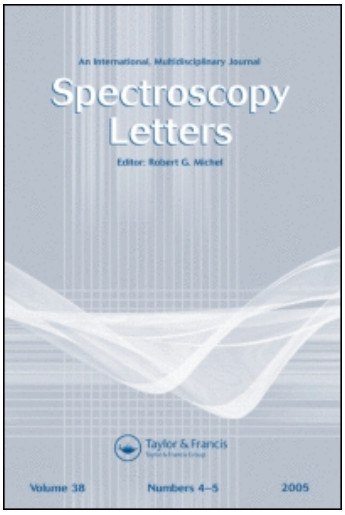


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# THE INTERACTION VECTOR MODEL AND THE SECONDARY TRANSITION OF THE PHTHALIC ANHYDRIDE CHROMOPHORE

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The interaction vector model [1-3] (IVM) has been used to calculate on a very simple basis, and a good accuracy, the intensity of the secondary transition of the benzene chromophore of more than 80 molecules. In this paper we shall study the phthalic anhydride chromophore. Such a molecule is interesting in the frame of the IVM, since it displays a five membered ring, fused to the benzene ring, which imposes to that benzene ring a strong strain and a classical conjugation. No previous molecule displaying these two joined effects, which could cancel their respective influence on intensity, has been studied. The phthalic anhydride molecule will allow to study these effects and test the IVM in such a case. Furthermore, the whole molecules which have been studied till now display only $\pi$ donating substituents. So, before studying the phthalic anhydride molecule, it is necessary to determine the values of the IVM parameters necessary for that study ; that is to say : to study the behaviour of $\pi$ withdrawing substituents such as $-CO_2R$.

## I - THE BASIS OF THE IVM

The secondary transition lies towards 255 nm for the benzene molecule itself. It is electronically forbidden because of the $D_{6h}$ symmetry of the benzene molecule. Thus, the intensity of the transition is low and very sensitive to the interactions with the surrounding parts of the molecule likely to perturb the symmetry.

Within the IVM [1,2] the SKLAR's [4] simple vector scheme approach is used (Fig. 1) with basis vectors $\mathbf{n}$ [1,2] (Figure 1) whose moduli n depend on the nature of the substituents. But several concepts of major importance have been introduced and they completly change the approach : the *interaction vector* (Fig. 1), which takes into account the interaction of two given substituents, the *strain vector* which takes into account the strain imposed by fused rings. 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

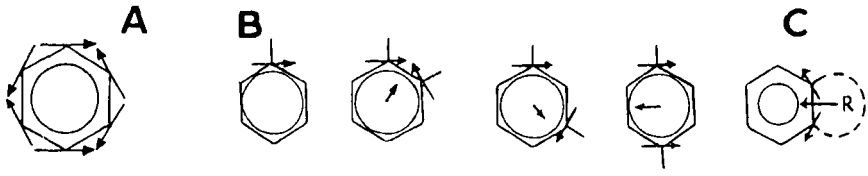



**FIGURE 1.** Direction of the basis vectors. A) The Sklar's basis virtual vectors pattern. B) The basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. C) Direction of the strain vector when there is a ring fused to the benzene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



$\pi$ system enlarge the $\pi$ system increasing its efficiency to capture photons (see S, $\sigma$ underneath).

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

A vibrational component [1,2,5]: V has been used. S and $\sigma$ ($\sigma = S^{1/2}$) are functions of the number and of the nature of substituents ($n_C$ is the number of alkyl substituents, $n_O$ the number of -OR ones) :

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

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

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

Intensity is given as $\varepsilon_{sm}$, the maximum of the smoothed absorption curve (BALLESTER and RIERA [5]) (the calculated value is : $\varepsilon_{sm,c}$). This approach minimizes the incidence of the vibrational fine structure on the measure of intensity. A general relationship has been obtained[1,2] :

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

In a preceding work (when $\pi$ donating substituents are involved) it has been shown that empirical relationships could be used to approach n and V for a given substituent for monosubstituted molecules : [6]

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

## II - BENZOIC ACIDS AND ESTERS

Measuring the intensity of the secondary transition of benzoic acids and esters needs to take into account the overlap of the secondary

transition with its neighbour lying at lower $\lambda$ and arising from the benzene primary band. This correction decreases the accuracy of the value obtained. The values given hereunder are the average of several selected values (since literature displays sometimes quite surprising and completely wrong values as concerns $-CO_2R$ and $-CO_2H$ derivatives) determined from literature,[7] and each one is also the average of benzoic acids and esters with aliphatic substituents on the carboxylic function (apart from the tetrasubstituted derivative [7a], whose only one spectrum has been used), since a carboxylic function and its corresponding ester one display similar effects on a benzene chromophore :

| | $\varepsilon_{sm}$ |
|---|---|
| $\phi$-$CO_2R$ | 725 |
| $\phi$-$(CO_2R)_2$ ortho | 1075 |
| $\phi$-$(CO_2R)_2$ meta | 725 |
| $\phi$-$(CO_2R)_2$ para | 1700 |
| $\phi$-$(CO_2H)_4$ (sites : 1,2,4,5) | 2550 |

In literature, there are few benzoic derivatives with $-CO_2R$ substituents only. The intensity of $\phi$-$CO_2R$ (benzoic acid if R = H) has been used to calculate S for $-CO_2R$. The S values for the other molecules can derive from this one.

