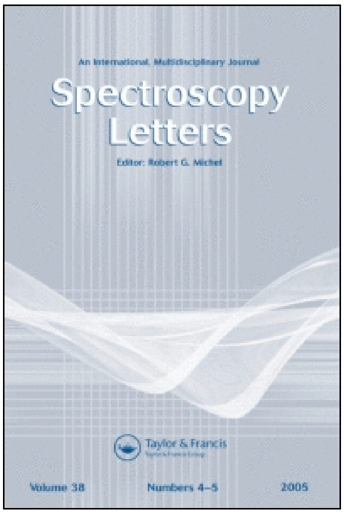

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The Interaction Vector Model and the Secondary Transition of Diphenylether, and of Some of Its Natural Derivatives: Enneaphylline, Pilocereine, Chondrocurine, Daphnandrine, Daphnoline, Tiliacorine

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THE INTERACTION VECTOR MODEL AND THE SECONDARY TRANSITION OF DIPHENYLETHER, AND OF SOME OF ITS NATURAL DERIVATIVES : ENNEAPHYLLINE, PILOCEREINE, CHONDROCURINE, DAPHNANDRINE, DAPHNOLINE, TILIACORINE

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Using the interaction vector model [1,2] (IVM), it is possible to calculate the intensity of the secondary transition of the benzene chromophore (towards 255 nm for the benzene molecule itself), on a very simple basis. This transition is electronically forbidden because of the D_{6h} symmetry of the benzene molecule. Many spectra have been studied with the IVM, specially those of natural products since they are the main concern of the laboratory. Alkyl, amino, hydroxy, alkoxy substituents, fused rings effects have been taken into account. The present work will be devoted to the study of diphenylether (ϕ-O-ϕ) derivatives which display an interesting challenge to the IVM since the two phenyl rings are "conjugated" through the oxygen non bonding electrons.

I - THE BASIS OF THE IVM

The IVM [1,2] uses the SKLAR's [3] simple vector scheme (Fig. 1-Aa), but it has been introduced three concepts of major importance which strongly change the approach : the *interaction vector* (Fig. 1-Ab), takes into account the interaction of two given substituents, the *strain vector* (Fig. 1-C), takes into account the fact that a ring fused to the chromophore imposes a strain distorting the symmetry, and thus inducing intensity changes. Furthermore, a component related to a sort of *photonic cross section* of the molecules has been introduced. Its value increases as much as the substituents coupled to the π system enlarge the π system increasing its efficiency to capture photons (see S, σ underneath).

The vector moduli n of the basis vectors **n** [1,2] (Figure 2) for the substituents are :

	-CH3 (homo)	-OR (homo)	-OR ⇔ -CH$_3$ (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	$n_{c,p} = 0.0120$	$n_{o,p} = 0.1800$	$n_{oc,p} = 0.0630$

An interaction vector lies on the line bisecting the angle of the two basis vectors involved in the interaction. Their directions (figure 1-Ab) show that, as far as transition moments are concerned, the ortho substitution increases the transition moment more than a simple addition of the effects, and the para substitution less than addition.

n_C is the number of alkyl substituents, n_O the number of -OR ones. V is a vibrational component [1,2,4]. S and σ ($\sigma = S^{1/2}$) are functions of the number and of the nature of substituents :

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

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

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 : $d = |n - \sigma|$.

R is related to the fused ring effect. The calculation is done for the corresponding parent molecule with -CH$_3$ (or isopropyl) and -OR, and no fused ring. This leads to S, σ, n, p, V. Strain is taken into account as a vector **R**, then as **S'** : **S'** = **S** + **R**. **R** is the sum of all the individual $\mathbf{R}_i$. The direction of a $\mathbf{R}_i$ proceeds from the basis vector pattern (Figure 1-B). 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 one, **+ 0.55** for a benzodioxole type one (methylenedioxy fused rings), and : **– 0.1** for a benzodioxanne type one. If there is no fused ring : S' = S and S'/S = 1.

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

$$\varepsilon_{sm,c} = 4905\,[1.025\,p(S'/S) + V]$$

II - DIPHENYLETHER

The modulus of the basis vector **n** for a given type of substituent ($n_c = 0.0980$, $n_o = 0.3900$, see above) as well as the interaction vectors, and as well as S, have been established on an empirical basis, [1,2] using the spectra of several molecules as references. Nevertheless, when considering a monosubstituted chromophore : ϕ-X, and drawing S or n against some electronic parameters (for example : the number of π electrons, the π bond order between ϕ and the substituent) which can be considered as varying as the perturbation imposed by the substituent (the perturbation imposed to the D_{6h} symmetry for which the transition is electronically forbidden), it appears that n and S for ϕ-X increase when these parameters increase. There are only three points to be used to establish a relationship : one for which n and S are 0 corresponding

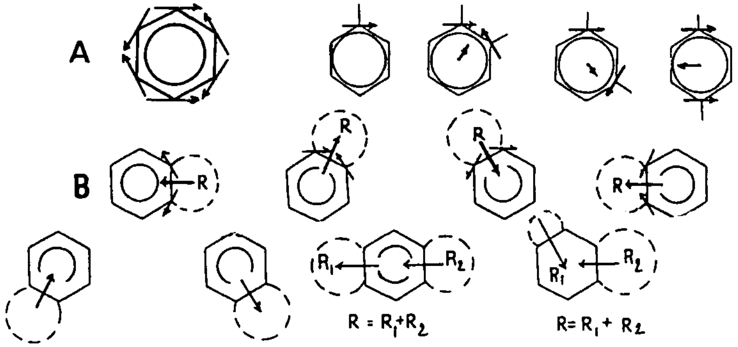

FIGURE 1. A) Direction of the basis vectors. First drawing : the Sklar's basis virtual vectors pattern. Other drawings : the basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. **B)** Strain vectors corresponding to the fused ring. The basis vectors at the positions of substitutions have also been drawn, since the direction of a given strain vector depends on the direction choosen for the basis vector pattern.

