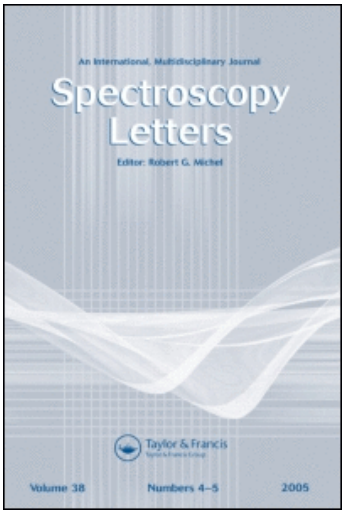

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THE INTERACTION VECTOR MODEL AND THE INTENSITY OF THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE IN STRAINED NATURAL MOLECULES : SESAMOL, MELACACIDIN, TETRAHYDROPAPAVEROLIN, RENIFOLIN, PTEROCARPIN, PELTOGYNOL

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A method (the New Vector Model : NVM) designed to approach the intensity of the secondary transition of the benzene chromophore with $-CH_3$ and -OR substituents, has been recently published. [1] This method is based on MNDO calculations. It has been applied to strained chromophores with fused rings, [2] assuming that it is possible to take into account the incidence of strain on intensity in introducing a strain vector in the vector scheme used to calculate the transition moment vector. In another step it has been derived a much simpler method which avoids the quantum calculations. It can be brought into play using graphically simple vector addition rules. [3] This method is based on a new concept : the interaction vector (underneath, the method is called the Interaction Vector Model : IVM). It has been designed to study alkyl and -OR substituents, since we are mainly involved in the study of natural products and many natural products display such substituents. This IVM has not been designed to take into account the perturbations induced by the strain on intensity. The present work is devoted to the adaptation of the IVM to strained benzene chromophores. It is given several examples on the way it can be used on strained natural molecules.

Experimental intensity is given in the present work as ε_{sm}, the maximum of the smoothed absorption curve, as it has been defined by BALLESTER and RIERA [4] (the calculated value is : $\varepsilon_{sm,c}$).

I - THE NEW VECTOR MODEL [1]

The NVM leads to the simple relationship for the calculated molar extinction coefficient : $\varepsilon_{sm,c} = 4905\ (TS + V)$. V is the vibrational component of intensity which is based on the BALLESTER and RIERA's work. It has been designed for -OR groups as well as methyl ones, and systematized :

$$V = 0.0180 + 0.0390\ K + 0.0030\ (n_c + n_O)$$

where n_c is the number of methyls substituting the chromophore, and n_O the number of -OR groups. When $n_O = 0$: K = 0 ; when $n_O \neq 0$: K = 1.

S is an increasing function of the number of substituents and of their ability to capture photons. It is related to the UV cross section of the molecule, increasing when the UV cross section increases :

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

T, which arises in the calculation of $\varepsilon_{sm,c}$, is the modulus of a vector **T** related to the electronic transition moment. It is based on the distorsion that the π electronic charges display from a pure D_{6h} symmetry scheme. T is an average of the moduli of $\mathbf{t}_1$ and $\mathbf{t}_2$, which are two complementary approaches to the transition moment. The first one put emphasis on the whole π electrons involved in the π bond orders between the substituents and the chromophore, and the second is related to the distorsion from a pure D_{6h} scheme, of the part of the π bond orders which is related to the HOMOs, those which are degenerated in the benzene molecule itself.

The SKLAR's model [5] assumes that the vectors, related to the substituents, and composing the transition moment vector, are additive, independently of interactions among the substituents. The NVM takes into account these interactions in the ground state of the transition.

II - THE INTERACTION VECTOR MODEL [3]

The vector moduli used (Figure 1) for the different substituents are :

	-CH3 (homo)	**-OR** (homo)	**-OR ⇔ -CH3** (hetero)
basis vector	$n_c = 0.0980$	$n_o = 0.3900$	
ortho interaction vector	$n_{c,o} = 0.0060$	$n_{o,o} = 0.1330$	$n_{oc,o} = 0.0520$
meta interaction vector	$n_{c,m} = 0.0060$	$n_{o,m} = 0.0450$	$n_{oc,m} = 0.0240$
para interaction vector	$n_{c,p} = 0.0120$	$n_{o,p} = 0.2000$	$n_{oc,p} = 0.0630$

One of these values differs slightly from the value used in preceding calculations ($n_{o,p} = 0.2000$ instead of 0.1800). Actually, the new value leads to slightly better results for -OR and $-CH_3$ substituted benzenes (calculations not given here).

The vector taking into account the interaction of two substituents lies on the line bisecting the angle of the two basis vectors involved in the interaction (this bisectrix splits up the angle into two equal parts whatever the respective lengthes of the two basis vectors are. The resultant of the two basis vectors lies on the bisectrix only when the two

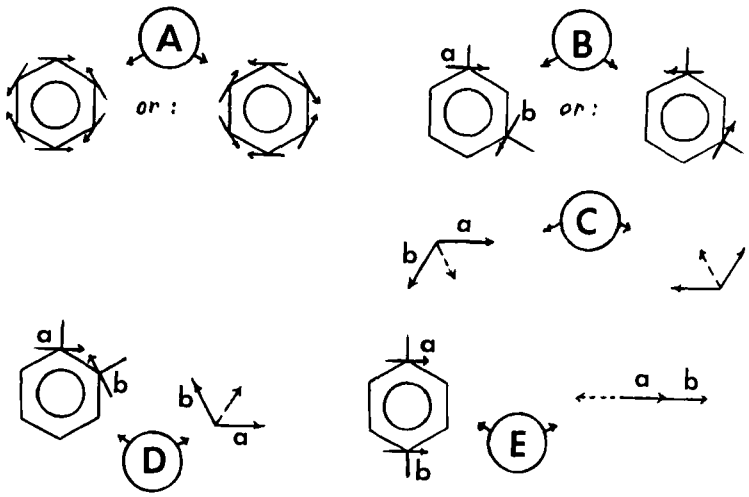

Figure 1. A) Vector pattern for the basis vectors. B) An example of vector orientation for two π donating substituents in meta positions. C) Directions of the interaction vectors (dotted vectors) corresponding to part B. D) Vectors for two ortho donating substituents and direction corresponding to the interaction vector (dotted vector). E) Vectors for two para substituents and direction of the interaction vector (dotted vector).

basis vectors have equal lengthes). The ortho interaction vector points to the same direction as the projection, on that bisectrix, of the resultant of the two ortho interacting vectors. The meta interaction vector points to the same direction as the projection on that bisectrix of the resultant of the two meta vectors. It is the contrary for two para substituents : the para interaction vector points to the direction opposed to the direction of the resultant of the two para vectors (Figure 1).