When using S = 0.5830 for $\phi$-$CO_2R$, the value for $\sigma$ is : $\sigma$ = 0.7635, and using the above formula to derive n and V from S for the monosubstituted chromophore : n = 0.2517, V = 0.0343. Thus : a = 0.1103, b = 0.1277, $d^6$ = 0.01797, and : p = 0.1106. Thus :

$$\varepsilon_{sm,c} = 4905\,[1.025 \cdot 0.1106 + 0.0343] = 725$$

Using the above empirical value for S (S = 0.5830) (calculated when there is one substituent), allows to calculate S for any number of $-CO_2R$ substituents : $S = K \cdot n_{CO2R}/(4{,}8 + 0.2\ n_{CO2R}{}^2)$, where K has to be calculated. Precisely, when $n_{CO2R} = 1$, S = 0.5830, thus K = 2,915 and :

$$S = 2.915\ n_{CO2R}/(4{,}8 + 0.2\ n_{CO2R}{}^2)$$

When there are two substituents on the chromophore : S = 1.041, and $\sigma$ = 1.020. An interaction vector taking into account the interaction of the two substituents has to be determined. Considering that, for low perturbations, $\pi$ attracting substituents should display an effect symmetric to $\pi$ donating ones,[8] it is possible to use the fact, as it has already been explained in a preceding work,[3] that the modulus of the interaction vector is proportional to the product of the moduli of the two interacting vectors. To determine the modulus of the interaction vector it is possible to use the -OR substituent whose parameters are known with a good accuracy. The modulus of the basis vector for an -OR substituent is 0.3900, and the modulus of the interaction vector for two -OR substituents in ortho position is 0.1330.[1-3] Thus : $0.1330 = k\ 0.3900^2$, and : k = 0.8744. As the basis vector for $-CO_2R$ is 0.2517 one obtains :

$n_{CO2R,ortho}$ = 0.0554. Thus, for the ortho derivative (phthalic acid if R = H), as the interaction vector and the resultant of the basis vectors are colinear, the modulus of **n** is : n = 0.2517 + 0.0554 = 0.3071. Thus : a = 0.1719, b = 0.2038, $d^6$ = 0.1316, p = 0.1756. As V = 0.0343 for one $-CO_2R$, and as V increases only by 0.003 for each substituent added [1,2] : V = 0.0343 + 0.003 = 0.0373. Calculation leads to :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.1756 + 0.0373] = 1065 \text{ (experiment : 1075)}$$

When studying the meta disubstituted derivative, as the interaction vector for two -OR in meta positions is 0.0450 : $n_{CO2R,meta}$ = 0.0187. Thus : n = 0.2517 + 0.0187 = 0.2704, since the interaction vector and the resultant of the basis vectors are colinear. S and σ are the same as what has been calculated for the ortho disubstituted derivative since they depend only on the number and the nature of the substituents. Thus : a = 0.1420, b = 0.1745, $d^6$ = 0.1778, p = 0.1469 :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.1469 + 0.0373] = 920 \text{ (experiment : 725, } \Delta = +27\%)$$

The difference between calculation and experiment is 27%. This result is particularly wrong, although it leads to a value lower than the value obtained for the ortho disubstituted derivative and the para one. There is no specific reason to suspect the experimental value, which is based on several ester molecules and the acid one. This is the greatest discrepancy ever observed in our calculations. This point is discussed hereunder.

As concerns the para disubstituted derivative, as the modulus of the interaction vector for two -OR substituents in para positions is 0.1800, the modulus for the interaction vector of two $-CO_2R$ in para position is $n_{CO2R,para}$ = 0.0750. Not forgetting that the interaction vector of two para like substituents opposes the direction of the basis vectors of the substituents : n = 0.2517·2 - 0.0750 = 0.4284. Still σ = 1.020. Then : a = 0.2833, b = 0.3103, $d^6$ = 0.0430, p = 0.2844, and :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.2844 + 0.0373] = 1613 \text{ (experiment : 1700, } \Delta = -1\%)$$

As concerns the tetrasubstituted benzene molecule, the vector scheme is given in figure 2. Vector addition gives : n = 0.5766. $S = 2.915 \cdot 4/(4.8 + 0.2 \cdot 4^2) = 1.4575$, σ = 1.2073. Thus : a = 0.4811, b = 0.5143, $d^6$ = 0.0629, p = 0.4831. As there are three substituents added to the one appearing in benzoic acid : V = 0.0343 + 0.003·3 = 0.0433, and :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.4831 + 0.0433] = 2640 \text{ (experiment : 2500 ; } \Delta = +5{,}6\%)$$

Only the result concerning the meta disubstituted chromophore is not accurate enough, although it is far better than what could be obtained by the SKLAR'S original method. One should question the way the meta interaction vector is calculated. It is possible that a specific interaction occurs. In order to take into account that interaction it would be necessary to reverse the direction of the meta interaction vector as well as strongly change its modulus. This would lead to too a low value for the tetrasubstituted derivative.

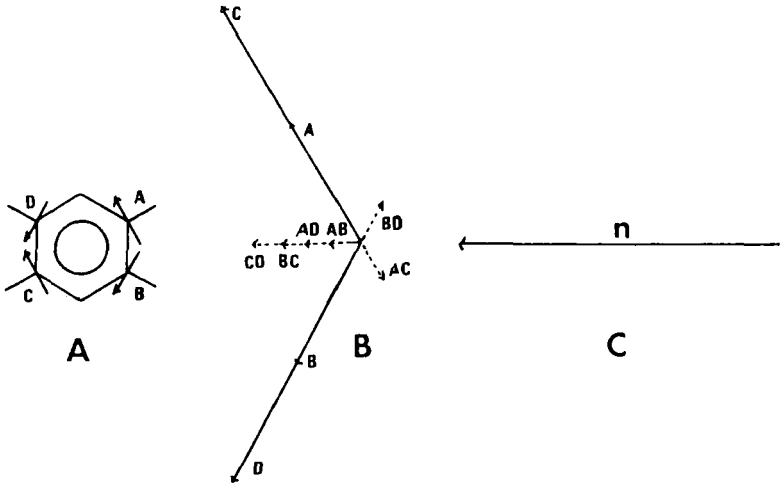



**Figure 2.** Vector scheme for the calculation of the intensity of the secondary transition of 1,2,4,5-benzenetetracarboxylic acid tetramethyl ester. A) Directions of the basis vectors. B) Vector addition. Baisis vectors : plain vectors. Interaction vectors : doted vectors. C) resultant **n** of the vector addition (n = 0.5766).



