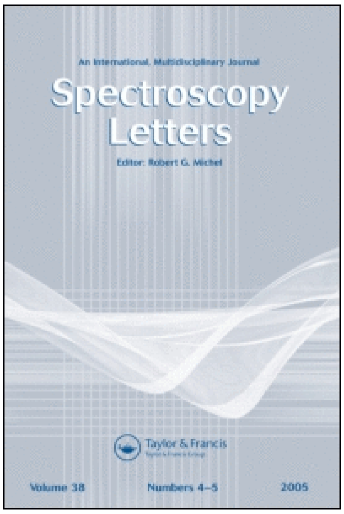

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A NEW APPROACH TO THE INTENSITY OF THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE WITH -CH_3, -OH, -OCH_3, SUBSTITUENTS

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Since the beginning of the UV absorption spectroscopy, the intensity of the secondary transition of the benzene chromophore in organic derivatives has been a puzzling challenge. The well known vector model has led to some qualitative evaluation of intensity, but accuracy is very low, and sometimes leads to no less than 50% or 100% error. [1-8] It is designed for very weak perturbations only, as in methylbenzenes. But, even in that latter case, it is not completely satisfactory. Nevertheless, that model is very easy to use ; it allows to determine the sensitive positions around the benzene nucleus : those which could enhance or quench intensity for a given pattern of substitution. On that ground it has been of much help for qualitative evaluations. With SCF methods and CI calculations, evaluation of transition moments for several benzene derivatives has been possible on a firmer ground. In fact, such an approach is useful mainly from a theoretical point of view, when accuracy is not the first aim, for some choosen molecules at the same time, since the involvement of computation is far from being negligible, and since the method is not part of the ones that are of common use in organic chemistry [9,10] (for a recent example on oscillator strength calculations of π systems see : [11]). In other words, it is not perfectly valuable on a large scale and routine approach and, from that point of view, UV spectroscopy of benzene derivatives appeared sometimes, from 1965 till now, as being in a *cul-de-sac*, although it was under thorough examination (for example : [12-30]). Until recently *ab initio* calculations have failed to reach a fit with experiment better than 1 eV for the spectrum of the benzene molecule [31-32]).

As we are mainly concerned by UV spectroscopy applied to natural products, we need a method as simple as possible for interpreting spectra, relating the data to some simple concepts. As phenols and alkoxybenzene derivatives are very common in natural products, we decided to study these molecules, more exactly to study a benzene nucleus with substituents such as : $-CH_3$, -OH, $-OCH_3$. Molecules with strain (rings fused to the benzene nucleus) have not been taken into account in the present state of our work.

I - THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE

Many problems related to the intensity of the secondary transition of the benzene chromophore have been studied in other works (for example : [12-25]). One can find, hereunder, the main characteristics of that transition.

The secondary transition of the benzene chromophore lies towards 250-260 nm, when considering the free benzene molecule. It is a $^1B_{2u}$-$^1A_{1g}$ type transition ; and it is electronically forbidden because of the D_{6h} symmetry of the molecule. Nevertheless, the coupling of the electronic motion with a e_{2g} vibration in the $^1B_{2u}$ excited state allows to observe that transition with a low intensity, as a progression of the a_{1g} breathing vibration of the excited state. When substituents perturb the D_{6h} symmetry of the chromophore, the selection rules linked to that symmetry are weakened. The transition becomes allowed, and a new progression of the a_{1g} breathing vibration superimposes to the preceding one. The intensity of the secondary transition depends on the extent of the distorsion of the benzene chromophore, and on the nature of the new symmetry which is reached. Thus, intensity can be considered as having two components. The first one is linked to the vibrational coupling ; the second one is more purely electronic. This latter is the most important one for -OR substituted benzenes, since the "non bonding" electrons of the oxygen atom are coupled to the π_ϕ system. The charges are strongly modified in the benzene nucleus because of such a conjugative interaction.

II - THE FORMER SIMPLE VECTOR MODEL

In this model, the intensity changes in substituted benzenes can be explained by a diagram shown in figure 1. This diagram display the symmetry of the transition, which is linked to the symmetry of the ground and of the excited state. As the ground state is completely symmetric, that diagram displays the symmetry of the excited state. It allows to calculate the transition moment vector (intensity is proportional to the square of that vector) by calculating the sum of the component vectors of the diagram, taking into account the amplitude of the perturbation of each substituent to use component vectors on the sites of the substitutions proportional to the estimated perturbation. That perturbation, for a given substituent, is empirically evaluated from the spectrum of the monosubstituted chromophore. This empirical spectroscopic approach involves, of course, the ground and the excited state.

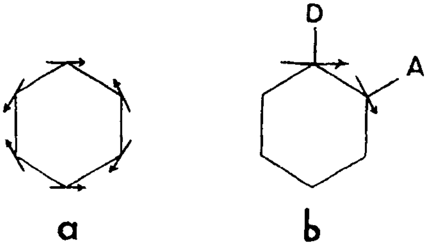

FIGURE 1 a) The vector pattern used in the simple vector model. b) The vector pattern used for two ortho substituents, one being π donating (D), the other being π withdrawing (A).

