3363 | q = 0 | **3040** | **3080** | -1.6 |
| | | a = 0.5373 | b = 0.5809 | V = 0.063 | | **3100** | |
| | | d = 0.7363 | p = 0.5433 | | | | |

*(continued)*

**TABLE I Continued**

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| o . o . o | (5) | n = 0 | σ = 1.5076 | q = 0.006 | **353** | **330** | +7.0 |
| | | a = 0 | b = 0 | V = 0.066 | | | |
| | | d = 1.5076 | p = 0 | | | | |
| | | $\varepsilon_{sm,c}$ = (0 + 0.006 + 0.066) 4905 | | | | | |
| o o o | (6) | n = 0.0880 | σ = 1.5076 | q = 0 | **656** | **680** | -3.5 |
| | | a = 0.03205 | b = 0.07021 | V = 0.066 | | **680** | |
| | | d = 1.4196 | p = 0.0661 | | | | |
| o o . o | (7) | n = 0.6971 | σ = 1.5076 | q = 0 | **3976** | **3650** | +8.9 |
| | | a = 0.7146 | b = 0.7684 | V = 0.066 | | | |
| | | d = 0.8105 | p = 0.7265 | | | | |
| o c | (8) | n = 0.3976 | σ = 1.0954 | q = 0 | **1646** | **1650** | -0.2 |
| | | a = 0.2624 | b = 0.2968 | V = 0.063 | | | |
| | | d = 0.6978 | p = 0.2660 | | | | |
| o . c | (9) | n = 0.3767 | σ = 1.0954 | q = 0 | **1549** | **1500** | +3.8 |
| | | a = 0.2420 | b = 0.2773 | V = 0.063 | | **1480** | |
| | | d = 0.7187 | p = 0.2463 | | | | |
| o . . c | (10) | n = 0.4250 | σ = 1.0954 | q = 0 | **1781** | **1900** | -3.7 |
| | | a = 0.2900 | b = 0.3231 | V = 0.063 | | **1800** | |
| | | d = 0.6704 | p = 0.2927 | | | | |

The experimental value of this phenol molecule could be overestimated. The actual value could be nearer to 1850 than to 1900. Several values are given in literature. The highestones are given by BERLMAN [18] for the phenol molecule : 2250 in cyclohexane, 2150 in ethanol (for the corresponding anisole molecule : 1850 in cyclohexane, 1950 in ethanol)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| o c c | (11) | n = 0.3249 | σ = 1.1564 | q = 0 | **1377** | **1450** | - 2.7 |
| | | a = 0.1992 | b = 0.2406 | V = 0.066 | | **1380** | |
| | | d = 0.8315 | p = 0.2095 | | | | |
| c o c | (12) | n = 0.3380 | σ = 1.1564 | q = 0 | **1434** | **1450** | - 1.1 |
| | | a = 0.2113 | b = 0.2526 | V = 0.066 | | | |
| | | d = 0.8184 | p = 0.2208 | | | | |
| o c . . c | (13) | n = 0.4045 | σ = 1.1564 | q = 0 | **1745** | **1820** | -4.1 |
| | | a = 0.2766 | b = 0.3157 | V = 0.066 | | | |
| | | d = 0.7519 | p = 0.2826 | | | | |
| o c . c | (14) | n = 0.4269 | σ = 1.1564 | q = 0 | **1857** | **1930** | - 3.8 |
| | | a = 0.3000 | b = 0.3380 | V = 0.066 | | | |
| | | d = 0.7295 | p = 0.3050 | | | | |
| c . o o | (15) | n = 0.5653 | σ = 1.4092 | q = 0 | **2932** | **3000** | - 2.3 |
| | | a = 0.5046 | b = 0.5581 | V = 0.066 | | | |
| | | d = 0.8439 | p = 0.5188 | | | | |

when c is $-CH_2-CH=CH_2$ instead of $-CH_3$ and o is methoxy : $\varepsilon_{sm}$ = 2900. When only the group in meta position to the c group is a methoxy group : $\varepsilon_{sm}$ = 3000.