The discrepancy observed when considering calculations and experiment for the meta disubstituted chromophore could arise in fact, at least for a part, from the way S, and consequently $\sigma$, are calculated. Actually, for benzoic acid : n = 0.2517 ; for the ortho disubstituted chromophore : n = 0.3071 ; for the meta one : 0.2704, and for the para one 0.4284. These values change from one molecule to the other following to the changes of intensity. Nevertheless, the value for the meta disubstituted derivative still is higher than the value calculated for the benzoic acid. Of course S values do not follow the same pattern : S increases when the number of substituents increases, since it is related to a sort of photonic cross section whose nature impose to increase when the number of substituents increases. Consequently, if S is overemphazised in the IVM calculations it can overwhelm the information arising from n, and $\varepsilon_{sm,c}$ will mirror too tightly the changes of S. Furthermore, the way S is calculated for $-CO_2R$ could be questionned too since this group is a $\pi$ withdrawing one when the relationship used has been established for $\pi$ donating groups. The behaviour of the calculated values follows what has been observed for -OR substituents,[1-3] where the experiment for the meta disubstituted chromophore leads to a value between the values observed for the monosubstituted and the ortho disubstituted chromophore [$\varepsilon_{sm}$ are given in the order : monosubstituted chromophore, ortho disubstituted one, meta dis. and para dis. For methyle substituents : 192-234-234-425. For -OH

substituents : 1450-2550-2000-3080]. Such a problem concerning the meta derivative could be seen as the necessity of parametrizing on a different basis the interaction vectors when $\pi$ electronwithdrawing substituents. It is perhaps too much ambitious to proceed as it has been done here above, deducing $\pi$ electronwithdrawing substituent parameters from $\pi$ donating substituents.

In order to evaluate further the nature of the problem, the simplest approach to "reshape" $\sigma$ has been investigated in order to obtain a relationship in which $\sigma$ evolves as n does, for the $-CO_2R$ substituents. The simplest relationship to investigate is : $\sigma = k\ n$, where k is a constant. As $a = n^{1.5}\sigma^{0.5}$, this leads to $a = k^{0.5}\ n^2$. As concerns b : $b = n(\sigma + n)/2$, thus : $b = n^2(k + 1)/2$. As : $d = |n - \sigma|$, $d^6 = n^6\ |k - 1|^6$. Using benzoic acid to evaluate k one sees that b would introduce only a very small correction to a in calculating p [$p = (a + d^6b)/(1 + d^6)$] since $d^6$ would be about 0.003. Thus p simplifies to : $p = a$, and $\sigma = 2.5\ n$. This leads to : $\varepsilon_{sm,c} = 4905\ [1.5811 \cdot 1.025 \cdot n^2 + V] = 4905\ [1.620 \cdot n^2 + V]$. This leads to the values : 670 ($\Delta$ = - 7.7%) - 933 ($\Delta$ = - 13.2%) - 764 ($\Delta$ = + 5.4%) - 1641 ($\Delta$ = - 3.5%) - 2854 ($\Delta$ = - 11.9%) for the $\varepsilon_{sm,c}$ calculated values in the same order as in the above table. These results are almost satisfactory. The ortho derivative and not the meta one displays the worse fit. The problem still lies in the fact that the calculated value for the meta derivative is *still* higher than experiment, whatever the approach used, the above ones and others which have been tried.

Nevertheless, the constant feature is that n appears has being in all the cases a good parameter (although the meta interaction vector should be reevaluated) ; $\sigma$ has to be "reshaped" and adapted to $\pi$ withdrawing substituents if one wants to obtain a satisfactory result for the meta derivative. It is possible to lower its "cross section" identy which binds it to increase when the number of substituents increases. The relationship : $\varepsilon_{sm,c} = 4905\ [1.620 \cdot n^2 + V]$, which derives directely from the IVM, shows that good results can be obtained when assuming empirically that $\sigma$ behaves exactly like n, that is to say that the vector approach of the transition moment, for the $-CO_2R$ $\pi$ electronwithdrawing substituent, has to supersede the more rustic "cross section" one. The cross section is related only to the number of collisions photons-molecules. Absorption needs a collision, but every collision does not lead to absorption. This is not surprising since the transition moment do has a vector nature related to the symmetry of the chromophore, and the way the cross section parameter is used in the IVM is destinated to compensate for deficiencies caused by the simplicity of its vector approach.