III - A NEW VECTOR MODEL TO CALCULATE INTENSITIES

As the vector pattern of the vector model can take into account the excited state – at least its symmetry, which is an important point –, one can try to use that vector pattern with quantum parameters of the ground state. Then, we can try, with a proper further empirical parametrization, to reach the important parts of the excited state – and of the ground state – which are not taken into account in such a vector pattern. As a principle, the whole information on a molecule can be reached from whatever electronic state this molecule diplays. The differences between states are a matter of energy, and of symmetry if we choose to study the molecule with MO obeying to the symmetry of that molecule (which is the general case).

The quantum parameters necessary for our calculations have been obtained by the MNDO method after geometry optimization. In fact, it is not sure that optimization is absolutely necessary, but when starting that study we wanted to be sure of the consistency of our calculations as far as geometry is concerned. Although MNDO geometry is not always the actual geometry – since, sometimes, it overemphazises nuclear repulsions – it is the geometry which leads to some reference MNDO quantum parameters. Furthermore, as concerns substituents, the geometries which have been used are not exactly identical with the actual conformations. Actually, we adopted a standard conformation for the methyles, with a C-H bond in the plane of the benzene chromophore, to ensure a standard hyperconjugative coupling between the substituent and the π cloud of the benzene molecule. But, the whole other parameters were optimized. The O-H and the O-C(H_3) bonds where also in the plane of the benzene molecule. When crowding, around the benzene ring, was too great, we allowed some of the methyles to an optimization of their HCC=C dihedral angles.

We did not try to calculate transition moments but some function which could vary as intensity does, whatever that function could be. We were happy enough to reach a linear variation, but this was not really our aim when that work began.

Our approach has also taken into account the very crude picture of the absorption process that considers that a photon has to reach the molecule to be absorbed by that molecule, a "collision" has to occur: and the probability for such a collision increases when the area of the π system increases.[33] In other words the probability of the absorption process increases – all other factors being equal – when the UV cross section increases.

The intensity of the secondary transition of the benzene chromophore has been evaluated by ε_{sm}, the maximum of the smoothed absorption curve, as it has been defined by BALLESTER and RIERA.[34] This method leads to values consistent with the integrated intensities. It avoids the problems linked to the vibrational fine structure which depends strongly on the relative importance of the two progressions of the secondary transition, on the interactions of the molecule with the medium : the "height" of a "peak" depends, for a given integrated intensity, on its width. Although intensity could be the same for two different molecules, the width can be different. The molar extinction coefficient of the OO band (ε_{00}) of the secondary transition is not always visible in phenols because of its width and because of its burying under the rest of the transition. It is of no use in the present work. Furthermore, the molar extinction coefficient of the maximum of the absorbtion curve (ε_{max}) does not correspond to the same vibrational transition in the different molecules studied. Thus, only ε_{sm} has been used in that work.

The first step we did to find a new method to evaluate the intensity of the secondary transition, has been to assume that the vector model can be improved. On that ground we had to find how to evaluate the modulus of the component vectors. As we did not want really to calculate effective transition moments, we decided to use, for a given substituent, the π bond order (BO_π) between the p_π orbital of the atom which, in the substituent, is bonded to the benzene moiety, and the p_π orbital of the atom to which it is bonded in the benzene moiety. Actually, although that BO_π is not equal to the modulus of the corresponding component vector, it is characteristic of the perturbation brought upon the π_ϕ system. Its modulus – its length – should increase when the actual component of the transition moment increases, and decrease when the actual component decreases. The modulus of the resultant vector for a given substitution pattern is t_1. Our results show that such an approach has to be strongly improved to be much more useful than the simple vector model. The present model displays the same defects as the simple vector model. The intensities of the secondary transition of phenol, o-dihydroxybenzene, m-dihydroxybenzene, are : ε_{sm} = 1450, 2550, 2000, and the values of t_1 are 0.300, 0.302, 0.321. This is not satisfactory. The scattering of the results could lead to think that there is not much hope. In fact, t_1 overemphasizes the part of the molecule which is outside of the benzene ring, that part which imposes the perturbation. The π_ϕ system of the benzene ring is not enough taken into account. That model overemphasizes the whole π electrons involved in the partial π bond between the substituents and the π_ϕ system. External symmetry too, is certainly overemphazised, since the only component vectors taken into account are those evaluated at the sites of the substitutions, and their moduli are evaluated from data arising mainly from the substituents.

Symmetry distorsions, electronic density distorsions, inside the nucleus are not taken into account. These defects have to be corrected. Thus, another parameter (t_2) has been calculated in order to put emphasis on the π_6 system itself. Then, it will be possible to use a combination of t_1 and t_2 to reach a better parameter displaying a better balance between the π system inside the chromophore and the part which is outside.