**TABLE I Continued**

| | | | | | | |
|---|---|---|---|---|---|---|
| o . c . c | (16) | n = 0.3100 σ = 1.1564 q = 0 | **1313** | **1430** | - 8.2 |
| | | a = 0.1856 b = 0.2273 V = 0.066 | | | |
| | | d = 0.8464 p = 0.1968 | | | |
| o . o . c | (17) | n = 0.3130 σ = 1.4092 q = 0 | **1565** | **1550** | + 1.0 |
| | | a = 0.2079 b = 0.2695 V = 0.066 | | | |
| | | d = 1.0962 p = 0.2470 | | | |
| o . $c_1$ o | (18) | n = 0.6080 σ = 1.4092 q = 0 | **3206** | **3450** | - 7.1 |
| | | a = 0.5628 b = 0.6132 V = 0.066 | | | |
| | | d = 0.8012 p = 0.5733 | | | |
| | | $\varepsilon_{calc}$ = (0.5733·1.025 + 0 + 0.066) 4905 | | | |
| o . o $c_2$ | (19) | n = 0.5054 σ = 1.4092 q = 0 | **2570** | **2850** | - 9.8 |
| | | a = 0.4265 b = 0.4838 V = 0.066 | | | |
| | | d = 0.9038 p = 0.4467 | | | |
| o c c c c c | (20) | n = 0.3050 σ = 1.1458 q = 0 | **1328** | **(1200)** | +10.7 |
| | | a = 0.1803 b = 0.2212 V = 0.075 | | | |
| | | d = 0.8408 p = 0.1910 | | | |
| o . c c | (21) | n = 0.4064 σ = 1.1564 q = 0 | **1754** | **1850** | - 5.2 |
| | | a = 0.2786 b = 0.3176 V = 0.066 | | | |
| | | d = 0.7500 p = 0.2845 | | | |
| o c c c | (22) | n = 0.3790 σ = 1.1743 q = 0 | **1652** | **(1860)** | -11.2 |
| | | a = 0.2528 b = 0.2944 V = 0.069 | | | |
| | | d = 0.7953 p = 0.2612 | | | |
| o c c c | (23) | n = 0.3111 σ = 1.1743 q = 0 | **1347** | **(1440)** | - 6.5 |
| | | a = 0.1880 b = 0.2310 V = 0.069 | | | |
| | | d = 0.8633 p = 0.2006 | | | |

$c_1$ is an hydantoin group as concerns the experimental value

$c_2$ is n-hexyl as far as the experimental value is concerned

The experimental value has been evaluated from a logarithmic spectrum whose $\varepsilon_{max}$ = 1250. [15] The value given here (1200) is the lowest estimated limit.

The experimental value inside the brackets, for that molecule (22) and the next one (23) has been obtained from a logarithmic spectrum whose accuracy is low. [16]

## II - INTENSITY EVALUATION

Two approaches have been tried in evaluating the transition moment. The first one is based on two separate elements : n and σ, with : $\varepsilon_{sm,c}$ = 4905 (nσ + V) corresponding to what has already been done within the MNDO calculation frame. n is the modulus of the vector determined