The root of the problem lies in the fact that improving the IVM to obtain a better adequacy for $\pi$ electronwithdrawing substituents can be done only if a larger experimental basis could be available to check hypothesis, calculations, as it has been possible for aliphatic and -OR derivatives. This would allow a pure empirical evaluation of the interaction vectors, and a better shaping for S. Of course, one could use -CHO or -COR carbonyl substituents to increase the experimental basis. In fact, there is no more available experiments on the carbonyl derivatives (displaying several -COR groups and no $\pi$ donating substituents) than on the acid ones. Furthermore, the overlap with the higher energy transition is more pronounced for the aldehydes and ketones, thus $\varepsilon_{sm}$ is less accurate. There is too an overlap with the $n \rightarrow \pi^*$ transition, a lower

energy one. The intensity of that transition is weak (it is a symmetry forbidden one) but high enough to cause an increase of the indeterminacy in the calculation of the intensity of the secondary transition of the benzene chromophore. Another point which prevents to reach precise values is that $-CO_2R$ is bigger than -OH or $-CH_3$. Using empirical parameters for a substituent imposes that the parameter does not change much when increasing the number of substituents on the chromophore, when the surroundings become more and more crowded. That means that $-CO_2R$ should stay in the plane of the chromophore in order to maintain the same interaction with the chromophore, whatever its neighbours, whatever the number of $-CO_2R$ groups substituting the chromophore. Actually, the acid group can rotate and decrease its conjugation with the benzene chromophore when its neighbours are bulky. Furthermore, no other $\pi$ withdrawing substituent exists which could be compared to $-CO_2R$ in the same way as $-CH_3$ is to -OH, allowing to cover a wide range of effects.

## III - INTENSITY OF THE SECONDARY TRANSITION OF PHTHALIC ANHYDRIDE AND PHTHALIMIDE



Although the IVM in its present structure does not lead to an accurate enough result for the intensity of one of the benzoic acids (the meta disubstituted one), it is possible to improve that model since results are good for the other molecules studied. Nevertheless, our aim being to study phthalic anhydride the discrepancy which is observed for the meta disubstituted molecule is not too a strong limitation.

It has been established, [2] for $\pi$ donating substituents, that a strain vector **R** has to be added to the vector **S** (**S** displays the same direction as **n**) leading to $\mathbf{S'} = \mathbf{R} + \mathbf{S}$. Then p obtained for the unstrained parent molecule is multiplied by S'/S. The modulus of the strain vector is + 1.920 in indane (five membered aliphatic fused ring) and + 0.550 in benzodioxole (five membered oxygenated fused ring). It has been observed [9] that the spectroscopic efficiency of the strain depends on the conjugative interaction, on the $\pi$ bond order in $\phi$-X between the atom X of the substituent and the atom to which it is bonded in the chromophore. The spectroscopic efficiency of strain decreases when the $\pi$ bond order increases. In the 1,3-benzodioxole molecule the $\pi$ bond order is 0.2680, in indane : 0.1467, and in phthalic anhydride 0.1947 [MNDO calculations ; this work]. Assuming a linear relationship, in that latter molecule R will be : R = 1.3779. Owing to the symmetry of the molecule, **S** displaying the same direction as **n**, bisects the angle of the two substituents. **R** too displays the same direction (see fig. 1). Thus : S' = S + R = 1.0411 + 1.3779 = 2.419. As p for the phthalic acid is p = 0.1756 :

$$\varepsilon_{sm,c} = 4905\,[1.025 \cdot 0.1756(2.419/1.0411) + 0.0373] = 2234$$

The values from experiment are : $\varepsilon_{sm}$ = 2010, (measured from : [10]) and 2100, (measured from : [11]) that is to say an average value of : 2060. Calculation is 8.5% higher than experiment. This is a satisfactory result. [Note that the fused ring is an anhydride group : it is very sensitive to moisture and if not enough cautions are taken to work in a dry medium

(solvent and atmosphere) a part of the anhydride is changed in phtallic acid whose intensity is much lower. Sensitivity to moisture should increase with increasing strain.] This result allows to understand the strong increase of the intensity when cyclizing the acid parent molecule. This phenomenon will be more studied underneath.

The same calculation can be done for the amide corresponding molecules.

The intensity of the secondary transition of the benzamide molecule is lower than the intensity of benzoic acid and it needs a higher correction from the overlap with another transition, thus it is less accurate (overlap can be evaluated roughly to 1/3 of the intensity), which leads to a value : $\varepsilon_{sm}$ = 450 (measured from : [7b]). In order to obtain from the IVM this value of intensity S has to be given the value S = 0.4000 [thus : $S = 2n_{CONH2}/(4.8 + 0.2\ n_{CONH2}{}^2)$]. This leads to : $\sigma$ = 0.6324, n = 0.1825 and V = 0.0267 for the monosubstituted molecule. These values being established, an ortho interaction vector is deduced — as above for the benzoic acids — whose modulus is : 0.0291. Thus, for the ortho disubstituted chromophore : n = 0.1825 + 0.0291 = 0.2116. S = 0.7142 and $\sigma$ = 0.8452 and : a = 0.0895, b = 0.1118, $d^6$ = 0.0647, p = 0.09085. Owing to the the $\pi$ bond order between the first atom of the substituent and the chromophore in phthalimide : 0.1905 [MNDO calculations ; this work], the assumed linearity of the relationship relating R to that $\pi$ bond order, R will be : R = 1.4253, and S' = 0.7142 + 1.4253 = 2.1395. This gives :

$$\varepsilon_{sm,c} = 4905\ [1.025 \cdot 0.09085(2.1395/0.7142) + (0.0267 + 0.003)] = 1514$$

instead of 1390 (measured from : [7c]). The difference is $\Delta$ = + 8.9%. Again this result can be considered as a satisfactory one. Thus the IVM is able to take into account strain when there are $\pi$ withdrawing substituents.