to the benzene molecule, one for the toluene molecule and the other for the phenol one. Nevertheless, the functions have to be regular and in another work [5] it has been shown that interpolation is possible leading to a good fit with experiment. So, the next relationships — which are valid only for π donating substituents whose behaviour is near to that of an alkyl or an alkoxy group — have been settled in that work to evaluate the basis vectors and the basis parameters of a given type of substituent :

$$S = 5.2812(D \cdot P^{1.43})^{(1/2.43)}$$

where *D* is the increase of the number of π electrons caused by the substituent. *P* is the π bond order between the substituent and the chromophore. This relationship is no more than a sort of geometric average. Furthermore :

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

MNDO calculations on diphenylether lead to the next number of π electrons for a given benzene moiety : n_π = 6.06295 (thus *D* = 0.06295). The π bond order between O and a given ϕ is $P_{O\text{-}\phi}$ = 0.26221. This allows to calculate $S_{O\text{-}\phi}$ = **0.6795** and $n_{O\text{-}\phi}$ = **0.2858** for the modulus of the basis vector, and V = **0.0392** for the vibrational contribution of the substituent. One sees that the value for $n_{O\text{-}\phi}$ is much lower than the value for an -OR substituent (which is 0.39). This is the same for $S_{O\text{-}\phi}$ which is lower than the value of -OH (S = 1). O-ϕ is a substituent which is far from being as efficient as an OR group to perturb the D_{6h} symmetry of the benzene chromophore. Diphenylether is not a planar molecule. It is like a propeller [6] preventing the non bonding electrons on the oxygen atom to couple strongly with the π_ϕ system. MNDO calculations lead to a dihedral angle of 130° for $C_{\phi 2}$-O-$C_{\phi 1}$-$C_{\phi 1}$.

Using the basis values obtained here above, calculations concerning the chromophore ϕ-O lead to : a = 0.1389, b = 0.1588, d^6 = 0.0243 and p = 0.1394. Thus :

$$\varepsilon_{sm,c} = 4905\,[1.025 \cdot 0.1394 + 0.0392] = 893$$

This value corresponds to a benzene moiety under the influence of an -Oϕ substituent, that is to say under the influence of an oxygen atom whose efficiency is lowered compared to an -OR one. Diphenylether is composed of two such moieties, each one displaying a benzene moiety under the perturbation of an oxygen whose efficiency is reduced :

$$\varepsilon_{sm,c} = 893 \cdot 2 = 1785 \text{ (experiment, from }^{7} : \varepsilon_{sm} = 1750)$$

Calculation agrees with experiment, within the range of 10% which has been considered as satisfactory in preceding works.

It is possible to calculate what quantity of a phenolic oxygen a ϕ-O-ϕ oxygen is. For one substituent -OR and no alkyl substituent, S simplifies to : $S = 5n_O/(4{,}8 + 0.2\, n_O^2)$, [where n_O is the number of -OR substituents on the chromophore] . The number of -OR groups is 1 : n_O = 1, thus S = 1. For an O-ϕ chromophore it has been calculated here above : $S_{O-\phi} = 0.6795$, this means that : $n_{O(O-\phi)}$ = **0.6643**. The oxygen in diphenylether is similar to 0.6643 of an -OR oxygen, as concerns the present intensity calculations.

III - DIPHENYLETHER DERIVATIVES

When a given benzene moiety is substituted by several groups, the problem of the interactions between the substituents arises. One lacks experimental data to calculate empirical accurate values for calculating the moduli of the interaction vectors between an -Oϕ substituent and the others. Should one approximate the interaction vectors as if the -O-ϕ substituent is an -OR one ? Should one calculate, as it has been done in a preceding work, these vectors — where distorsion from alkyl substituents were weaker —, considering that they depend on the product $n_1 \cdot n_2$ of the two interacting substituents ? This would decrease their moduli since $n_{O-\phi} = 0.2858$, when : $n_{O-R} = 0.39$. But experiment shows that interaction is certainly not decreased. One part of the problem lies in the fact that one cannot be sure that the conformation is conserved around the oxygen atom whatever the other substituents are. Nevertheless, it will be assumed that the possible changes of conformation can be neglected (nevertheless for chondrocurine and daphnandrine two conformations will be studied). This is a rough approach but it is necessary for the sake of simplicity. The assumption that there is no conformational change leads, in order to reach the best fit experiment-calculations, to assume too that the interactions are increased and that the contribution to the interaction vectors moduli are multiplied by 1.118 each times that the -O-ϕ substituent is involved. This increase of the lengthes of the interaction vectors could be linked to the greater volume of the -O-ϕ substituent compared to an -OCH_3 one, but also to the fact that interaction between substituents is also an interaction between chromophores (since an -O-ϕ substituent is also a chromophore) and also to the fact that the oxygen atom is a bridge allowing the two chromophores to which it is bonded to interact. As the problem is complex it has been decided to priviledge an empirical approach. The next results are obtained : -OR$\Leftrightarrow$-O-ϕ ortho : $0.1330 \cdot 1.118 = 0.1487$; -OR$\Leftrightarrow$-O-ϕ meta : $0.0450 \cdot 1.118 = 0.0503$. -OR$\Leftrightarrow$-O-$\phi$ para : $0.1800 \cdot 1.118 = 0.2012$; For -O-$\phi$$\Leftrightarrow$-O-$\phi$, ortho : $0.133 \cdot 1.118 \cdot 1.118 = 0.1662$; meta : 0.0562, para : 0.225. For alkyl$\Leftrightarrow$-O-ϕ, ortho : 0.0581, meta : 0.0268, para : 0.0704.