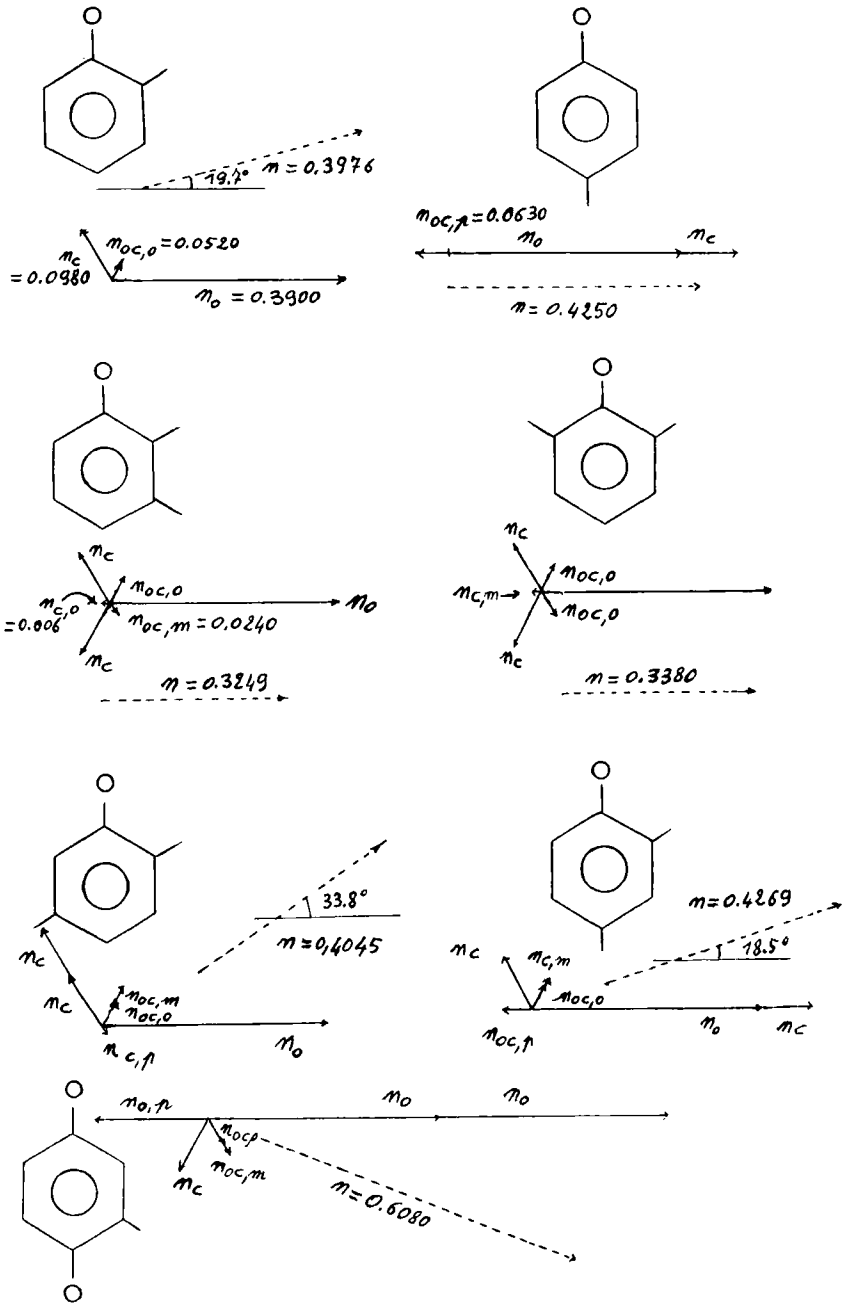


**Figure 2.** Vectors for hetero interactions (-OR and -$CH_3$).

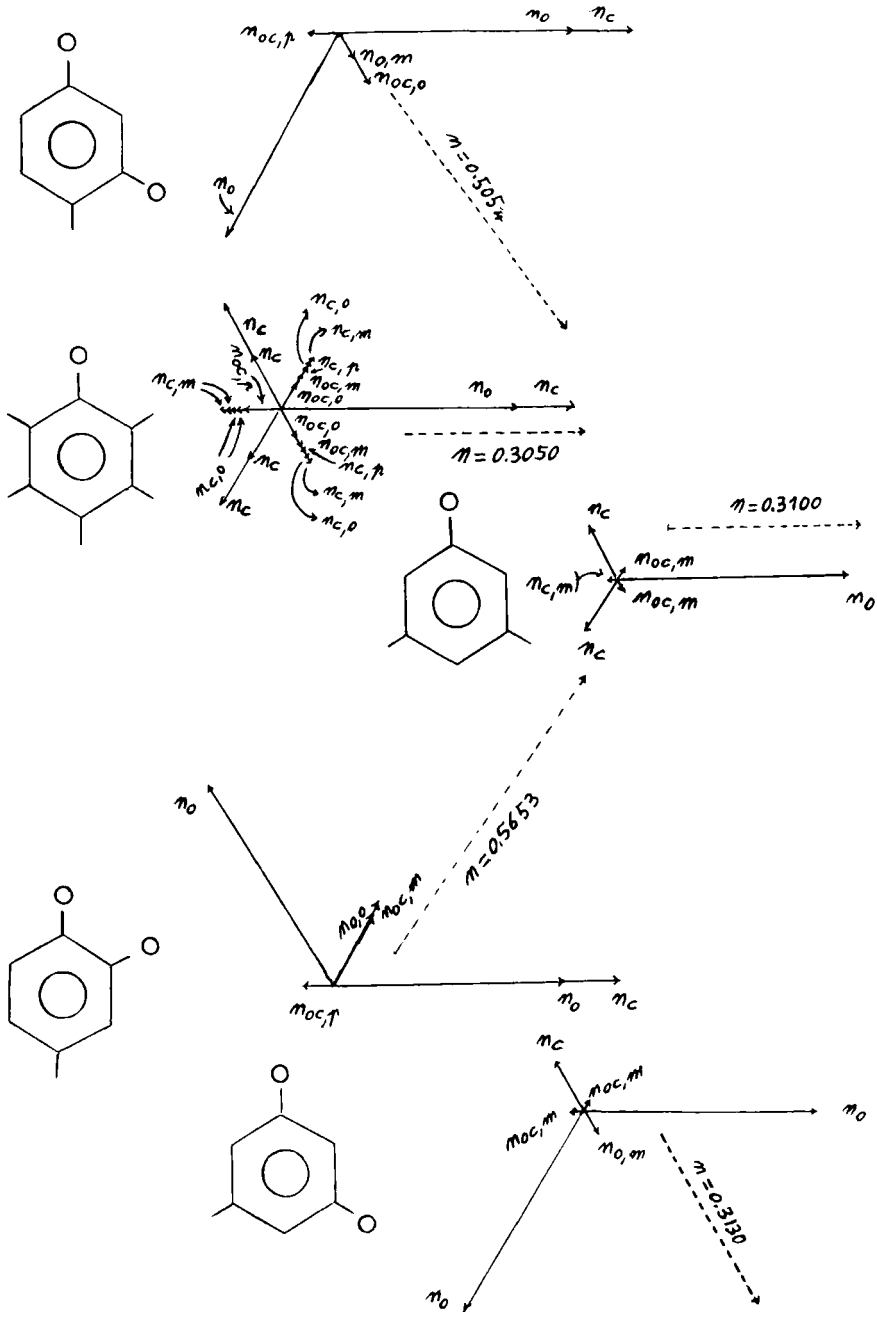


Figure 2. Continued.

by the vector model (taking into account the interactions vectors). $\sigma$ is linked to the number of substituents and to their efficiency to capture photons. It has been taken as $\sigma = S^{1/2}$ in order to reduce the variation amplitude of the function linked to the shape of the molecule, linked to its naive UV cross section picture. Actually, it has been proved easier to evaluate n in doing so. There is nothing which prevents to make this choice since the value used for n should take into account at least for a part what is not taken into account by $\sigma$. n depends for its values on the policy used to determine $\sigma$ and *vice versa*.

Another approach has been investigated too : $\varepsilon_{sm,c} = 4905\ (n^2 + V)$. Such an approach does not mix the vector approach and the cross section approach, to the absorption process. In fact, it appears that the both of them display complementary fits. Thus, it has been decided to take into account these two approaches in a same relationship. Is it better to choose a geometrical combination : $a = (n\sigma \cdot n^2)^{1/2} = n^{1.5}\sigma^{0.5}$, or an arithmetical one : $b = (n\sigma + n^2)/2 = n(n + \sigma)/2$ ? There is no theoretical point to take into account to help us. The two approaches ($n\sigma$ and $n^2$) would be perfect on a theoretical point of view, each of them would