It is known that the secondary transition in the benzene chromophore arises mainly from electrons belonging to the two degenerate HOMO orbitals and much less from deeper electrons. Thus we tried another approach, in the benzene derivatives, using only the two highest MO arising from the degenerate orbitals of the free benzene molecule. Among these two MO, the highest energy one will be noted MO_1, the lowest one : MO_2. Furthermore, we tried to build a parameter evaluating the distorsion from the D_{6h} symmetry, keeping in mind the logic and the structure of a transition moment (but not trying really to reach the actual transition moment, not trying to fit exactly the structure of the transition moment).

The structure of the transition moment is, for an absorption from the ground state ϕ_g towards an excited state ϕ_e : $<\phi_g | \Sigma er_k | \phi_e>$. r_k is the vector distance from a given electronic charge e, to the center of gravity of the positive charges. Σ is the summation over all the k. That center of gravity will be assumed, here, at the center of the benzene chromophore, whatever the substituents are. Summation is done over all the charges. Using only the ground state – and parametrizing to take into account the excited state – needs, to keep consistency, the assimilation of ϕ_g^2 to the product $\phi_g\phi_e$ which appears in the transition moment. Furthermore, the transition moment being a *moment* we have to take into account an electronic charge as much as it is farther from the center of gravity of the positive charges. Actually, using a naive picture, we can say that the symmetry of a given object is all the more perturbed as its extensions are farther from its previous center of symmetry.

When considering the circle circumscribing the benzene ring all the carbon atoms of the benzene chromophore are situated at a unit radius distance from the center of the benzene ring. The atoms C, of the $-CH_3$, O of the OH or OR substituents, are considered as being at twice that radius taken as a unit.

In the simple vector model, when a substituent is π donating its corresponding component vector is oriented in the direction of a previously fixed reference vector pattern (Figure 1a). Of course, changing the direction of the whole vectors would be valid too. When the substituent is π withdrawing, its component vector is oriented in the opposite direction. The figure 1b gives an example with D as a donating substituent, and A an electron withdrawing substituent. In fact, when one of the substituents is π donating and another one π withdrawing the simple vector model leads often to completely unreliable previsions.

In the free benzene molecule, the π densities arising from the two degenerate HOMO (MO_1 and MO_2) is 0.3333 on each carbon atom when considering **one** electron in each one of these two MO (we could have used two electrons in each one of these MO of course, but one more calculation is not useful). In a benzene derivative, when that density calculated from MO_1 and MO_2, arising from the two degenerate MO of the benzene molecule, is higher than 0.3333 at a given position, that means that this position has received electrons. Using the same convention as in the simple vector pattern (see underneath part IV-Comment), the component vector is oriented as it is in the reference pattern for the same position. When the density is lower than 0.3333, the component vector is oriented in the opposite direction. The modulus of the component vector is assumed as being the difference between 0.3333 and the actual density d (calculated as explained above with one electron in each one of the two concerned MO) : $|0.3333 - d|$.

The calculation of the component vector linked to a given position involves not only the densities from the carbon atoms of the benzene nucleus, but also the π densities, in the two concerned MO, which could arise from the substituents. The contribution of a given substituent is taken into account with a weight depending on the efficiency of the bonding of that substituent with the corresponding carbon of the benzene ring, since it is the efficiency of the perturbation imposed to the benzene ring which has to be taken into account. That is to say : the density involved by the substituent in one of the two MO - say MO_1 - is multiplied by the fractional bond order internal to that MO (the same arises for MO_2). Furthermore, that contribution has to be multiplied by two, in order to take into account the nature of the *moment*, since the sustituent is situated at twice the unit radius from the center of the benzene moiety. One has to consider also that there is no substituent in the benzene molecule, no density to take into account outside the ring. That is to say : the value to take into account is 0. Thus, the density arising at the level of the substituent is always greater than the value arising from the benzene molecule in the same place. In the begining of the calculation, the vector arising from a substituent for each one of the two MO will be in the same direction as that of the reference pattern. Nevertheless, as in all the cases observed here the fractional bond order is negative, its directionchanges to point to the opposite direction. Thus, in almost all the cases, the contribution of the two vectors arising from a given substituent (the vector from MO_1, and the vector from MO_2) is in the same direction as that obtained for the vector arising from the carbon of the benzene moiety to which the substituent is linked.

To be clearer we shall develop the elements necessary to realize a calculation. Furthermore, we shall give an example calculation for an actual molecule, in part IV.

A, B, C, D, E, F, a, b, c, d, e, f, are the coefficients involved in the highest molecular orbital arising in a benzene derivative from one of the degenerate HOMO of the free benzene molecule (not forgeting their signs, of course) : MO_1. A', B', C', D', E', F', a', b', c', d', e', f' are the coefficients involved in the other molecular orbital arising from the other degenerate HOMO of the benzene molecule : MO_2 (Figure 2(1) and Figure 2(2)).

The first step in calculating t_2 is to calculate the densities corresponding to these coefficients (that is to say we have to calculate the square of these coefficients). a, b, c, d, e, f, a', b', c', d', e', f' are 0 if there is no substituent in the corresponding position.