The next entities have been used to calculate intensities. n is the modulus of the vector **n** obtained in using the IVM. It is the resultant obtained when adding the basis vectors, within the SKLAR's vector pattern, and the interaction vectors. σ is linked to the number of substituents and to their efficiency to capture photons. It has been taken as $\sigma = S^{1/2}$. a is defined as being : $a = n^{1.5}\sigma^{0.5}$, and b : $b = n(n + \sigma)/2$. Then : $p = (a + kb)/(1 + k)$, with $k = d^6$, and : $d = |n - \sigma|$.

When the pure electronic evaluation of the electronic transition moment leads to : n = 0, there is still a weak absorption to take into account. It has been evaluated as being : $q = 0.006^{1+10n}$. This is designed to have non zero values only for very small n.

$$\varepsilon_{sm,c} = 4905\ (1.025\ p + q + V)$$

with : $p = (n^{1.5}\sigma^{0.5} + d^6\, n(n + \sigma)/2\ )/(1 + d^6)$ and $q = 0.006^{1+10n}$.

III - APPLICATION OF THE IVM TO MOLECULES WITH RINGS FUSED TO THE BENZENE CHROMOPHORE

a) The method

Many natural molecules display rings fused to the benzene moiety. The strain induced by these rings distorts the structure of the chromophore. The π densities are changed. The D_{6h} symmetry of the benzene chromophore being decreased, the secondary transition - which is electronically forbidden for a D_{6h} symmetry - becomes allowed. Intensity can increase under strain. [6]

A method to approach the intensities of strained molecules has been obtained within the frame of the NVM.[2] The approach is the same within the IVM, but no quantum calculation has to be done. Weak differences arise only in the numerical values of the parameters to be used.

In the NVM, S is used to take into account the fused ring effect. First of all, the calculation is done for the corresponding molecule with $-CH_3$ and -OR, and no fused ring : orthoxylene is used for indane or tetraline, pyrocatechol for benzodioxole etc. T, S, V are calculated. Then, the strain is taken into account as a vector increment **R** added to the resulting vector **S** whose modulus is S : $\mathbf{S'} = \mathbf{S} + \mathbf{R}$. Thus, **S** is given the direction of $\mathbf{t}_1$ a component of **T**, since the direction of **T** is not calculated in the NVM (in reference [2] p.1445, line 2, read : "**S**" instead of "**R**"). **R** points, in the NVM, to the same direction as the resultant of the two component vectors of the two positions of substitutions. Thus, the direction of **R** proceeds from the SKLAR's vector pattern, when adding two by two the vectors (each one with one of its neighbourgs) of that pattern. The direction of the resultant - and thus the direction of **R** (Figure 2) - is related to the position of the fused ring on the chromophore. **R** can display two directions : from the chromophore towards the fused ring, or from the fused ring towards the chromophore. This depends on the direction which has been choosen for the SKLAR's vector pattern in figure 1A (the directions of the whole vectors could be reversed), and for the position of the fused ring.

R has been given the next values in the NVM : 1.82 for an aliphatic five membered fused ring, 0.50 for an aliphatic six membered fused ring, 0.65 for a benzodioxole type fused ring (methylenedioxy fused rings). No correction is necessary for a benzodioxanne type fused ring. The vector addition being calculated, the value of T calculated for the molecule with no fused ring is used to calculate TS'. Then V (calculated for the molecule with no fused ring) is added to the result.

In the IVM, the approach to the intensity is based on n and σ and not on T and S (NVM). Nevertheless, it is possible to use the same approach to take into account the effects of strain. Now, it appears that the simplest way to proceed is to calculate p within the IVM model. So as to be consistent : 1.025 p (within the IVM) should be the same as TS (within the NVM) ; knowing S, T is known : $T = 1.025p/S$. The direction which has to be given to **S**, is no more known since $\mathbf{t}_1$, one of the components of **T**, is not calculated in the IVM. In fact, on a theoretical ground, the direction of $\mathbf{t}_1$ is very near to the direction of **T**. Furthermore, within the IVM, **n** plays a similar part as **T** in the NVM. So, **S** can be given the same direction as **n**, the vector whose modulus is n

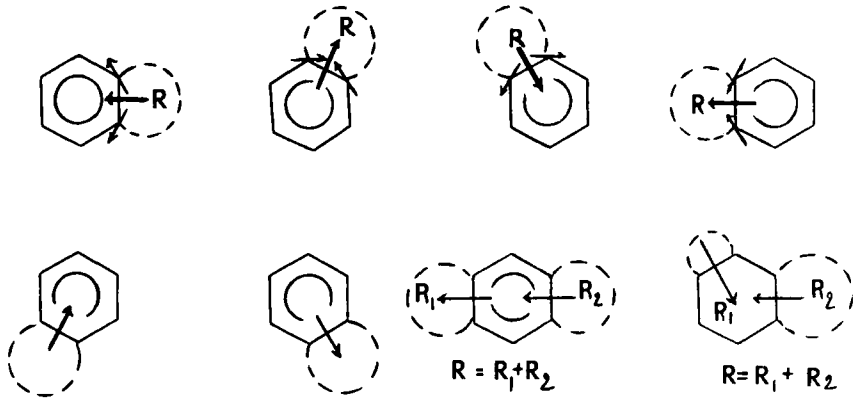

Figure 2. Directions of the basis vectors, and of the strain vectors **R**, according to the position of the fused rings around the chromophore. When several fused rings, the resulting vector **R** is the vector addition of the whole individual strain vectors.