lead to the same value of intensity, and we should have too : a = b. As these two approaches are not perfectly equivalent they cannot fit perfectly with the experiment. Their weaknesses have been studied and it has been decided to combine them in order that the weaknesses of one be corrected by the other when necessary. When n and $\sigma$ are very different the experiment is nearer to b than to a. The contrary is true for small differences between b and a. Thus, some relationship as $(a + kb)/(1+ k)$ should be used. k depends on the difference $d = |n - \sigma|$. k has to be important only for high d values. We choose $k = d^6$. This is not the only possibility : we could have based the combination on $d' = a/b$. The relationship would have had another structure.

Experiment shows that when the pure electronic evaluation of the electronic transition moment leads to : n = 0, there is still a weak absorption to take into account apart from the pure vibrational component V. It is difficult to say if this is linked to the vibration or to some electronic behaviour. It has been evaluated as being : $q = 0.006^{1+10n}$. This is designed for having non zero values only for very small n. Thus, fitting the numerical parameters :

$$\varepsilon = 4905\ \left(((n^{1.5}\sigma^{0.5} + d^6\, n(n + \sigma)/2\ )/(1+ d^6))\cdot 1.025 + 0.006^{1+10n} + V\right)$$

V is obtained from our preceding work, [1] $\sigma$ too, since it is $\sigma = S^{1/2}$. Some examples of vectors calculations of n are given in figures 1 and 2.