[Note : The strong decrease of the π donating effects when the alkyl substituent is isopropyl like (-CH(CH_2-)$_2$) has led to decrease the basis vector modulus from 0.0980 to 0.0650 in that latter case, assuming that the contributions to the other parameters are unchanged.[1,2]]

These new moduli lead to 2183 for the intensity of the CH_3O-ϕ-O- part of **CH_3O-ϕ-O-ϕ** (substituents in para position), value to which has to be added 893 for the -O-ϕ part. Thus, calculations would lead to $\varepsilon_{sm,c} = 3076$ when experiment is only 2375. (from : 8a) This is quite a strong difference ($\Delta = + 29.5\%$).

Considering **CH_3O-ϕ-O-ϕ-OCH_3** (all substituents in para positions) one would wait for the same difference. On the contrary agreement is quite good. Calculation is easy since it needs only take twice the above 2193 value : $\varepsilon_{sm,c} = 4365$ when experiment is 4150 (from : 8b) ($\Delta = + 5.2\%$).

When considering : **ϕ-O-ϕ-O-ϕ**, with the two O-ϕ substituents on the central ϕ in meta positions, calculation gives : $\varepsilon_{sm,c} = 3105$ (with V calculated considering that there is no -OR group, thus K = 0 ; if K is considered on the contrary as K = 1 : $\varepsilon_{sm,c} = 3207$) when experiment is 3270 (from : 8c) ($\Delta = - 5.3\%$).

As concerns the molecule with two substituents in the ortho positions only the **1,4-dioxine** molecule has been found in the literature. This molecule displays a fused ring separating the two chromophores and the incidence of that fused ring on the intensity has to be evaluated. The effect of strain on intensity should be weak since for an aliphatic six membered fused ring (such as in tetraline) R = + 0.55, and when there are two oxygen atoms in the α position, such as in benzodioxanne, R is reduced to - 0.10. The difference is 0.65. If, in an -O-ϕ substituent, the oxygen would have the efficiency of half an oxygen atom the value to use would be $0.55 - 0.65/2 = 0.225$. In fact the oxygen atom of an -O-ϕ substituent is worth 0.6643 (see above calculations concerning diphenylether). Thus R = 0.1182. This is a very rough but reasonable estimate. Actually, such a small value has not to be known with great accuracy since it will be involved only in additive or soustractive process, and since it will contribute for only a small part of the intensity. As S = 1.2891, this leads to S' = 1.4468 and to a molar extinction coefficient : 2051 (with $V = 0.039 + 0.003 = 0.042$ considering that K = 0) for each chromophore, thus to $\varepsilon_{sm,c} = 4100$ for the 1,4-dioxine molecule. Experiment gives 3960. (from : 8d) Difference is only : $\Delta = + 3,5\%$.

Apart from the strong discrepancy for CH_3O-ϕ-O-ϕ — for which one has no explanation — calculations can be considered as satisfactory. This has led to try to use this rustic approach, not taking into account conformational changes, to some much more complex molecules of natural products.