(this vector arises from the vector addition of the basis vectors and the interaction vectors).

R is given the next values in the IVM : + **1.92** for an aliphatic five membered fused ring, + **0.55** for an aliphatic six membered fused ring, + **0.55** for a benzodioxole type fused ring (methylenedioxy fused rings), and : - **0.1** for a benzodioxanne type fused ring. The vector addition being done, the value of T calculated for the molecule with no fused ring is used to calculate TS'. Then V (calculated for the molecule with no fused ring) is added to the result. The values for R are slightly different in the NVM and the IVM. This arises from the fact that the approximations are different. In fact, one could use in the IVM the same values as in the NVM, on the price only of a slightly lower accuracy.

For the IVM a general relationship can be written :

$$(I)\quad \varepsilon_{sm,c} = 4905\,(1.025\,p(S'/S) + q + V)$$

$$\text{or : } \varepsilon_{sm,c} = 4905\,(1.025\,p(\sigma'/\sigma)^2 + q + V)\ ;\ \text{or } \varepsilon_{sm,c} = 4905\,(TS' + q + V)$$

with : $\sigma' = S'^{1/2}$, and p being calculated for the unstrained molecule with methyls and -OR groups. When there is no strain S' = S. The nature of q is ambiguous. If it is a vibrational factor the above equation (I) is theoretically consistent. If it is an electronic factor it has to be included in T, and we should write :

$$(II)\quad \varepsilon_{sm,c} = 4905\,((1.025\,p + q)(S'/S) + V)$$

In fact, the value of q is usually 0. q is of interest only when n is very weak, near to 0, then its value is near to 0.006, which is weak too. The

problem of choosing among (I) and (II) will be unusual, and (I) and (II) will give about the same value. The problem arises for the molecule 7 in table I and molecule 13. In fact, in molecule 7, the contribution **R** to **S'** vanishes for symmetry reasons : S = S', and the two relationships leads to the same value. As concerns molecule 13 relationship (I) leads to $\varepsilon_{sm,c}$ = 194, and relationship (II) : 198. Experiment gives 250. There is such a bad fit with experiment that choosing the right relationship is devoided of interest. The value given in table I is from (II). q is usefull when studying unstrained chromophores. It seems that its value is too much lower when there is strain.

b) applications

The formulæ of the strained molecules studied by the IVM are in figure 3, and the values are given in table I. Δ is the difference with experiment in % of the experimental value. All the molecules of table I have already been studied using the NVM (in reference 2, p.1447, molecules G and H should be exchanged). The IVM is quicker and simpler to use. From here to the end of the paper, apart from some values, references concern the data on which the experimental ε_{sm} values have been determined. When ε_{sm} display the same value as the ε_{max} given in literature, it has been assumed that the fine vibrational structure could be neglected.

IV - NATURAL PRODUCTS

1) Sesamol

As concerns sesamol (Figure 4), the values for the unstrained molecule (1,2,4-trihydroxybenzene) are : n = 0.6831, S = 2.2729, σ = 1.5076,
V = 0.066, p = 0.7063. Thus : T = 0.3185. Calculation shows that there is a 13,9° angle between **S** and **R** (R = 0.55). This leads to : S' = 2.8099, TS' = 0.8950, and to : $\varepsilon_{sm,c}$ = 4905(0,8950 + 0.066) = 4713. This is higher than the experimental value : 4400, by 7.1 %. This is good, but it is possible to get it better. Actually the experimental value is $\varepsilon_{sm,c}$ = 3650 for the unstrained molecule. It is possible to use this value to calculate T : 3650 = 4905(2.2729 T + 0.066), thus : T = 0.2984. Then : TS' = 0.2984•2.8075 = 0.8378 ; and the new value for the strained molecule is : $\varepsilon_{sm,c}$ = 4433, which is quite a good fit with experiment (4400). [7]

2) Melacacidin

Melacacidin (Figure 5) displays two independent benzene chromophores. The diol (chromophore I ; part B in figure 5) displays an "aliphatic" substituent which is in fact substituted on the α carbon atom by an oxygen atom. The oxygen atom is in a position where its σ-attracting power decreases the π donating hyperconjugative character of the substituent, [8] decreasing the perturbation ability of the substituent towards the chromophore. So, it is better to calculate the $n_{subst.}$ contribution of that substituent from α-methylbenzylalcohol

TABLE I : IVM CALCULATIONS ON STRAINED MOLECULES (Fig. 3)

Molecule	p	S	σ	V	S'	T	$\varepsilon_{sm,c}$	ε_{sm} (exper.)	Δ%
1	0.02608	0.3571	0.5976	0.024	2.277	0.07488	954	1040	-8,3
2	0.08000	0.5000	0.7071	0.030	4.340	0.1640	3638	3700	-1,7
3	0.02608	0.3571	0.5976	0.024	0.907	0.0749	451	465	-3.0
4	0.08000	0.5000	0.7071	0.030	1.600	0.1640	1434	1450	-1.0
5	0.08000	0.5000	0.7071	0.030	2.970	0.1640	2536	2525	+0.4
6	0.02415	0.5000	0.7071	0.030	2.420	0.04951	735	700	+5.0
7	0.00000	0.5000	0.7071	0.036	0.500	(q = 0.006)	206	270	-23.7
8	0.08000	0.5000	0.7071	0.030	2.420	0.1640	2094	1900	+10,2
9	0.08000	0.5000	0.7071	0.030	1.050	0.1640	992	950	+4.4
10	0.4482	1.7857	1.3363	0.063	2.336	0.2572	3256	3330	-2.2
11	0.2660	1.2000	1.0954	0.063	2.435	0.2272	3023	2900	+4.2
12	0.5188	1.9858	1.4092	0.066	2.512	0.2678	3623	3670	-1.3
13	0.0000	0.4545	0.6742	0.027	1.005	(q = 0.006)	198	250	-20,1
14	0.05788	0.4545	0.6742	0.027	0.970	0.1305	754	760	-0.8
15	0.05788	0.4545	0.6742	0.027	2.324	0.1305	1620	1490	+8,7
16	0.2095	1.3373	1.1564	0.066	0.583	0.1606	783	740	+5,8
17	0.4482	1.7857	1.3363	0.063	1.686	0.2573	2437	2350	+3,7