Then, inside the benzene moiety, the sum of these densities is calculated for each carbon. If $A^2 + A'^2 > 0.3333$, the component vector in that position is in the direction of the vector of the reference pattern,

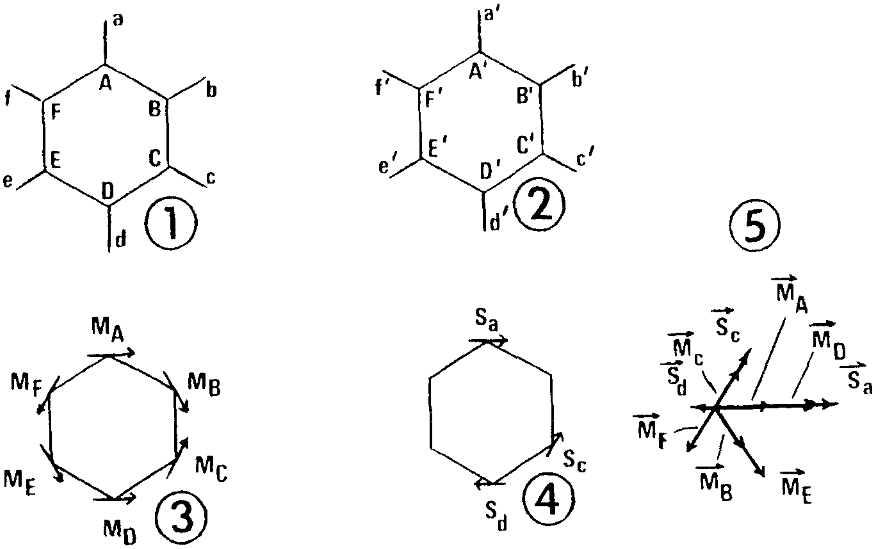

FIGURE 2 Process to follow to calculate t_2. 1) MO_1 coefficients for a given molecule. 2) MO_2 coefficients. 3) The vector pattern related to the carbon atom of the benzene moiety for a given given set of substituents (see text). 4) The vector pattern related to the substituents. 5) Addition of the vectors involved in "3)" and "4)".

and its modulus – its length – is : $| A^2 + A'^2 - 0.3333 |$. On the contrary if : $A^2 + A'^2 < 0.3333$, it will point to the opposite direction, with the same modulus. If : $B^2 + B'^2 > 0.3333$, the component vector is as given in the reference pattern. Its modulus will be : $|B^2 + B'^2 - 0.3333|$. The opposite direction will be used if : $B^2 + B'^2 < 0.3333$, etc.

Let us assume that there is a substituent in the first position. The p_π density to use in that position is a^2. This is greater than 0, which is the value to take into account for the free benzene molecule. This charge being situated at twice the unit distance from the center of the chromophore, we take into account $2a^2$. The evaluation of its involvement in the spectroscopic process leads to multiply by Aa, the partial π bond order, then : $2a^2(Aa)$, not forgeting the signs of A and a. If $2a^2(Aa) > 0$ the direction of the corresponding vector is the same as that of the vector pattern in that region of space, if: $2a^2(Aa) < 0$ it is the opposite direction which has to be used. As it is explained above this is very often the case, and, as, very often too : $X^2 + X'^2 < 0.3333$ (X standing for the corresponding coefficient in the position concerned), the contribution of a substituent adds to that of the carbon of the ring. Thus, at the first position we have to add three colinear vectors whose moduli are :

$$| A^2 + A'^2 - 0.3333 | \ ; \ 2a^2(Aa) \ ; \ 2a'^2(A'a')$$

with the proper directions. The same operation is done for the five other directions. Then the six vectors obtained are added. The modulus – the length – of the resulting vector is t_2.

Sometimes there are great differences between t_1 and t_2. As it has been explained above, t_1 overemphasizes the substituents, and the whole π electrons involved in the π bond order between the substituents and the benzene moiety ; t_2 takes into account the highest MO of the benzene moiety. The actual parameter linked to intensity should participate from the both. Thus, we can use a combination of t_1 and t_2. We have been unsuccessful in searching the quantum factor which could be involved to balance the combination, allowing the weight of the two parameters to change from one molecule to the other. So, we were led to use the same sort of combination for the whole studied molecules : $(t_1 + \alpha\, t_2)/(1 + \alpha)$. The denominator : $(1 + \alpha)$, normalizes – in a classical way – the average. We found empirically that the best parameter was :

$$t = \frac{t_2 + (0.3214/t_2)\, t_1}{1 + 0.3214/t_2}$$

although the consistency is not very sensitive to the numerical value 0.3214.