## III - VECTORS MODULI

### 1) -CH3

modulus of the basis vector : $n_c = 0.0980$

modulus of the interaction vector between: two *ortho* -$CH_3$ : $n_{c,o} = 0.0060$
two *meta* -$CH_3$ : $n_{c,m} = 0.0060$
two *para* -$CH_3$ : $n_{c,p} = 0.0120$

The *ortho* (modulus : $n_{c,o}$) and *meta* (modulus : $n_{c,m}$) interaction vectors point to the direction of the resultant of the two corresponding interacting vectors. The *para* interaction vector (modulus : $n_{c,p}$) is opposed to the direction of the resultant of the two para vectors.

**2) -OR**

modulus of the basis vector : $n_0 = 0.3900$

modulus of the interaction vector between: two *ortho* -OR : $n_{o,o} = 0.1330$
two *meta* -OR : $n_{o,m} = 0.0450$
two *para* -OR : $n_{o,p} = 0.1800$

The behaviour of these vectors is the same as above for $-CH_3$.

**3)** Interaction between **-OR** and **-CH3** (hetero interaction) :

$$n_{oc,o} = 0.0520 ; \quad n_{oc,m} = 0.0240 ; \quad n_{oc,p} = 0.0630 ;$$

The *ortho* (modulus : $n_{oc,o}$) and *meta* (modulus : $n_{oc,m}$) hetero interaction vectors point to the direction of the projection of the resultant of the two corresponding interacting vectors on the line bissecting these two vectors. The *para* interaction vector (modulus : $n_{oc,p}$ ) is opposed to the direction of this projection (Figure 2).

Apart from pentamethylphenol, calculated intensities are almost systematically lower than the experimental ones when there is an hetero interaction. The calculated values could be improved in using higher values for the hetero parameters but this would increase the distorsion with the experiment for pentamethylphenol (molecule (20)).

## IV - ANILINE LIKE MOLECULES

As concerns the intensity of the secondary transition of the aniline like molecules there is a lack of reliable experimental data. Experience in that field [19-21] has shown that it is difficult to purify to a spectroscopic level anilines : carbonatation, polymerisation are very important since many of the resulting products superimpose their absorptions to the secondary transition, and surprising results are obtained with not recently and not carefully produced - although nice loking - chemicals. Sometimes too, anilines are not in a basic enough medium. A part of the experimental data of the handbooks is erroneous, and each value has to be carefully checked. Comparison of data from different origins is not enough since the same neglect leads to the same errors. Old data in literature papers sometimes are better than recent handbooks' ones. Nevertheless, very often spectra curves are not given, and it is difficult to evaluate $\varepsilon_{sm}$. Furthermore, there is often an overlap with the so called "charge transfert band" appearing at lower wavelengthes, and corrections have to be taken into account. So, it will be given underneath only some tests to check if it is possible to adapt the interaction vector model to the aniline like molecules. This is only a preliminary approach.

There is a problem of structure concerning the nitrogen atom. That problem could prevent systematisation. Actually, rotation around the $C_\phi$-N bond is possible and it decreases the coupling of the non bonding electrons with the $\pi_\phi$ system. This is quite important in N-substituted molecules when there are strong steric ortho interactions.

In this preliminary approach, it has been postulated that, in the molecules in which there is no specific interactions, the $-NH_2$ group behaves as an -OH one, as far as the intensity of the secondary transition is concerned. Actually the $\pi$ bond order of the coupling of the non bonding electrons to the $\pi_\phi$ system is almost the same in phenol (0.300) and in aniline (0.297). This leads to think that perturbations are almost