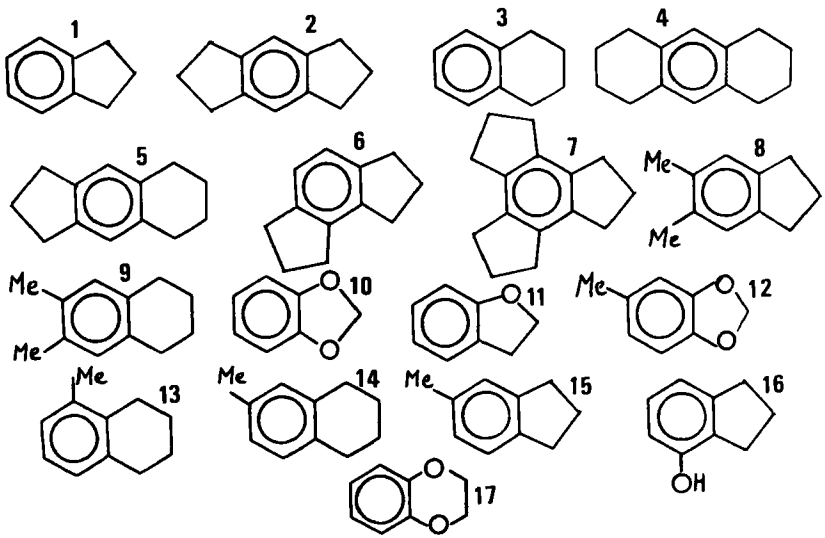

Figure 3. Formulæ of the molecules which are studied in table I.

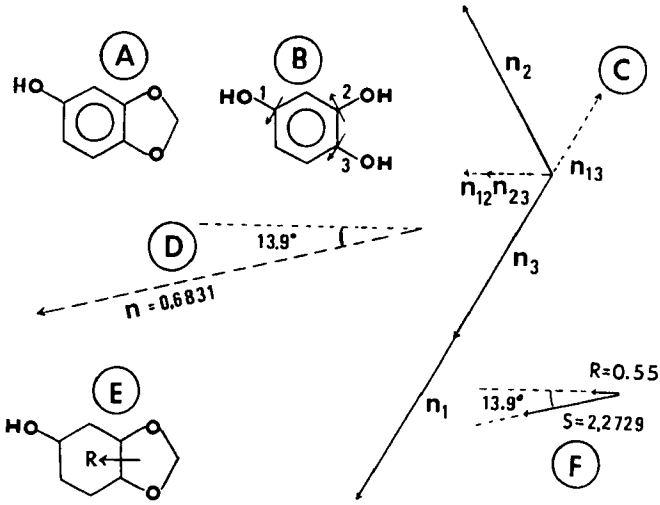

Figure 4. A) The sesamol molecule. B) The unstrained corresponding parent molecule. The direction used for the basis vector pattern is shown. C) The vector pattern used to calculate the intensity of the secondary transition of sesamol. The dotted vectors are interaction vectors. The indices are related to the substituents as numbered in part B. $n_1 = n_2 = n_3 = 0.3900$. $n_{13} = 0.2000$. Since $\mathbf{n}_{13}$ is a para interaction vector its direction is opposed to the direction of $\mathbf{n}_1$ and $\mathbf{n}_3$ the two interacting vectors. $n_{23} = 0.1330$ since $\mathbf{n}_{23}$ is an ortho interaction vector, $n_{12} = 0.0450$ since $\mathbf{n}_{12}$ is a meta interaction vector. D) The resulting vector of part C displays a length : $n = 0.6831$. It displays too a 13.9° angle with the direction shown by a dotted line. E) The direction of the strain vector is shown. F) **S** points in the same direction as **n** in part D. $\mathbf{S}' = \mathbf{R} + \mathbf{S} = 2.8099$.

(ϕ-$CH(CH_3)OH$) than using the contribution of a methyl. The intensity of the α-methylbenzylalcohol is $\varepsilon_{sm} = 155$ instead of 192 for toluene. This leads to decrease the basis contribution for the substituent to approximately $n = 0.065$ instead of 0.098 for a methyle. We assume that the vibrational contribution is not changed, which is our general assumption when there are branched substituents, and that S too is the same as for a methyl, in order to be simple (n bears all the changes). Calculation leads to a vector having a length : $n = 0.5480$ (instead of 0,5653 if the substituent is a methyl). Having : $\sigma = 1.4092$ one obtains : $a = 0.4816$, $b = 0.5363$, $d^6 = 0.408$, $p = 0.4975$. As : $V = 0.066$, the calculated intensity is for the chromophore I : $\varepsilon_{sm,c\ (I)} = 2825$. (It would be 2932 if considering a methyl instead of the actual substituent).

For chromophore II (part C in figure 5) there is (part E and F) an "aliphatic" substituent not purely aliphatic, as in chromophore I, and one will use as above : $n_{subst.} = 0.065$. The vector addition for the unstrained molecule leads to $n = 0.0521$ (it would be 0.0595 if there was a