We could have used instead of t_1 a parameter similar to t_2 but extended to deeper MO. In fact, calculations are far more longer when the number of substituents increases, since the number of π MO increases, and the relative importance to give to the different MO is difficult to evaluate. t has proved to be a good parameter when corrected from a defect linked to the fact that when t_1 and t_2 are strongly different its value is too much high. So, we had to correct its value using an empirical factor : $\delta = 1/(1 + \Delta)^{1/2}$ where Δ is the relative gap between t_1 and t_2 [$\Delta = 2|t_1 - t_2|/(t_1 + t_2)$]. We shall use the corrected parameter :

$$T = t\delta.$$

We said also, here above, that a different approach was possible in taking into account a sort of effective UV cross section linked in a some naive way to the area of the molecule.[33] If that parameter has to be linked to the area of the molecule it has to be linked to the number of the substituents, using a different efficiency for substituents differing in nature. For example, $-CH_3$ and -OR should not have the same efficiency since a methyle is less π bonded (only through the $\sigma\pi$ hyperconjugative coupling) than -OR, to the benzene chromophore. Although such a parameter should increase with the number of substituents, there is no indication that it could be a linear function of the number of substituents. On the contrary, efficiency could increase quicker, or more slowly, than the number of substituents. Experiment shows that the efficiency of a given substituent decreases when there are already more substituents of the same species. The best experimental law obtained is : $S_1 = k\, n/(4.8 + 0.2\, n)$, n being the number of substituents of a given nature, and k is linked to the "efficiency" of that substituent. k has been evaluated as being five times greater for -OR than for $-CH_3$. Thus :

$$S_2 = 5\,n_O/(4.8 + 0.2\,n_O^2) + n_C/(4.8 + 0.2\,n_C^2)$$

where n_O and n_C are the number of -OR groups and methyles. A saturation seems to be reached for a given species for four substituents. The maximum number of substituents of a given species being six, we are not concerned by the behaviour of the function when n_O or n_C is greater than six ; in fact : when it is greater than five, since for six identical substituents the symmetry of the molecule imposes : T = 0.

Experiment seems to show too, that the efficiency of the methyles decreases when -OR is present in the molecule, as if -OR – let us use a naive picture – diverted the flow of photons to capture them. Thus, the parameter used was slightly corrected from S_2:

$$S = 5\,n_O/(4.8 + 0.2\,n_O^2) + n_C/(4.8 + 0.2\,n_C^{(2 + 0.5\,n_O)})$$

In fact, the correction involved is small for the molecules which have been studied here, and it could be neglected. It should have perhaps also to be reestimated if a greater number of phenols could be studied.

The two parameters, T and S, emphasizes two different approaches to the problem. Each one of them is imperfect in a specific manner. There is a sort of compensation. Our studies have shown that when one of them is too weak the other could be too strong. The parameter used has been : M = TS.

In fact we studied several other parameters differing more or less from the preceding ones. We tried to improve them in a parallel way – each one of them following its own logic – in taking into account the others, and trying to simplify the set of parameters, keeping only those which could not be replaced by a simple modification of the others. All along that work we used products rather than linear combinations. A linear combination has been used for t instead of some products of functions because we could not obtained something simpler in using products. Thus, the fact that we are led to a product involving T and S arises from the way used, and not from some final intuition.

There is another theoretical point to take into account : the vibrational component of intensity. This component has been studied by BALLESTER and RIERA for methylbenzene derivatives. [34] The vibrational contribution to the intensity of the secondary transition is quite important for these molecules, since it can be of the same order of magnitude as the pure electronic component, or in some cases higher. This is not important for -OR derivatives, since the electronic part of intensity is much higher than the vibrational part. Nevertheless, for the sake of consistency we had to study it. When studying it on methylbenzenes, in order to see how to take it into account for -OR deerivatives, we found that methylbenzenes could be easily inserted in our work without modifying the previous parameters calculated for the phenols derivatives. As the intensity ranges are very different when considering phenols and methylbenzenes, the fact that the parameters obtained for phenols were valid for methylbenzenes appeared as a confirmation of the consistency of our approach to the problem of the intensity of the secondary transition.

To determine the vibrational components for methylbenzenes and phenols or methoxybenzenes we used the approach and the values of BALLESTER and RIERA for methylbenzenes.[34] Nevertheless, these authors published a table and no analytical formula. We smoothed their values, decided to simplify the graphical law obtained, writing it in an analytical form adapted to our case :

$$v_1 = 0.018 + 0.003\ n_C$$

where n_C is, as above, the number of methyles. As the vibrational component is certainly linked to the mass of the atom which in the substituent is directly linked to the benzene ring, we decided to use the same increment (0.003) for all the substituents, since the difference in mass between C and O is not fundamental in that work, the vibrational component being of a weaker importance for the spectroscopy of phenoxy molecules. As O is more π linked to the benzene ring, it appeared that we had to introduce a parameter linked to that specificity :

$$V = 0.018 + 0.039\ K + 0.003\ (n_C + n_O)$$

when $n_O = 0$: $K = 0$; when $n_O \neq 0$: $K = 1$. Thus, since the vibrational component of the intensity adds to the intensity coming from the electronic absorption we have to write : $\varepsilon_{sm} = = f(m) = f(M + V) = f(TS + V)$, with $m = TS + V$. The result is given in Figure 3. The law can be written :

$$\varepsilon_{sm} = 4906\ m\ ;\ \text{or} :\ \varepsilon_{sm} = 4906\ (TS + V)$$

On that ground, intensity can be explained with four parameters : t_1, t_2, S, V. t_1 is mainly linked to the whole electrons involved in the π bonds with the substituents, t_2 is mainly linked to the higher energy electrons of the π_0 system. S is linked to the efficient UV cross section, to the bulk of the molecule, to the number of substituents. V, the vibrational component, is of small importance for -OR derivatives. V would not be taken into account for these molecules, the law would be simpler, and only three parameters would be needed. The curve obtained would be almost parallel to the preceding one, with the value of 1,3,5-trimethoxybenzene for ε_{sm} at $TS = 0$.