## IV - PHTHALIC ANHYDRIDE AND PHTHALIMIDE STRUCTURES RELATED TO THE INTENSITY OF THE SECONDARY TRANSITION

The structure of phthalic anhydride (Figure 3) has been calculated in this work by the MNDO method. These calculations correspond to isolated pseudo-free molecules in a pseudo gaz phase. When comparing the results one sees that the main phenomenon to be underlined is an alternation of the bond lengthes inside the benzene moiety. Such a phenomenon has been known for a long time for indane (Mills-Nixon effect) and more recently for 1,3-benzodioxole.[12-13] It has been shown that it is the strain, imposed by the five membered fused ring on the bridgehead bond, which lengthens that bond, changes the values of the angles situated between the substituents. Under strain the structure is driven towards a Kekulé like structure. In fact, increasing infinitely the length of the bridgehead bond would lead to open the benzene ring and reach a $\pi$ structure somewhat similar to that of hexatriene. Actually, the hexatriene molecule shows a strong alternation of bond lengthes, but this alternation differs from a pure Kekulé structure. Nevertheless, to be short, in benzene derivatives it will be refered to as a Kekulé structure.

The alternation of bond lengthes destroys the $D_{6h}$ symmetry of the molecule distorting it towards a $C_{2v}$ one. As concerns the $C_2$ operation, in

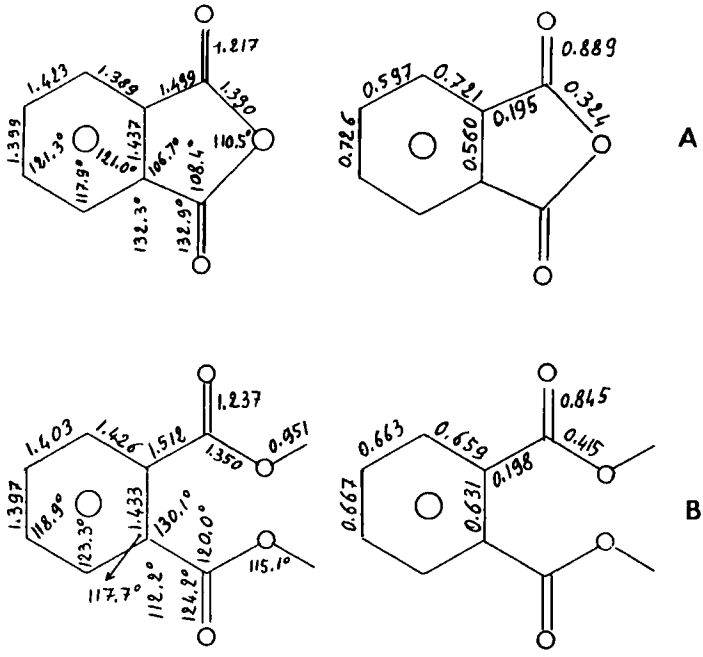



**Figure 3.** A) MNDO structure of phthalic anhydride. Left drawing : bond lengthes (Å) and bond angles (degrees). Right drawing : π bond orders. B) phthalic acid.



the phthalic acid molecule, on the one hand the long bonds are symmetric, the same for the short ones on the other hand. As far as the intensity of the secondary transition is concerned, the nearer to a $C_{2v}$ symmetry the molecule is, the higher the intensity is, since the transition is electronically forbidden for the $D_{6h}$ group ($^1B_{2u} \leftarrow {}^1A_{1g}$), and allowed for the $C_{2v}$ one. Thus, intensity is increased when the two substituents are part of a fused ring compared to the molecule displaying two free substituents. That phenomenon is taken into account using the vector **R**, as a strain vector, in the IVM.

Geometry being the result of a quantum behaviour, a distorsion is also observed in the electronic distribution. Actually, there is an alternation of the π bond orders within the benzene moiety : 0.560 (bridgehead bond) — 0.721 — 0.597 — 0.726 — 0.597 — 0.721 for phthalic anhydride. The bond orders are lower than 0.667 — which is the benzene value — when the corresponding bond length is increased, since the lengthening weakens the bond. They are greater than 0.667 when the bond is shortened.

As concerns phthalic anhydride, closing the angles external to the benzene moiety, between the two substituents, causes the benzene

moiety to contract towards the fused ring, increasing the angles at the sites of substitutions inside the benzene moiety, and decreasing them in the positions neighbouring these ones (Figure 4).

The fused ring tends to release its strain by opening its geometry and consequently lengthening the bridgehead bond. The behaviour of phthalic acid is different. In that latter molecule, in the benzene moiety, although the bond between the two $-CO_2H$ is increased compared to the free benzene molecule in order to lower the repulsion between the substituents, this repulsion opens the angles external to the benzene moiety between the substituents, and closes the complementary angles external to the benzene moiety (Figure 4). This tends to decrease the angles inside the benzene moiety at the sites of substitution. Thus, when considering the angles inside the benzene moiety : the angles which are increased when there are two $-CO_2R$ substituents are decreased when there is an anhydride fused ring and vice versa. This can be understood on a purely mechanical basis as it is shown in figure 4.

In a preceding work [13] two alternation indices have been defined in order to quantify the distorsion, one is based on the bond lengthes, the other on the bond orders :

$$A_L = 100(L - l)/L \quad \text{and} \quad A_\pi = 100(\Pi - \pi)/\Pi$$

$A_L$ is related to the geometry of the molecule : $L$ is the average length of the three longest alternating bond lengthes and $l$ the average of the three shortest ones in the benzene moiety. $A_{L,n}$ is $A_L$ normalized to 100 for the Kekulé structure ($A_L$ = 13.64, using : $L$ = 1.54 Å, $l$ = 1.33 Å). $A_L$ has been previously used [13] but it appears that $A_{L,n}$ is more interesting, since it shows that very often the geometric index and the electronic one ($A_\pi$) are very close. Actually, they measure the same phenomenon seen from two different point of view. As concerns $A_\pi$ : $\Pi$ is the average of the three highest $\pi$ bond orders within the benzene moiety and $\pi$ the average of the three weakest ones. For a pure Kekulé structure : $A_\pi$ = 100(1-0)/1 = 100. The values are given in table I.