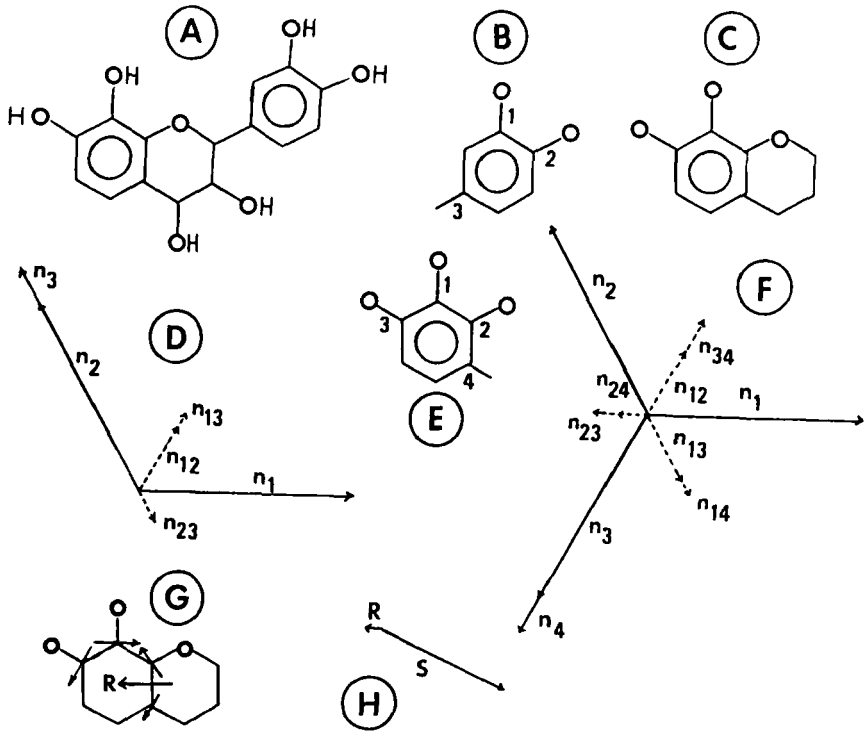

Figure 5. **A**) The melacacidin molecule. **B**) Chromophore I. **C**) Chromophore II. **D**) The vector pattern used to calculate the intensity of the chromophore I (part B). The dotted vectors are the interaction vectors. The indices are related to the substituents as numbered in part B. For example n_{13} is $n_{oc,m}$ = 0.0240, n_{23} (n_{23} = 0.0630) being a para interaction vector points to the direction opposed to n_2 and n_3. $n_1 = n_2$ = 0.3900, n_3 = 0.0650 (see text), n_{13} = 0.0240, n_{12} = 0.1330. The length of the resulting vector is n = 0.5480 (it would be 0.5653 for n_3 = 0.098 (the methyl value)). **E**) The unstrained model corresponding to chromophore II. **F**) The vector pattern for E. The dotted vectors are interaction vectors. $n_1 = n_2 = n_3$ = 0.3900, n_4 = 0.0650 (see text), $n_{12} = n_{13}$ = 0.1330, n_{14} = 0.0240 n_{34} = 0.0630 (para interaction vector), n_{23} = 0.045, n_{24} = 0.052. The length of the resulting vector is n = 0.05210 (it would be 0.0595 if n_4 would be given the value 0.098 (methyle)). **G**) The direction of **R**. The strain contribution is shown. Its direction has to be consistent with the vector pattern used for the individual substituents. The lengthes of the vectors are not proportional to the actual lengthes. The vectors show only the directions. **H**) Addition of **R** to **S**. (angle **R**,**S** = 154.27°) (length of the resulting vector S' = 2.2721).

methyl). As S = 2.4727 and σ = 1.5725 : a = 0.01491, b = 0.04232, d^6 = 12,353 and p = 0.04027. T = 1.025 p/S = 0.01669. Considering the strained chromophore, one uses R = 0.55 for a tetraline like strain and - 0.1 for a benzodioxanne one. Thus the R value to be used will be : R = (0.55 - 0.1)/2 = 0.225 (the average of the two corresponding symmetric fused rings is used when there is an unsymmetric fused ring). The direction of **R** is given in figure 5-G. As the vector **n** displays a 154.27° angle with the direction of $\mathbf{n}_{24}$ (part F of figure 5), as **R** has the same direction as $\mathbf{n}_{24}$ and **S** the same direction as **n**, **R** and **S** display a 154.27 °angle. This leads to S' = 2.2721 and TS' = 0.03792. $\varepsilon_{sm,c\ (II)}$ = 4905 (0.03792 + 0.069) = 524. Thus, considering that $\varepsilon_{sm,c} = \varepsilon_{sm,c\ (I)} + \varepsilon_{sm,c\ (II)}$, $\varepsilon_{sm,c}$ = 2825 + 524 ; $\varepsilon_{sm,c}$ = 3349. The experiment gives 3160. [9a] Calculation is 5.9% higher.

If considering a methyl in chromophore II, instead of a -O(-C)CH- substituent, one should have had : n = 0.0595, S = 2.4727, s = 1.5725, V = 0.069. Thus p = 0.04621 and T = 0.01916. The angle **R**,**S** is 120°, thus : S' = 2.3682. This leads to $\varepsilon_{sm,c\ (II)}$ = 561 for the strained molecule. Thus for melacacidin when using a methyl : $\varepsilon_{sm,c}$ = 2932 + 561 = 3493. Calculation would have been 10.4% higher than experiment.

One sees that it is better to take into account the actual nature of the "aliphatic" substituent. Nevertheless, considering a methyl would lead to an acceptable evaluation of intensity.