IV - AN EXAMPLE CALCULATION

The conformation used for the molecule under study (2,3-dimethylmethoxybenzene) is given in figure 4(A). The O-CH_3 bond is in the plane of the benzene moiety since RX studies have shown that it is approximately the general case for that substituent, when there is no peculiar intramolecular or intermolecular interactions in a molecule. In fact, the solid state conformation is sometimes different from the pseudo free gazeous state used in calculations, and the solvated state from which spectra are obtained. Particularly, free rotation is not taken into account and the actual molecule should be an average of the whole possible geometries and conformations. Nevertheless, this conformation seems to

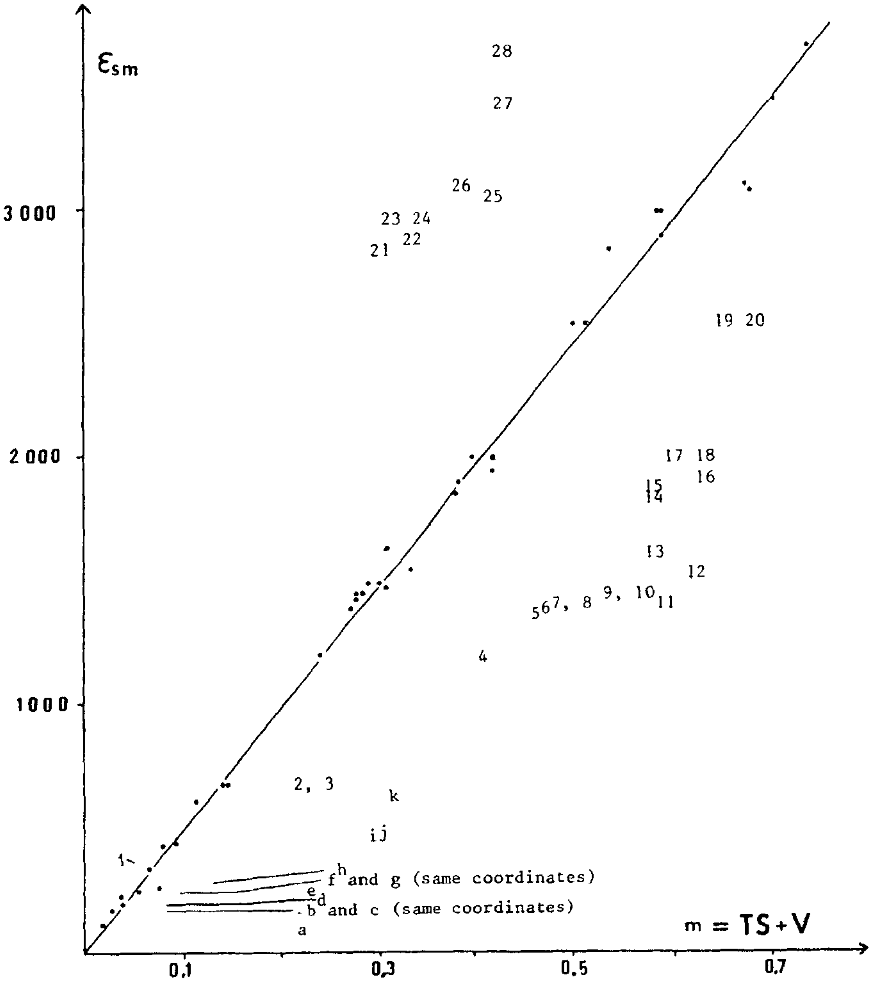

FIGURE 3 ε_{sm} versus m = TS + V.

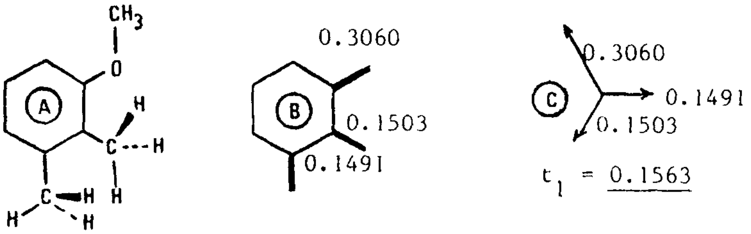

FIGURE 4. An example calculation. Calculation of t_1. A) The formula of the molecule studied. B) The π bond orders involving the bonds between the substituents and the π_0 moiety. C) The vector pattern corresponding to the π bond orders of part "B)".

be a good approach, and it allows to use a sort of reference interaction between the oxygen atom and the benzene chromophore. The same could be said for the methyles substituents with a C-H bond lying in the plane of the benzene molecule in order to obtain a reference hyperconjugative interaction.