Till now, 1,3-benzodioxole has been known to display the strongest effect. This work shows that the alternation of bond lengthes and bond orders in phthalic anhydride (and phthalimide) is greater than what is observed in benzodioxole. This is quite surprising since the anhydride molecule displays a much lower overall electronic interaction between the benzene moiety and the fused ring. For the anhydride molecule the fused ring withdraw 0.046 electron from the $\pi_\phi$ cloud. 0.148 electron is given in benzodioxole to the benzene moiety. One could argue that in the anhydride case a decrease of $\pi_\phi$ electrons occurs, and, on the contrary, an increase in the benzodioxole case. Of course, although one could not, at first, neglect a possible incidence on the alternation effect, of the number of $\pi$ electrons in the benzene moiety, if this number was strongly differing from 6, it is more important to consider the ability of the whole structure, with the substituents, to display a conjugated pattern as long as possible and as efficient as possible. Actually, the two C=O bonds outside of the fused ring and outside of the benzene moiety, support the alternating structure : the $\pi$ bond order is naturally strongly marked in C=O (0.851 in benzoic acid, 0.845 in phthalic acid, and 0.888 in the anhydride molecule), and weak in the $C_\phi—C_{C=O}$ bond space (0.212 in

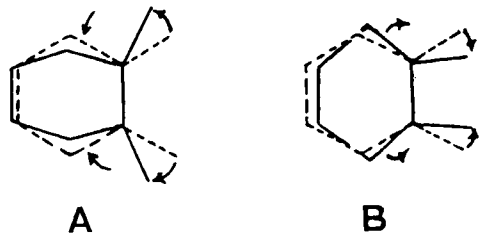


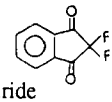
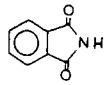
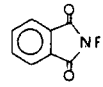
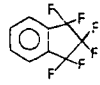
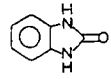
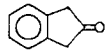
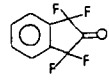
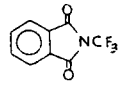
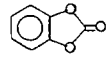
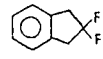
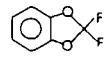

**Figure 4.** A) Distorsions of the benzene moiety under the change of the angles between the chromophore and the substituents, when the substituents are not part of a fused ring. B) when the substituents are part of a fused ring.



the benzoic acid, 0.198 in phthalic acid, and 0.195 in the anhydride). This begining of alternating structure outside of the benzene ring will tend to impose its continuity inside the benzene ring. This explains why the tendency towards an alternating structure, already induced by strain, will be enhanced by the conjugation of the benzene moiety with the C=O bonds. Furthermore, in benzoic acid, the $\pi$ bond orders of the two benzene bonds involving the same carbon (C-C=O) bonded to the C=O group are decreased from 0.667, value corresponding to the free benzene molecule, to 0.644. Actually, these bonds are the first ones, inside the benzene moiety, to be under the influence of the $\pi$ electron withdrawing character of C=O (the other $\pi$ bond orders in benzoic acid are 0.673 and 0.663 as distance increases from the position of substitution). Thus, when there are two $-CO_2R$ in ortho positions the $\pi$ bond order of the benzene bond between the two substituents will be much more decreased than when there is only one electron withdrawing substituent. This is what happens in phthalic acid : the $\pi$ bond order is only 0.631. Nevertheless, in that latter case there is also the repulsion of the substituents which tends to increase that bond length, thus to decrease the $\pi$ bond order. Consequently, in order to isolate the pure conjugative electronic effect, calculations have been done on a "standard" disubstituted benzene chromophore with 1.400 Å bond lengthes and 120° angles, the $-CO_2R$ substituents displaying also 120° angles with the benzene moiety. These parameters have been kept constant. Although its length cannot be increased by the repulsion of the substituents, since its length is not allowed to vary, the $\pi$ bond order of the bond situated between the two substituents is : 0.628 much weaker than the value of the free benzene molecule (0.667). The other $\pi$ bond orders inside the benzene moiety show that, although the geometry is kept constant, there is a natural tendency to display an alternating structure (0.628, 0.665, 0.658, 0.671) owing to the only conjugative effect of the substituents.

A similar alternation effect is observed in phthalimide. The five membered amide fused ring is slightly less efficient to induce alternation of bond lengthes than the anhydride ring. At first, this could seem to parallel the fact that the intensity of the secondary transition in

**TABLE I : Alternation indices**

| | | $A_{L,n}$ | $A_\pi$ | |
|---|---|---|---|---|
| Kekulé structure |  | 100 | 100 | |
| [1-indanone |  | 9.02 | 8.99] | |
| [Phthalide |  | 10.31 | 10.32] | |
| 1,3-indandione |  | 11.77 | 12.80 | 1 |
| |  | 11.58 | 13.48 | 2 |
| phthalic anhydride |  | 17.96 | 19.14 | 3 |
| phthalimide |  | 16.70 | 18.15 | 4 |
| |  | 14.40 | 16.29 | 5 |
| indane |  | 9.09 | 8.98 | 6 |
| 1,3-benzodioxole |  | 14.93 | 14.90 | 7 |
| |  | 7.72 | 9.40 | 8 |
| |  | 9.64 | 8.76 | 9 |
| |  | 7.51 | 10.06 | 10 |
| |  | 10.49 | 6.76 | 11 |
| |  | 9.96 | 9.89 | 12 |
| |  | 9.02 | 11.01 | 13 |
| |  | 14.66 | 16.68 | 14 |
| |  | 12.90 | 10.43 | 15 |
| |  | 6.68 | 5.68 | 16 |
| |  | 8.11 | 8.08 | 17 |
| |  | 14.46 | 13.68 | 18 |
| |  | 12.92 | 12.69 | 19 |
| |  | 13.73 | 15.44 | 20 |