3) Tetrahydropapaverolin

Tetrahydropapaverolin (Figure 6) displays a secondary transition lying at 286 nm with ε_{sm} = 6700.[10] In fact two secondary transitions overlap since there are two chromophores : one is unstrained (chromophore I - figure 6, part B) the other is strained by a fused ring (chromophore II - figure 6, part C, neglecting the influence of the nitrogen atom on the intensity and assuming that the strain, when there is a nitrogen atom on the α carbon atom, is the same as it is in tetralin). Considering the aliphatic substituent in chromophore I as a methyl, the intensity of the secondary transition is readily known since it has been calculated for melacacidin : $\varepsilon_{sm,c\ (I)}$ = 2932. The strained chromophore (chromophore II) as approximated by C in figure 6 gives : n = 0.6120 (figure 6-D). Knowing that S = 2.0985, σ = 1.4486, calculation gives : a = 0.5762, b = 0,6305, d6 = 0,3429 and p = 0.5901. Thus : T = 1.025 p/S = 0.2882. As the direction of the resulting **n** is the same as that of $\mathbf{n}_{12}$, $\mathbf{n}_{34}$ etc. in figure 6-D, the direction of **R**, the strain vector, being as given in figure 6-E (owing to the direction used for $\mathbf{n}_3$ and $\mathbf{n}_4$ (see figure 6-C and D)) **R** and **S** are colinear and in the same direction : **S'** = **R** + **S**. As R = 0.55 and S = 2.0985 the value for S' is : S' = 2.6485. Here, the strain increases intensity, since it increases the S contribution. As V = 0.069 : $\varepsilon_{sm,c\ (II)}$ = 4905(0.2882•2.6485 + 0.069), $\varepsilon_{sm,c\ (II)}$ = 4082. The two secondary transitions overlaping, intensity is : $\varepsilon_{sm,c} = \varepsilon_{sm,c\ (I)} + \varepsilon_{sm,c\ (II)} \Rightarrow \varepsilon_{sm,c}$ = 7014. This value is only 4.7% higher than experiment (6700). Nevertheless, it has been used in chromophore I a methyl as the aliphatic like substituent (figure 6-B). An ethyl like substituent would have been nearer to the actual substituent. When considering toluene ε_{sm} = 192 and n_c = 0.098. It has been seen here above that when ε_{sm} = 155 (as in α-methylbenzylalcohol) this aliphatic contribution decreases to 0.065. Thus, as ethylbenzene displays ε_{sm} = 184, the ethyl contribution can be

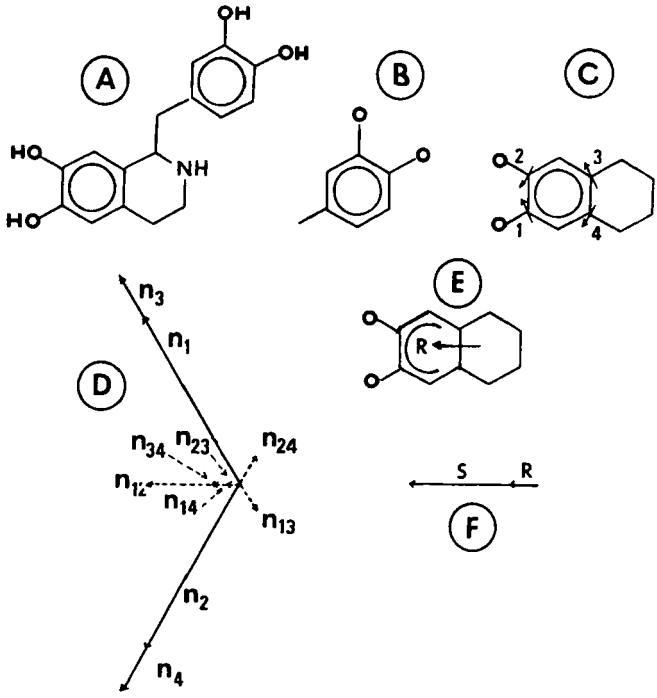

Figure 6. **A**) Tetrahydropapaverolin. **B**) Chromophore I. **C**) Chromophore II. **D**) Vector pattern for the intensity of chromophore II : $n_1 = n_2 = 0.3900$; $n_3 = n_4 = 0.0980$ (when the third substituent is not approached in the unstrained parent molecule by a methyl like substituent but by an ethyl like : $n_3 = 0.0900$) ; $n_{12} = 0.1330$; $n_{34} = 0.0060$; $n_{14} = n_{23} = 0.0240$; $n_{24} = n_{13} = 0.0630$. **E**) Direction of **R** according to the vector pattern used in part C. **F**) Addition : **S'** = **R** + **S** (R = 0.55, S = 2.0985).

decreased to $n_{ethyl} = 0.090$. Using this latter value for chromophore I, n decreases from 0.5653 to 0.5601. Thus a = 0.4976, b = 0.5515, $d^6 = 0.3612$, p = 0.5119 (V = 0.066). This leads to $\varepsilon_{sm,c\ (I)'} = 2897$ (instead of 2932 when using a methyle like substituent).

As concerns chromophore II, the aliphatic like substituent is near to an isopropyl like one. For isopropylbenzene $\varepsilon_{sm} = 157$. This is near to what has been observed for α-methylbenzylalcohol and we can use the same value for the substituent contribution : $n_3 = 0.065$. The nitrogen atom should not have too much effect on intensity since there is only one hyperconjugative hydrogen atom to allow the σπ-coupling. The fact that n_4 corresponds to an ethyl like substituent, instead of a methyl one, has not to be considered, although an ethyl is less π donating as a methyl

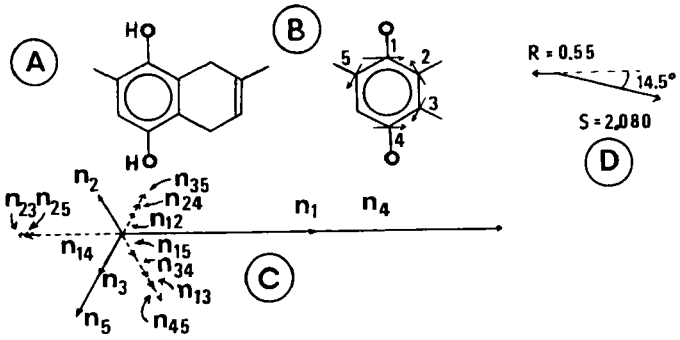

Figure 7. A) Renifolin. B) The unstrained parent chromophore with the direction of the basis vectors. C) The vector pattern : $n_1 = n_4 = 0.3900$; $n_2 = n_3 = n_5 = 0.0980$; $n_{23} = 0.0060$; $n_{14} = 0.2000$; $n_{12} = 0.0520$; $n_{24} = 0.0240$; $n_{35} = 0.0630$; $n_{15} = 0.0520$; $n_{34} = 0.0520$; $n_{13} = n_{45} = 0.0240$. D) Addition of **R** and **S**.

since R takes into account the ring nature of this substituent, and the fact that it is not a methyl one. Thus, in figure 6-D, only n_3 has to be modified and decreased to 0.065. This leads to : n = 0.5962. As $\sigma = 1.4486$, it is obtained : a = 0.5541, b = 0.6096, $d^6 = 0.3836$, p = 0.5695, T = 0.2782. **S** and **R** display a 177,25° angle. Thus, with the above value for S (S = 2.0985) : S' = 2.6480. $\varepsilon_{sm,c\ (II)} = 4905(0.2782 \cdot 2.6480 + 0.069) = 3952$. This leads to : $\varepsilon_{sm,c} = \varepsilon_{sm,c\ (I)} + \varepsilon_{sm,c\ (II)} = 2897 + 3952 = 6849$. This is only 2.2% higher than experiment. Once more one sees that it can be possible, to use the methyl value to approach the aliphatic like substituent.