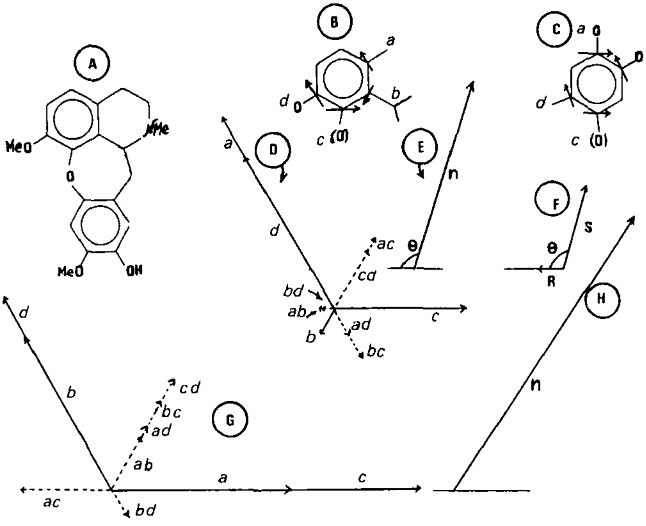

FIGURE 2. **A)** Enneaphylline. **B)** Chromophore I. The parent unstrained analog. The directions of the basis vectors are shown. O stands for -OR, and (O) stands for -Oϕ. **C)** Chromophore II. The parent unstrained analog. The directions of the basis vectors are shown. O stands for -OR, and (O) stands for -Oϕ. **D)** The basis vectors (plain arrows) and the interaction vectors (dotted arrows) pattern of chromophore I. Letters correpond to the letters in part B. The interaction vectors are labelled by the two letters of the two interacting vectors. a = 0.0980, b = 0.0650 (isopropyl substituent), c = 0.2858, d = 0.3900 ; ab = 0.0060, ac = 0.0268, ad = 0.0630, bc = 0.0581, bd = 0.024, cd = 0.1487. **E)** The vector resulting from the vector addition of D : Θ = 107.15°, n = 0.4327. The calculation of S takes into account the fact that an -Oϕ like substituent is equivalent to 0.6643 of an -OR one, thus the chromophore displays 1.6643 -OR like substituents ; it displays two alkyl substituents, thus : $S = [5 \cdot 1.6643/(4.8 + 0.2 \cdot 1.6643^2)] + 2/[4.8 + 0.2 \cdot 2^{(2 + 0.5 \cdot 1.6643)}] = 1.8756$ and $\sigma = 1.3695$. Thus : a = 0.3331, b = 0.3899, d^6 = 0.6760, p = 0.3560. **F)** Calculation of S'. **S** is given the direction of **n** (part E). The contribution **R** (R = + 0.55) of the strain of the six membered fused ring is added to **S** with the direction shown in figure 1 (the direction bisecting the angle of the basis vectors in position a and b in part B of the present figure). The contribution of the strain of the seven membered oxygenated fused ring is neglected. Thus S' = 1.7922. As : $\varepsilon_{sm,c}$ = 4905 [1.025 p(S'/S) + V] it needs V : V = 0.0180 + 0.0390 K + 0.0030 ($n_C + n_O$) ; as there is at least one -OR substituent : K = 1. The number of substituents is 4, thus V = 0.0180 + 0.03900 + 0.0030·4 = 0.069. Thus $\varepsilon_{sm,c}$ = 4905 [1.025·0.3560(1.7922/1.8756) + 0.069] = **2050**. One sees that S'/S being lower than 1 the strain of the six membered ring lowers intensity. **G)** The basis vectors pattern of chromophore II (part C of this figure). a = 0.3900, b = 0.3900, c = 0.2858, d = 0.0980 ; ab = 0.1330, ac = 0.2012, ad = 0.024, bc = 0.0503, bd = 0.063, cd = 0.0581. **H)** The vector addition of the part G leads to n = 0.7164. As there are two -OR and one -Oϕ the number of equivalent -OR is 2.6643. There is one alkyl substituent. Thus : $S = 5 \cdot 2.6643/(4.8 + 0.2 \cdot 2.6643^2) + 0.2 = 2.3418$ and σ = 1.5303. a = 0.7501, b = 0.8048, d6 = 0.2907, p = 0.7624. V = 0.069. $\varepsilon_{sm,c}$ = 4905 (1.025.0.7624 + 0.069) = **4172**. No S' is calculated since the incidence of the seven membered ring is neglected. Thus, for enneaphylline $\varepsilon_{sm,c}$ = 2050 + 4172 = **6222** (experiment : 7080 ; Δ = - 12.1%)

Enneaphylline displays two chromophores (Figure 2). Chromophore I displays two fused rings and these rings are superfused. But one of them is a seven membered one which would be less efficient than a six membered one to distort the symmetry, furthermore it displays an oxygen atom which decreases the efficiency of the strain on intensity. Neglecting the seven membered fused ring effect, one is led to neglect the superfusion effect [9] which is difficult to take into account. Chromophore I gives 2050 and chromophore II 4172, which gives 6222 instead of the experiment 7080. [10] The difference is : $\Delta = -12{,}1\%$. This is near to the 10% range which is considered as a good fit for much simpler molecules.

Pilocereine displays three chromophores. Chromophore I leads to 937, chromophore II to 1304, and chromophore III to 3613. This gives : 5855 for pilocereine, when experiment is 5250.[11a] The difference is : $\Delta = +11.5\%$. The great crowding around the chromophores could prevent the oxygens to be in favourable position to conjugate with the π_{ϕ} systems and experiment could be lower than calculations.

Furthermore, there is another point which is worthy of notice : it has been shown in a preceding paper [5] that when an -OR group and an isopropyl one are in ortho position the lengthes of the basis vectors have to be increased : $n_0 = 0.5070$ and $n_c = 0.0845$ (factor : 1.3). If the same interaction has to be considered here, when an $-O\phi$ substituent is involved, instead of an -OR one, chromophore I and II should display intensities differing slightly from what has been calculated. Using the same factor (1.3) this would lead to the new length for the basis vector of $-O-\phi$: $n_{O\phi} = 0.2858 \cdot 1.3 = 0.3715$, n_c displaying the same value 0.0845. Calculation shows that the intensity of chromophore I would be drastically decreased to 568, and that of chromophore II decreased to 902. These strong decreases arise because the $-O\phi$ like substituents are in positions where the direction of their basis vectors are opposed to the resulting vector of the other substituents, thus an increase of the length of the $-O-\phi$ basis vectors decreases the resulting length. This leads to $\varepsilon_{sm,c} = 568 + 902 + 3613 = 5083$, and the difference with experiment is only : $\Delta = -3.2\%$. In fact, without other data it is not possible to maintain the factor 1.3 for the increase of the vectors of the two interacting substituents on another basis than the similarity with the -OR case. Of course, as an $-O\phi$ substituent displays a ratio 0.6643 for its efficiency compared to an -OR substituent, it is inviting to suggest a factor : $1 + 0.6643 \cdot 0.3 = 1.199$. This would lead to a value for intensity between the two preceding ones.

Notice that in enneaphylline it is not justified to consider the $-OR \Leftrightarrow$ isopropyl interaction. Actually, in part B of figure 2, substituent *b* is isopropyl like and it neighbourgs an $-O\phi$ substituent, but the two substituents are parts of a same ring : they do not act as two interacting free substituents. The ortho effect would have to be taken into account in a seven membered fused ring effect which precisely has been neglected in that molecule.