phthalimide is much lower than what is observed in phthalic anhydride (see above part III). In fact, one should not forget, first, that the amide function is less perturbating, on a spectroscopic point of view, than the carboxylic function : the intensity of the benzamide molecule is much lower than the intensity of the benzoic acid molecule : $\varepsilon_{sm}$ = 450 for the first one, and $\varepsilon_{sm}$ = 725 for the second one, and second that strain does not "create" intensity, but enhances, multiplies, the already existing intensity in the unstrained parent molecule. In other words : intensity in the fused molecule depends strongly on the value of the intensity in the unstrained ortho disubstituted derivative, and, consequently on the intensity of the monosubstituted derivative ; it depends on the already existing intensity that strain can enhance. Furthermore, the lengthes of the strain vectors have been calculated here above : R = 1.4253 for the phthalimide molecule and R = 1.3779 for phthalic anhydride. The effect of strain is higher in benzamide, although the amide group is less perturbing, less conjugated, precisely because the conjugation — which cancels the effects of strain on intensity — with the chromophore is less marked. But, as the enhancing factor is (S + R)/S, a given value for R will all the more lead to a great value of (S + R)/S, as S is low, that is to say as the substituting group is less perturbing. When comparing phthalimide and phthalic anhydride : S = 0.7142, for the first molecule, and 1.0411 for the other. These values lead respectively to the enhancing factors : 3.00 and 2,32. A lower alternation indice in phthalimide, compared to phthalic anhydride, leads to a stronger enhancement of intensity, but to a lower intensity because the enhancement, owing to the much lower intensity of the monosubstituted derivative, is not sufficient to reach the value of the phthalic anhydride. Thus, when there is a fused ring, the intensity of the secondary transition cannot be directly linked to the amplitude of the alternation of bond lengthes, or $\pi$ bond orders, within the chromophore.

One could think too that the fused ring of phthalimide being slightly less $\pi$ withdrawing (number of $\pi_\phi$ electrons : $n_{\pi\phi}$ = 5.9571) than the anhydride ring ($n_{\pi\phi}$ = 5.9541) the interaction of the substituents with the $\pi$ cloud of the benzene moiety is weakened, and that this could be the origin of the lower alternation of bond lengthes and bond orders in the benzene moiety. This reasoning would be wrong. In fact, in order to understand, one needs considering 1,3-indandione which displays a $-CH_2-$, instead of -O- in phtalic anhydride or -NH- in phthalimide, ($-CH_2-$ is less $\pi$ donating than -O- or -NH-). The number of $\pi_\phi$ electrons is : $n_{\pi\phi}$ = 5.9390 in 1,3-indandione. This number of electrons has been strongly decreased compared to the anhydride and to phthalimide, showing a stronger electronic intraction. Nevertheless, although the electronic interaction is increased, the alternation effect is much lower : $A_{L,n}$ = 11.77, instead of 17,96 (phthalic anhydride) and 16,70 (phthalimide). Thus, the loss of efficiency in imposing an alternating structure is not directly linked to the pure electron interaction of the fused ring on the $\pi$ benzene cloud.

In order to identify the origin of this loss of efficiency in imposing an alternating structure, several other molecules have been studied, introducing $\pi$ donating or $\pi$ withdrawing substituents in the fused ring, in order to vary the effects of the fused ring on the benzene moiety. Results are given in figure 5. That figure shows that when ploting $A_{L,n}$,

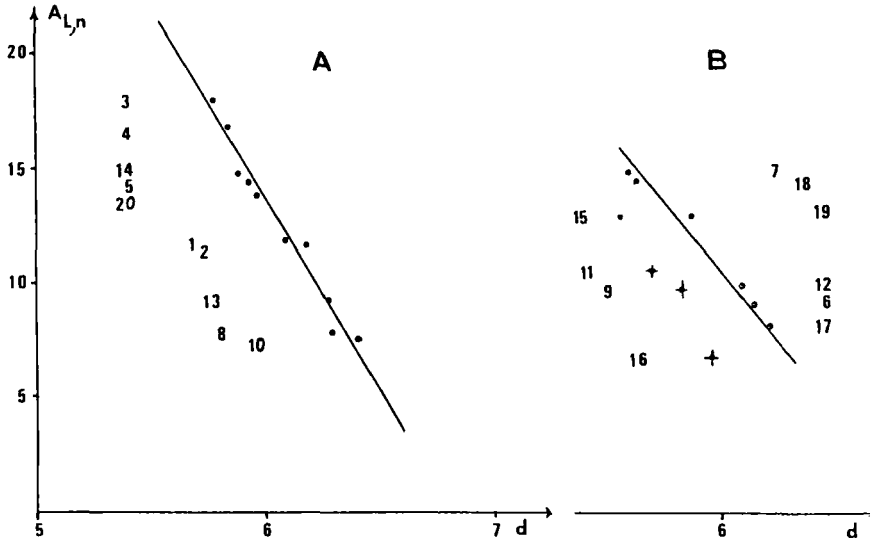



**Figure 5.** $A_{L,n}$ for various five membered fused ring (ordonate) versus the length d of the part of the fused ring external to the benzene moiety (four bonds). A) $\pi$ withdrawing fused rings. B) $\pi$ donating fused rings. The fused rings in molecules 11, 9, 16 are not plane.



which measures the alternation of bond lengthes, against the length d of the part of the fused ring outside of the benzene moiety (four bonds), a strong correlation is obtained for the fused rings which are $\pi$ withdrawing : the alternation of bond lengthes increases when the length d of the fused ring decreases. Actually, this decrease of the perimeter of the fused ring increases the strain in the molecule. The bridgehead bond, where the greater part of the strain is directed, lengthens to relieve it, and this lengthening, the change in the angles, as it has been explained here above, causes a distorsion towards a Kekulé like structure. All the more the five membered fused ring is short all the more it tends to open its structure.