4) Renifolin

Renifolin (Figure 7) displays a secondary transition lying at 283 nm with $\varepsilon_{sm} = 2000$.[9b] This is quite a low value when considering that the two -OH groups when alone in para positions in the molecule lead to about 3000. In fact the alkyl substituents of the six membered fused ring opposes to the effects of the -OH groups, and the strain of the ring too. One will assume that the fused ring, as far as strain is concerned, is similar to an aliphatic six membered ring without the ethylenic unsaturation (tetraline like ring). n = 0.5589, V = 0.072, S = 2.0798, σ = 1.4422, this leads to a = 0.5018, b = 0.5592, d6 = 0.4750 and p = 0.5203 (unstrained parent compound). As R = 0.55, S = 2.0798, and as **R** and **S** display a 165.5° angle : S' = 1.5536 and TS' = 0.3983. Thus : $\varepsilon_{sm,c} = 2307$. This is 15.4% higher than experiment. Although calculation is less satisfactory than what has been obtained above, one sees that the strain effect is well taken into account on a qualitative basis since it is shown as decreasing intensity as it is observed in experiment. The gap between calculation and experiment lies in the fact that the fused ring has been approached as a tetraline like fused ring. In fact, the double bond inside

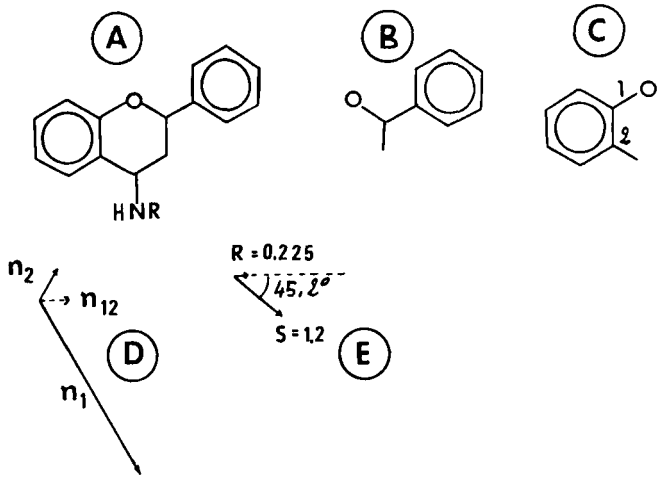

Figure 8 A) 4-aminoflavan-N-β-D-glucoside tetraacetate. B) Chromophore I. C) Chromophore II. D) The vector pattern used : n_1 = 0.03900 ; n_2 = 0.0650 (since de substituent is not methyl like but isopropyl like) ; length of the resulting vector : n = 0.3967. E) The resulting vector in the vector pattern for chromophore II, and the direction of $\mathbf{n}_{12}$ display a 45.21° angle. Thus, as **S** is given the same direction as **n**, **R** and **S** display a 45.21° angle too. This leads to S' = 1.3679. The value used (O.225) for R is the average of a pure tetraline like (0.55) and a pure benzodioxanne like fused ring (- 0.1).

the fused ring shortens the length of the ring, it decreases the fused ring ability to move. These two effects increase the strain on the chromophore. R should be higher than 0.55. As, in that molecule, **R** opposes **S**, this increase of R should decrease the intensity.

5) 4-aminoflavan-N-β-D-glucoside tetraacetate

The intensity of the secondary transition is ε_{sm} = 1930 (medium ethanol).[11] The two chromophores are distincts. As above, one shall use the value $\varepsilon_{sm,c\ (I)}$ = 155 for the chromophore I (Figure 8).

For chromophore II, the unstrained parent compound displays an -OR substituent, and an aliphatic like whose value can be approached by n_c = 0.065 (as above for tetrahydropapaverolin concerning an isopropyl like substituent or for melacacidin concerning an -O(-C)CH- substituent). The unstrained parent compound leads to n = 0.3967 (S = 1.2 and σ = 1.0954) a = 0.2615, b = 0.2960, d^6 = 0.1163, p = 0.2651. T = 1.025 p/S = 0.2264. For tetraline R = 0.55, and for benzodioxanne R = - 0.1. The value to be used for the fused ring will be : R = (0.55 - 0.1)/2 = 0.225 (as above for melacacidin the average of the corresponding two symmetric fused