Chondrocurine (Figure 4) is another challenging case. There are four chromophores. Chromophore I is the same as chromophore II of pilocereine. Thus its calculated intensity will be 1304. Chromophore III

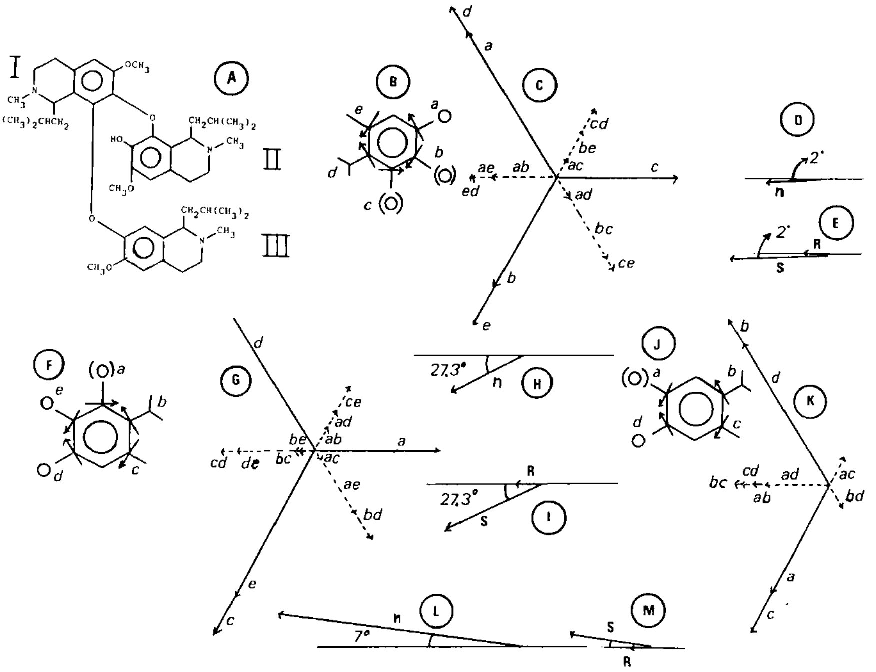

FIGURE 3. A) Pilocereine. B) Chromophore I. The parent unstrained analog. with the directions of the basis vectors. O stands for -OR, (O) for -Oϕ. C) Basis vectors (plain arrows), interaction vectors (dotted arrows) of chrom I. $a = 0.3900$, $b = 0.2858$, $c = 0.2858$, $d = 0.0650$ (isopropyl), $e = 0.0980$. $ab = 0.1487$, $ac = 0.0503$, $ad = 0.0630$, $ae = 0.0240$, $bc = 0.1662$, $bd = 0.0268$, $be = 0.0704$, $cd = 0.0581$, $ce = 0.0581$, $de = 0.0060$. D) The vector **n** resulting from the vector addition of C : n = 0.1218. θ = 2.44°. For S, an -Oϕ like substituent is equivalent to 0.6643 of an -OR one : the chromophore displays 2.3286 -OR like substituents, and two alkyl ones : S = 2.2820, σ = 1.5106. E) **R**, the strain vector, displays the direction shown in figure 1. R = + 0.55. Thus S' = 2.8316, since **S** displays the direction of **n**. a = 0.05225, b = 0.1244, $d^6 = 7.1749$. p = 0.09365. V = 0.0180 + 0.0390·1 + 0.0030·5 = 0.0720. $\varepsilon_{sm,c} = 4905$ [1.025·0.09365(2.8316/2.2820) + 0.0720] = **937**. F) Chromophore II (parent unstrained analog ; directions of the basis vectors). G) Basis vectors (plain arrows) interaction vectors (dotted arrows) of chromophore II. H) G leads to : n = 0.1888. θ = 27.33°. An -Oϕ like substituent being equivalent to 0.6643 of an -OR one, there are 2.6643 -OR like substituents. Thus : S = 2.4353 and σ = 1.5606. I) S displays the same direction as **n**. R = + 0.55. This leads to S' = 2.9348. a = 0.1025, b = 0.16516, $d^6 = 6.6636$, p = 0.1570. As V = 0.072 : $\varepsilon_{sm,c} = 4905$ [1.025·0.1570(2.9348/2.4353) + 0.0720] = **1304**. J) Chromophore III. K) The vector pattern of chromophore III. L) K leads to : n = 0.5623. θ = 7°. There are 1.6643 -OR like substituents and two alkyl ones, thus: S = 1.8756 and σ = 1.3695. M) S displays the direction of **n**. R = + 0.55. This leads to S' = 2.4225. a = 0.4935, b = 0.5432, $d^6 = 0.2765$, p = 0.5043. As V = 0.069, since there is one -OR (K = 0.039) and one substituent less than in chrom. I and II: $\varepsilon_{sm,c} = 4905$ [1.025·0.5043(2.4225/1.8756) + 0.0690] = **937**. Thus for pilocereine : $\varepsilon_{sm,c} = 1084 + 1304 + 3613 =$ **5855** (experiment : 5250 ; Δ = + 11.5%)