**TABLE II**

| | $\varepsilon_{sm,c}$ | $\varepsilon_{sm}$ |
|---|---|---|
| aniline | 1526 | 1400 measured from [15b] |
| *o*-phenylenediamine | 2562 | 2750 meas. from [17] |
| *m*-phenylenediamine | 2071 | 2100-2300 meas.from [15c, 14b] |
| *p*-phenylenediamine | 3040 | 1830 meas. from [14c] |
| This experimental value is not consistent with the aniline value itself, unless there is a specific interaction between two $-NH_2$ groups in the para positions. | | |
| *o*-amino-*p*-methylaniline | 2932 | 2600 meas. from [17b] |
| *m*-amino-*p*-methylaniline | 2850 | 2890 meas. from [14d] |
| *o*-amino-*p*-methoxyaniline | 3976 | 3690 meas. from [17c] |
| *m*-amino-*p*-hydroxyaniline | 3976 | 3200 meas. from [15c] |
| *o*-hydroxy-*m*-aminoaniline | 656 | 600-900 (1050)meas. from [15d] |
| This value has been evaluated from a logarithmic spectrum, because of a strong overlap a correction has been calculated. The experimental value is 1050. | | |
| *p*-methylaniline | 1781 | 1900 meas. from [14e] |
| *m*-methylaniline | 1549 | 1460 meas. from [14f] |
| *o*-methylaniline | 1646 | 3150 meas. from [14g] |
| This experimental value is quite surprising, since ortho interaction in aniline like molecules should lead to a weakening of the intensity of the transition. | | |



the same. So, within such a postulate, the above calculations concerning the phenol or methoxy molecules should be good for aniline like ones. This is what can be verified in table II on molecules having simple structures and being not too much overcrowded around the benzene chromophore. Then, the main difficulty, as far as the aniline like molecules are concerned, before trying to reach a better adequacy between calculation and experiment, seems to lie in obtaining more accurate data in a given medium, at a basic pH. This being done it will be possible to calculate interaction vectors on a large enough experimental basis.

## V - CONCLUSION

The method wich has been described here leads to calculated values very near to the experimental ones for methylbenzenes and methylmethoxybenzenes. This is completely satisfactory. An improvement could be obtained if experimental values could be known with a better accuracy. The method is easy to use although it needs more time than the Sklar's one, but it leads to better results than that latter, and it should supersede it when extended to other substituents.

## REFERENCES


1) B. VIDAL, *Spectroscopy Lett.* **26**, 621 (1993)

2) A. L. SKLAR, *J. Chem. Phys.* **10**,135 (1942)

3) A. L. SKLAR, *Revs. Modern Phys.* **14**, 232 (1942)

4) Th. FÖRSTER, *Z. Naturforsch.* **2a**, 149 (1947)

5) J. R. PLATT, *J. Chem. Phys.* **19**, 263 (1951)

6) J. PETRUSKA, *J. Chem. Phys.* **34**, 1111 (1961)

7) J. PETRUSKA, *J. Chem. Phys.* **34**, 1120 (1961)

8) P. E. STEVENSON, *J. Chem. Educ.* **41**, 234 (1964)

9) P. E. STEVENSON, *Ph. D. Thesis*, Part I, University of Chicago, 1964

10) M. BALLESTER, J. RIERA, *Tetrahedron*, **20**, 2217 (1964)

11) B. VIDAL, *Spectroscopy Lett.* (under press)

12) W. LIANG, J-M. YAN, R-H. HU, *J. Mol. Str. (Theochem)* **235**, 201 (1991)

13) American Petroleum Institute, *Research Project 44*, spectrum : 393

14) W. SIMONS, *Sadtler Handbook of Ultraviolet Spectra*, Philadelphia, Sadtler, 1979, a) spectrum : 194, b) spectrum 534, c) spectrum 535, d) spectrum 536, e) spectrum 490, f) spectrum 489, g) spectrum 488

15) *UV Atlas of Organic Compounds*, New York, Butterworth, 1966, a) spectrum : D 9/57, b) D6/3, c) D9/14, d) D9/15

16) R. A. FRIEDEL, M. ORCHIN, *Ultraviolet Spectra of Aromatic Compounds*, New York, J. Wiley, 1951, spectra : 45 and 46

17) L. LANG, *Absorption Spectra in the Ultraviolet and Visible Region*, Budapest, Akademiai Kiado, 1969, XII, a) spectrum 2105a ; b) spectrum 2107b, c) spectrum 2112b

18) I. B. BERLMAN, *Handbook of fluorescence spectra of organic molecules*, New York, Academic Press, 1971, p. 157-160

19) A. DARRY-HENAUT, B. VIDAL, *Spectroscopy Lett.* **19**, 265 (1986)

20) A. DARRY-HENAUT, B. VIDAL, C. CERF, *Spectroscopy Lett.* **19**, 1099 (1986)

21) D. DENIS-COURTOIS, B. VIDAL, *Spectrochim. Acta* **40 A**, 441 (1984)

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