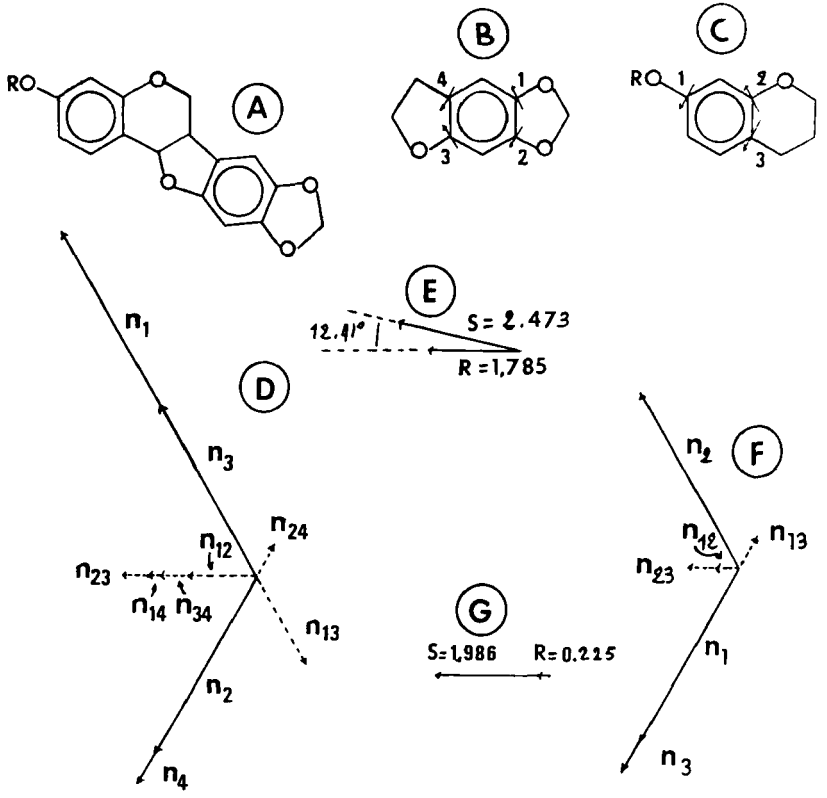

Figure 9. A) Pterocarpin. B) Chromophore I and the direction of the basis vectors. C) Chromophore II and the direction of the basis vectors. D) Vector addition for the unstrained equivalent of chromophore I (basis vectors (plain vectors) and interaction vectors (dotted vectors)). E) Addition of the strain vector (**R**) to **S**. F) Vector addition for the chromophore II. G) Addition of **R** and **S** for chromophore II.

rings is used for an unsymmetric one). As there is a 45.21° angle between **R** and **S**, the result will be : S' = 1.3679. Thus, as V = 0.063 : $\varepsilon_{sm,c\ (II)}$ = 4905 (0.2264·1.3679 + 0.063) = 1828. Thus : $\varepsilon_{sm,c}$ = $\varepsilon_{sm,c\ (I)}$ + $\varepsilon_{sm,c\ (II)}$ = 155 + 1828 = 1983. Calculation is only 2.7 % higher than experiment.

6) Pterocarpin

In pterocarpin (Figure 9), there are two chromophores whose secondary transitions partly overlap.When corrected from overlap, [12]

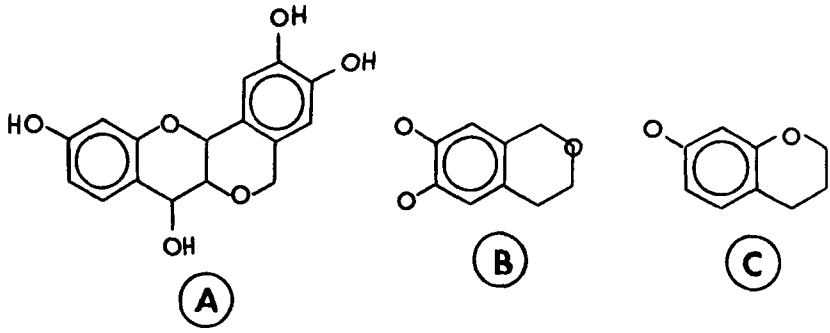

Figure 10. A) Peltogynol. B) Chromophore I. C) Chromophore II.

TABLE II :

INTENSITY OF THE SECONDARY TRANSITION FOR SOME STRAINED NATURAL MOLECULES

	$\varepsilon_{sm,c}$ Calculation(IVM)	ε_{sm} Experiment
Sesamol	4430	4400
Melacacidin	3350	3160
Tetrahydropapaverolin	6850	6700
Renifolin	2300	2000
4-aminoflavan-N-β-glucoside tetraacetate	1980	1930
Pterocarpin	7565	6600
	2715	2800
Peltogynol	6665	6950

the intensities are : chromophore I $\varepsilon_{sm} = 6600$, and chromophore II : $\varepsilon_{sm} = 2800$. The unstrained chromophore to be used for chromophore I is 1-methyl-2,4,5-trihydroxybenzene. Calculation gives for this unstrained molecule : n = 0.7577, S = 2.4731, σ = 1.5726, V = 0.069, a = 0.8271, b = 0.8828, d6 = 0.2928 p = 0.8397. The value of R is : 0.55 + (0.55 + 1.92)/2 = 1.785 (as above for melacacidin the average of the corresponding two symmetric fused rings is used for an unsymmetric one). As the **n**,**R** angle is 12.41°, the angle between **S** and **R** is 12.41° and the modulus of their resultant is S' = 4.2338. As : T =1.025 p/S, its value is : T = 0.3480. Thus TS' = 1.4735 and $\varepsilon_{sm,c\ (I)} = 7566$. This value is about 14,6 % higher than experiment.

For the unstrained equivalent to chromophore II : n = 0.4880, S = 1.9858, σ = 1.4092, V = 0.066, a = 0.4047, b = 0.4629, d^6 = 0.6111, p = 0.4268. R

= (0.55 - 0.1)/2 = 0.225. S' = 2.2108. Thus $\varepsilon_{sm,c\ (II)}$ = 2713 . This value is 3.1 % lower than experiment.

7) Peltogynol

For peltogynol (Figure 10) literature does not lead to a very accurate value. Two maxima are reported : ε_{sm} = 7415 (λ = 286 nm) and ε_{sm} = 6920 (λ = 280 nm) (no graph is given). [9a] As these two maxima are very near and similar to what can be observed for a vibrational structure in solvating medium, this structure has to be related to the vibrational structure of the secondary transition. Thus, the smoothed intensity, considering similar spectra, can be evaluated as being between 6800-7100, roughly 6950. Owing to the low accuracy of the experiment we only evaluate the intensity. The chromophore I is similar (not exactly identical) to the chromophore II of tetrahydropapaverolin, and the chromophore II is similar to the chromophore II of pterocarpin : $\varepsilon_{sm,c}$ = $\varepsilon_{sm,c\ (I)} + \varepsilon_{sm,c\ (II)}$ = 3952 + 2713 = 6665. This value is 4 % lower than the experiment.

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