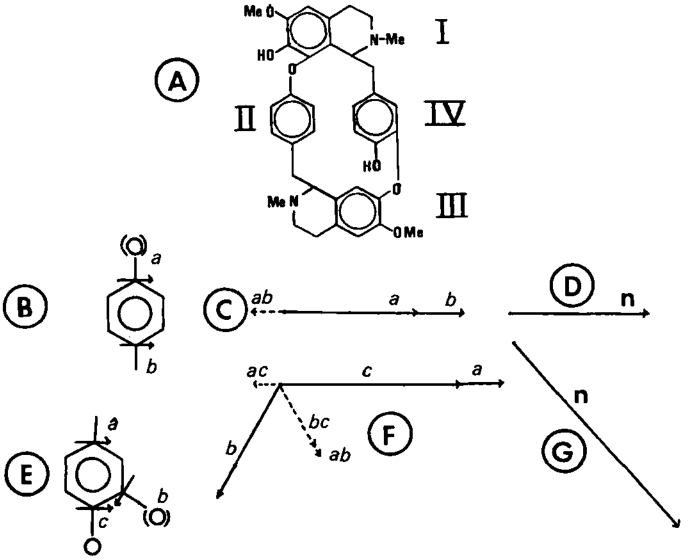

FIGURE 4. A) Chondrocurine. Chromophore I is the same as chromophore II of pilocereine : $\varepsilon_{sm,c}$ = **1304**. This value would be decreased to 917 when taking into account the possible changes in the lengthes of the basis vectors for the ortho -Oϕ⇔ipr interaction. Chromophore III is the same as chromophore III of pilocereine : $\varepsilon_{sm,c}$ = **3613**. **B)** Chromophore II. (O) stands for -Oϕ. The directions of the basis vectors are shown. **C)** Basis vectors and interaction vectors pattern of chromophore II. a = 0.02858, b = 0.0980, ab = 0.0704. **D)** The vector **n** resulting from the vector addition D : n = 0.3134. There is one -Oϕ substituent, thus the number of equivalent -OR is : 0.06643 ; there is one alkyl substituent, this leads to : S = 0.8795 and σ = 0.9378. a = 0.1699, b = 0.1961, d^6 = 0.05927 and p = 0.1714. Thus : $\varepsilon_{sm,c}$ = 4905(1.025.0.1714 + 0.0422) = **1070**. The value V = 0.0422 has been used since there is no -OR substituent : V = 0.0392 + 0.003 = 0.0422. **E)** Chromophore IV. O stands for -OR and (O) for -Oϕ. The directions of the basis vectors are shown. **F)** Basis vectors and interaction vectors pattern of chromophore II. a = 0.0980, b = 0.2858, c = 0.3900, ab = 0.0268, ac = 0.0630, bc = 0.1487. **G)** The vector **n** resulting from the vector addition F: n = 0.5444. There is one substituent -OR, one -Oϕ thus the number of -OR like substituents is 1.6643. There is one alkyl substituent thus : S = 1.7543 and σ = 1.3245. a = 0.4623, b = 0.5087, d6 = 0.2254, p = 0.4708. $\varepsilon_{sm,c}$ = 4905(1.025·0.4025 + 0.066) = **2690**. This leads for chondrocurine to $\varepsilon_{sm,c}$ = 1304 + 3613 + 1070 + 2690 = **8677** (experiment : 7030 ; Δ = + 23 %). Assuming 917 as the correct value for chromophore I would lead to $\varepsilon_{sm,c}$ = 917 + 3613 + 1070 + 2690 = 8290 which is only slightly improved (Δ = + 18 %) compared to the preceding value. Calculations are done assuming the same conformation for the -Oϕ substituents as in diphenylether. When calculations are done assuming an orthogonal conformation for the -Oϕ substituents (see text) the result is : 7994 which is only 13,7% higher than experiment. Furthermore, this result would be improved taking into account the -Oϕ⇔ipr interaction.

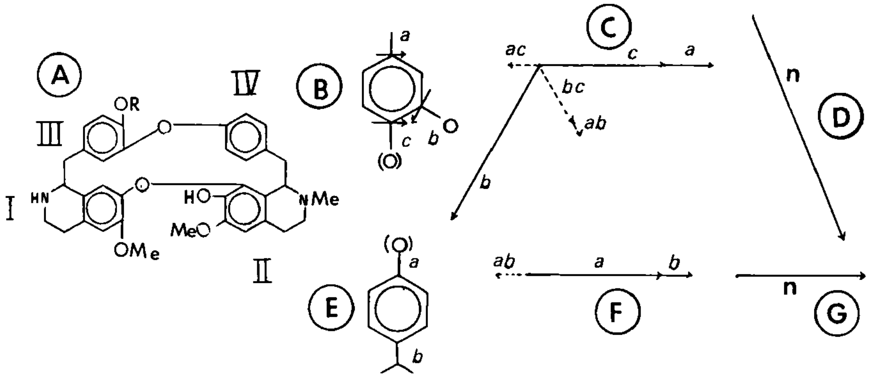

FIGURE 5. A) Daphnandrine (R = OCH3)-Daphnoline (R = OH). Chromophore I is the same as chromophore III of pilocereine thus $\varepsilon_{sm,c}$ = **3613**. Chromophore II is the same as chromophore II of pilocereine, thus $\varepsilon_{sm,c}$ = **1304. B)** Chromophore III. The parent unstrained analog showing the directions of the basis vectors. **C)** Basis vectors and interaction vectors pattern of chromophore III. a = 0.0980, b = 0.3900, c = 0.2858, ab = 0.02400, ac = 0.0704, bc = 0.1487. **D)** The vector **n** arising from the vector addition C : n = 0.5286. The number of -OR like substituents is 1.6643, thus S = 1.7543 and σ = 1.3245. a = 0.4423, b = 0.4898, d^6 = 0.2542, p = 0.4519. $\varepsilon_{sm,c}$ = 4905(1.025.0.4519 + 0.066) = **2595**. E) Chromophore IV. The parent unstrained analog showing the directions of the basis vectors. **E)** Basis vectors and interaction vectors pattern of chromophore III. a = 0.2858, b = 0.0650, ab = 0.0704. **F)** The vector **n** arising from the vector addition C : n = 0.2804. The number of -OR like substituents is 0.6643, thus S = 0.8795 and σ = 0.9378. a = 0.1438, b = 0.1708, d^6 = 0.0807, p = 0.1458. $\varepsilon_{sm,c}$ = 4905(1.025.0.1458 + 0.0392 + 0.003) = **940**. Thus for daphnandrine-daphnoline : $\varepsilon_{sm,c}$ = 940 + 2595 + 1304 + 3613 = 8450. Experiment : 8320 (R = OCH3) and 7945 (R = OH). Δ = + 1.6% and + 6.4%.