In part B of figure 4 are given the MNDO π bond orders for the three bonds of the substituents. In C, the vector addition pattern has been drawn and the length of the resulting vector too : $t_1 = 0.1563$. One should remind that in a triangle a, b, c, with the angle θ between a and c : $b = (a^2 + c^2 - 2ac\cos\theta)^{1/2}$.

In part A of figure 5 the MNDO coefficients of MO_1 (the highest energy orbital arising from the two degenerate HOMO of the free benzene molecule) are given. Part A' is devoted to the coefficients of MO_2 (the highest orbital arising from the other degenerate HOMO in the free benzene molecule). For example, in A, the coefficient 0.36686 is that of the MO_1 p_π orbital of the oxygen atom, 0.05418 is the coefficient of the p_π orbital of the carbon of the neighbouring substituent. In B and B' the values are the square of the preceding ones. In C are the sums of the values appearing in B and B' for the benzene moiety.

In part D, the distorsions to the values observed in the benzene molecule have been written. For example, the value 0.0154 is the difference between the value obtained in C for the same position and 0.3333 : $|0.3333 - 0.3487|$. The corresponding vector is oriented in the direction of the vector component of the reference pattern (Figure 4(D)) since 0.3487 is greater than 0.3333. The value 0.1062 comes from the difference $|0.3333 - 0.2271|$. The corresponding vector is in the direction opposite to that of the reference pattern since 0.2271 is smaller than 0.3333 etc. As concerns the oxygen atom, the density to take into account is 0.1346 from the part B. The distance from this charge to the center of the chromophore is roughly twice the distance from one of the atom of the ring to the center. Furthermore, it involves the partial bond order -0.47542×0.36686, calculated from the part A. The modulus of the vector linked to the contribution of the charge 0.1346 which arises from MO_1 is

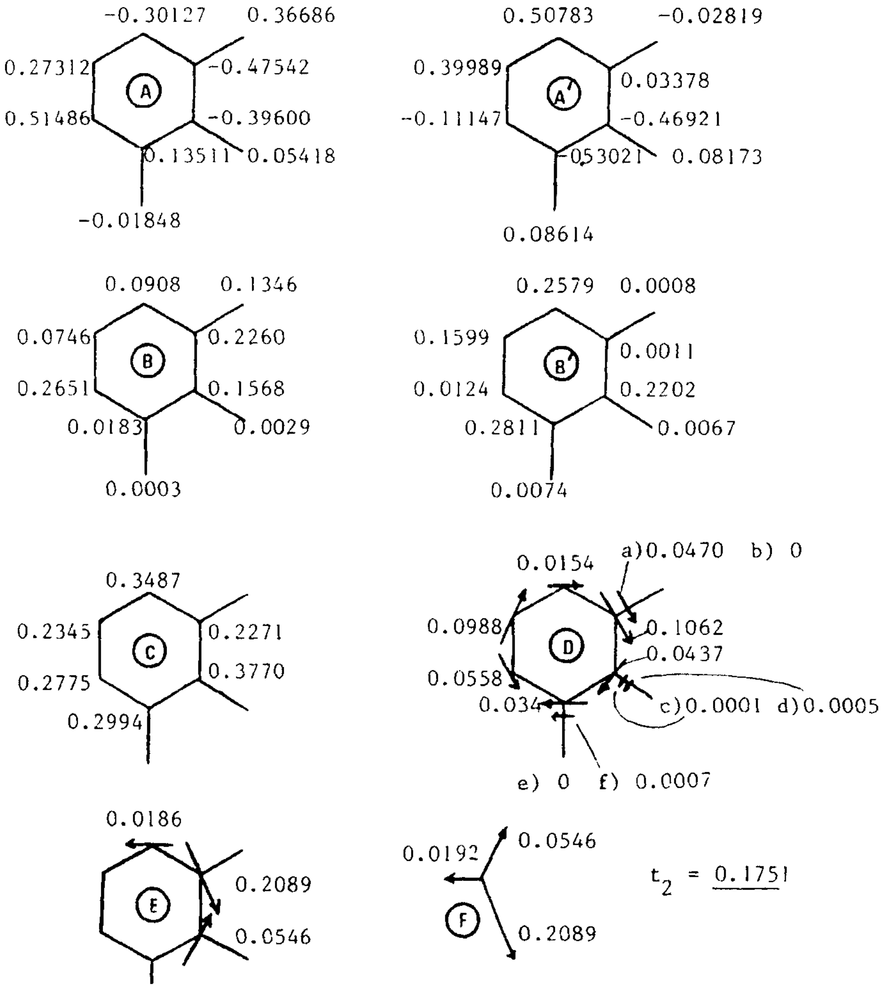

FIGURE 5. An example calculation. Calculation of t_2. A) MNDO coefficients of MO_1. A') MNDO coefficients of MO_2. B) The values of A have been squared. B') The values of A' have been squared. C) The sums, for a given position on the benzene moiety, of B and B'. D) The vector pattern obtained from the values of C. E) Partial addition of the vectors (the para positions have been added). F) Final addition.