$A_{L,n}$, has been choosen in figure 5, and not $A_\pi$, since the behaviour of $A_{L,n}$ related to geometry distorsions is easier to understand than the bond orders distorsions [some values of $A_\pi$ differ strongly from the corresponding $A_{L,n}$ ones (Table I : molecules 10 and 11). The origin of such a difference is difficult to explain].

This study on fused structures has been restricted to $C_s$ molecules (symmetric fused ring ; plane of symmetry perpendicular to the plane of the benzene moiety) considering the atoms of the benzene moiety and the five atoms of the fused ring, in order to limit the number of intervening factors. As concerns the $\pi$ donating fused rings, four

molecules display only a very low correlation (11, 9, 16, 15). The five atoms of the fused rings are not planar for three (11, 9, 16) of them. Although several of the $\pi$ electrons withdrawing fused rings are not perfectly plane, this lack of planarity does not introduce great discrepancies. Would planarity be a factor to take into account for the $\pi$ donating fused rings ? Apart from molecule 15 the plane ones obey to a decrease of the alternation of bond lengthes similar to the decrease observed for the $\pi$ withdrawing ones. The lack of planarity can release the strain in changing the dihedral angles within the fused ring as well as the length of the bridgehead bond. This could be one of the reasons why no tight correlation can be observed for these molecules.

## CONCLUSION

The alternation of the bond lengthes in phtalic anhydride display the highest index ever observed. Taking the phtalimide molecule as a basis for comparison, the index for the anhydride molecule is higher than what is observed in the phthalimide molecule because the length of the four bonds belonging to the fused ring outside of the benzene moiety, is shorter than the same perimeter in phthalimide. But, although the distorsion of the benzene moiety is lower in phthalimide than in phthalic anhydride ($A_{L,n(\text{phthalimide.})} < A_{L,n(\text{phthal.anh.})}$), this is not the reason why intensities are in the same order. The main factor inducing a higher intensity in phthalic anhydride lies in the fact that a $-CO_2R$ group induces a greaterer perturbation of $\pi_\phi$ (the intensity of the secondary transition of benzoic acid is much higher than the intensity of benzamide), and that strain enhances only existing intensity in the unstrained parent molecule. Nevertheless, although strain is lower in phthalimide, it is more efficient to increase the intensity.

Owing to the fact that S and $\sigma$ have been designed for $\pi$ donating substituents, the calculation of the intensity of the secondary transition of one of the molecules which have been studied does not lead to a good fit with experiment. Nevertheless, the IVM successfully helps to reach a clearer understanding of the behaviour of the benzene chromophore in the phthalic anhydride molecule, under the joined perturbation of strain and of $\pi$ withdrawing groups within the fused ring.

## REFERENCES

1) B. VIDAL, *Spectroscopy Lett.* **27**, 41 (1994)

2) B. VIDAL, *Spectroscopy Lett.* **27**, 709 (1994)

3) B. VIDAL, *Spectroscopy Lett.* **28**, 519 (1995)

4) A. L. SKLAR, *J. Chem. Phys.* **10**,135 (1942) ; A. L. SKLAR, *Revs. Modern Phys.* **14**, 232 (1942) ; Th. FÖRSTER, *Z. Naturforsch.* **2a**, 149 (1947) ; J. R. PLATT, *J. Chem. Phys.* **19**, 263 (1951) ; J. PETRUSKA, *J. Chem. Phys.* **34**, 1111 (1961) ; J. PETRUSKA, *J. Chem. Phys.* **34**, 1120 (1961) ;

P. E. STEVENSON, *J. Chem. Educ.* **41**, 234 (1964) ; P. E. STEVENSON, *Ph. D. Thesis*, Part I, University of Chicago, 1964

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

6) B. VIDAL, *Spectroscopy Lett.* (under press, **29**,1996)

7) W. SIMONS, *Sadtler Handbook of Ultraviolet Spectra*, Philadelphia, Sadtler, 1979. (a-spectrum 2920, b-spectrum 2288, c-spectrum 2380)

8) B. VIDAL, *Spectrochimica Acta*, **38A**, 367 (1982)
D. DENIS-COURTOIS, B. VIDAL, *Spectrochimica Acta*, **39A**, 735 (1983)

9) B. VIDAL, J-Y. CONAN, G. LAMATY, *Spectroscopy Lett.* **20**, 233 (1987)

10) *American Petroleum Institute*, Research Project 44. Spectra 102, 103

11) L. LANG, *Absorption Spectra In the Ultraviolet And Visible Region*, Akadémiai Kiodo, Budapest, 1975, spectrum 3685

12) B. VIDAL, J-Y. CONAN, G. LAMATY, J. VARDIN, *Australian J. Chem.* **41**, 1107 (1988)

13) B. VIDAL, J. VARDIN, A. DARRY-HENAUT, *Chem. Papers* **44**, 603 (1990)

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