is the same as chromophore III of pilocereine. Thus its intensity will be : 3613. Calculations on chromophore II gives : 1070. Calculations on chromophore IV : 2690. The sum of these values is : 8678, when experiment is 7030.[11b] The difference is : Δ = + 23%. In this molecule conformational changes could be important since the chromophores display a sort of ring. So, in order to evaluate the possible changes, it has been tried to calculate the intensity in the case where the -O-ϕ substituent would display a conformation with the O-ϕ bond of the substituent in a plane orthogonal to the plane of the concerned chromophore. A MNDO calculation has been performed on diphenylether for such a conformation to determine the excess of π electrons on the ϕ moiety, and the π bond order between that chromophore and the oxygen atom. The excess of π electron is 0.02676, and the π bond order is 0.20641 [interaction between the oxygen atom and the π orbitals is not completely cancelled ; this is not completely surprising since with a methyle the π bond order with a π system is about 0.15 (hyperconjugation)]. It is then possible to calculate S and n for the new conformation and use them in chondrocurine : $S = 0.4703$ and $n_{O\phi} = 0.2098$. This gives : $n_{O(O-\phi)} = 0.4554$ instead of 0.6643. This leads to a much better result : 7995 which is 13,7% higher than experiment. This is not completely satisfactory, nevertheless the molecule is complex and there are a lot of factors which cannot be mastered. Thus, owing to that complexity, although it would improve the results of the calculations, it is not useful to take into account the $-O\phi \Leftrightarrow ipr$ ortho interaction which arises in chromophore I (decrease from 1304 to 902).

Daphnandrine and **daphnoline** (Figure 5) exhibit four chromophores. They differ only in one of them by displaying an $-OCH_3$ (daphnandrine) or an -OH (dapholine). As the medium for the spectra is methanol there is no strong acido-basic effect to wait for, and as only one chromophore is slightly changed intensities should be the same. In fact they differ slightly : 8320 for daphnandrine and 7945 for daphnoline.[11c]

Calculation for the system daphnandrine-dapholine leads to 8450 which is a good fit : $\Delta = +1.6\%$ and $+6.4\%$. Nevertheless, as it has been done for chrondrocurin owing to the possibility of conformational changes from the diphenyl- ether type molecule, a calculation has been done using an $-O-\phi$ substituent with its $O-\phi$ bond in a plane orthogonal to the chromophore ϕ concerned. This leads to the value 7948 for the intensity [chromophore I and II (as in pilocereine) 3344 (intensity decrease) and 1696 (intensity increase), chromophore III : 2294, and IV : 614]. The difference is 4.5 % lower than the highest experimental value and 0% lower than the lowest one.

Tiliacorine (Figure 6) (experim. : $\varepsilon_{sm} = 8130$)[11d] displays four benzene moiety. Two of them are part of a 1,4-dioxine group which is particularly interesting to consider since, as concerns this type of molecule, only 1,4-dioxine itself is studied in that work. As concerns the biphenyl like bridge linking moieties III and IV, taking into account the steric effects imposed by the substituents, mainly by the -OR and the -OH groups in positions 2 and 2' there should be a high value for the dihedral angle between the two benzene rings, near to 70-80° at least, preventing any noticeable coupling through the biphenyl link. Actually, Biphenyl derivatives substituted at *ortho* positions by bulky substituents such as amino, carboxyl groups etc. display spectra quite similar to those of the two distinct parts of the molecule.[12] So, it will be considered in the present work that there is no coupling : the two chromophores are considered as independent, a benzene moiety being, for the other, only a substituent to take into account in the vibrational component with a standard contri- bution of 0.003, that is to say : almost nothing.

Chromophore I gives $\varepsilon_{sm.c} = 926$ using the value obtained here above in 1,4-dioxine for R (the strain effect). Such an intensity is a very weak contribution to the overall intensity for a chromophore displaying such a number of substituents, and specially three oxygens with high basis vectors, and two fused rings. In fact two of these three oxygens are of a diphenylether type and thus less efficient than an -OR one. Furthermore, the vector scheme shows that these two diphenylether oxygens oppose their action to that of the -OR group (remember that a

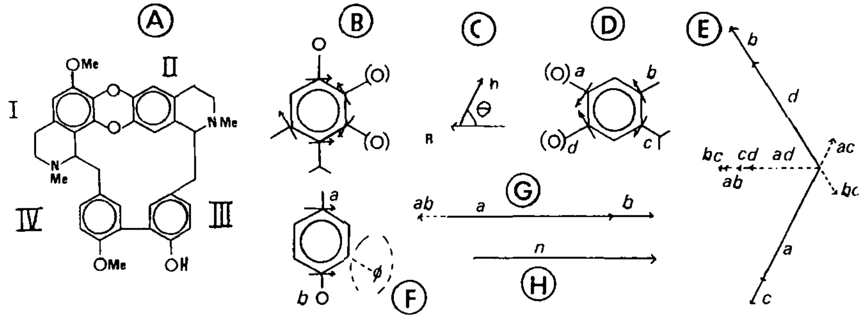

FIGURE 6. A) Tiliacorine. **B)** Chromophore I of tiliacorine. The unstrained parent analog is the same as the unstrained parent analog of chromophore I of pilocereine. **C)** The resulting vector **n** is the same as the resulting vector of chromophore I of pilocereine : n = 0.1218. θ = 62.44°. **S** is given the direction of **n**, and **R** (R = 0.1182 as in 1,4-dioxine), for the strain effect, adds to S giving S' = 2.7780 (which differs from pilocereine). The number of -OR like substituents is : 1 + 0.6643·2 = 2.3286. Thus : S = 2.2820, s = 1.5106. a = 0.05225, b = 0.09942, d6 = 7.1753, p = 0.09365. As there is one -OR substituent V = 0.072. $\varepsilon_{sm,c}$ = 4905(1.025·0.09365·2.778/2.2820 + 0.072) = **926**. **D)** Chromophore II of tiliacorine. The parent unstrained analog. Not to confuse with chromophore III of pilocereine which displays one -OR substituent. **E)** Vector pattern of chromophore II (part D) *a* = *d* = 0.2858, *b* = 0.0980, *c* = 0.0650. *ab* = *cd* = 0.0268, *bc* = 0.0060, *ad* = 0.1662, *ac* = *bd* = 0.0704. The resulting vector **n** is n = 0.5235, displaying a 3.13° angle with the direction of *ad*. The number of -OR like substituents is 1.3286, thus S = 1.61875, σ = 1.2723. As R = 0.55 + 0.1182 = 0.6682. The angle (**R**,**S**) being 3.13° : S' = 2.2862. V = 0.0392 + 0.003·3 = 0.048. a = 0.4272, b = 0.4700, d^6 = 0.1763, p = 0.4336. Thus : $\varepsilon_{sm,c}$ = 4905(1.025·0.4336·2.2862/1.6185 + 0.048) = **3315**. **F)** Chromophores III and IV. ϕ being considered as non conjugated to its neighbourg its contribution to S is 0 ; it is taken into account only as a vibrational component, thus V = 0.066 (three substituents). **G)** Vector pattern of chromophores III and IV. *a* = 0.3900, *b* = 0.0980, *ab* = 0.063. **H)** Resulting vector of G : n = 0.425. S = 1.2, σ = 1.0954, a = 0.2900, b = 0.3231, d^6 = 0.09078, p = 0.2928. $\varepsilon_{sm,c}$ = 4905(1.025.0.2928 + 0.066) = **1796**. As there are two chromophores $\varepsilon_{sm,c}$ = 926 + 3315 +1796·2 = **7832** for tiliacorine. Experiment : 8130, difference : Δ = - 3.6%.

1,2,3 -OR substituted chromophore owing to its symmetry has a very low intensity [1]). Furthermore, the strain induced by the 1,4-dioxine oxygens has little effect, and its vector display a 120° angle with the other fused ring vector. Thus, vector addition leads to a value lower than 0.55 which would be obtained for the second fused ring alone. Chromophore II leads to $\varepsilon_{sm,c}$ = 3315 (with V = 0.039 + 0.003·3). Intensity is very much higher than intensity of chromophore I, since the four substituents are in positions 1,2,4,5, since the strain vectors are colinear and in the same direction. As concerns chromophores III and IV, they are considered as independant and their quite weak contribution to the other intensity is taken into account in the vibrational component as a standard sustituent (V = 0.066). Their contribution to intensity should be $\varepsilon_{sm,c}$ = 1796 for each one of them. Thus calculated intensity for tiliacorine is :

$$\varepsilon_{sm,c} = 926 + 3315 + 1796 \cdot 2 = 7830$$

experiment being 8130, difference is only : - 3.6%.

In chromophore I there is an ortho interaction between an -Oϕ substituent and an isopropyl like one. Such an interaction could increase the lengthes of their basis vectors by a factor 1.3 : $n_{O\phi}$ = 0.3715 and : $n_{ipr} = 0.0845$. Assuming these values for the sake of simplicity, — although the factor 1.3 has been established for an -OR⇔isopropyl interaction, — the intensity of the chromophore I should decrease (instead of increasing as in thymol) from 926 to 562, which is a strong decrease, and would lead to 7470 for the intensity of tiliacorine which would be 8,1% lower than experiment, and which is still a good fit. Nevertheless, it has been used a very strong correction for the basis vectors, since it is not sure that such an interaction occurs with the same intensity when an -Oϕ substituent is involved instead of an -OR one, and intensity should lie within the range of the two calculated values.

CONCLUSION

Although some calculations on the intensity of the secondary transition of diphenylether and diphenylether derivatives differ appreciably from experiment (around 20-30%) the majority of them is quite satisfactory. This is worth of notice, since in the choice of the parameters it has been assumed in a first step that the interaction between the two phenyl group through the oxygen atom is kept constant, whatever the derivative, and in a second step it has been studied, for some of the molecules, another conformation where the bond linking the chromophore to the -Oϕ substituent would display a 90° dihedral angle with the plane of the chromophore. The success of these calculations on such big and complex molecules as those studied here must be said to the credit of the *Interaction Vector Model* which is apt to be applied to a large range of conditions.

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