$|2\text{x}0.1346\text{x}(-0.47542\text{x}0.36686)| = 0.0470$. This is the value which appears in D as : "a)", at the level of the oxygen atom. The orientation of the corresponding vector should be in the direction of the vector of the reference pattern, since 0.0470 is higher than 0 which is the value observed in the free benzene molecule where there is no substituent. Nevertheless, there is the negative sign coming from the partial bond order not to forget, and this leads to change the direction of the vector. Thus, the direction is opposite to that of the reference vector pattern, and it is the same direction as that observed for the contribution of the benzenic carbon to which the substituent is linked. The value 0 written after "b)", at the level of the oxygen, is the contribution of the charge 0.0008 which appears for the oxygen atom in B' (MO_2) : $2\text{x}0.0008\text{x}(-0.02819\text{x}0.03378) = -2\text{x}10^{-6}$.

In the part E, all the vectors have been reduced to three component vectors. In part F the vector addition is shown. The length of the resulting vector is : $t_2 = 0.1751$.

Then, t is calculated using the values : $t_1 = 0.1563$, $t_2 = 0.1751$:

$$t = (0.1751 + 0.3214\text{x}0.1563/0.1751)/(1 + 0.3214/0.1751) = 0.1629.$$

$$\text{Then : } \Delta = 2\,|\,0.1751 - 0.1563\,|\,/(0.1751 + 0.1563) = 0.1135.$$

$$\delta = 1/(1 + 0.1135)^{1/2} = 0.9477\ ;\ T = t\,\delta = 0.1544$$

$$S = 5\text{x}1/(4.8 + 0.2\text{x}1^2) + 2/(4.8 + 0.2\text{x}2^{(2+0.5\text{x}1)}) \approx 1.337\ ;\ M = TS = 0.2064\ ;$$

$$V = 0.018 + 0.039 + 0.003\text{x}3 = 0.066\ ;\ TS + V = 0.2724.\ (\varepsilon_{sm})_{calculated} = 1336$$

One will notice that t_1 and t_2 would have the same value if the approaches leading to them were perfectly equivalent, which is not the case, since the first approach emphasizes the substituents, and the second one the highest MO of the π_6 system. Differences will be all the more greater that the absorption process will be more located on the π_6 system, or more on the substituents.

Comment

The two resulting vectors t_1 and t_2 display, roughly, opposite directions, although they arise from two different approaches to the same phenomenon. This is only a matter of internal reference. When giving the definition of t_2 we said that, in a given position, the component vector is in the same direction as the corresponding vector of the vector pattern, when local density is higher than 0.3333 (which is the benzene value). We used such a convention not to confuse the reader. Actually, we had already used for the calculation of t_1 the direction of the vector pattern when the BO_π involved for a substituent is *higher* than the corresponding value for the benzene molecule. We had to use the same *apparent* convention for t_2. But, as in the benzene molecule there is no substituent, the reference value to which the BO_π of the substituents have to be compared will be 0. BO_π is always higher than 0, watever the nature of the substituent is : a π donating or a π withdrawing substituent. The correponding vectors are always in the direction given by the reference vector pattern. This is the reason why, for the time being, we do not study molecules substituted by π donating and π withdrawing substituents. We should have to use different convention for them depending on their nature. Another point is noteworthy. When calculating t_2 if we find a local density lower than 0.3333 at a site of substitution this does not imply that the corresponding vector component has to be in the direction opposed to the direction given by the vector pattern since, in fact, at a site of substitution density is often decreased for a π donating substituent. A substituent modifies the whole densities of the π system, and it is its whole contribution which should say in what direction should point any contributing vector. In practice it is difficult to find since we are concerned by MO_1 and MO_2 alone. Thus, to fit with the direction of t_1 we should have had taken the opposite convention, but this would have been troublesome if presented in part III.

V - RESULTS

Such a good fit between experiment and theory, for such an extended set of such different molecules (methylmethoxybenzenes and methylbenzenes), has never been obtained. The simple vector model predicts the same intensity for phenol, o-dihydroxybenzene, m-dihydroxybenzene, when they are quite different. The method used here predict the correct values. p-dihydroxybenzene is predicted by the simple vector model to be four times higher than phenol. Its intensity should be 5800, when experiment leads to 3100. Our calculations give 3300. Furthermore, 1,2,3-trimethoxybenzene is predicted by the simple vector model to have the same intensity as 1,3,5-trimethoxybenzene. Experiment leads in fact to 680 and 330, values which are correctly predicted by our present method. The intensities are quite different for these two molecules because in 1,2,3-trimethoxybenzene there is a distorsion of charges from additivity owing to the great π donating ability of the methoxy group, and to the fact that the methoxy in position 2 is not equivalent to the two others. Furthermore, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene are also correctly predicted to have the same intensity, since $-CH_3$ being less π perturbating than -OR the above distorsion is not observed . It has been claimed that 1,2,4,5-tetramethylbenzene has an anomalous high intensity.[34] In fact, our calculations fit with experiment and there is no need to think that such a molecule could display an anomalous behaviour.

The worst fits are obtained for the pentamethylbenzene molecule, p-dihydroxybenzene, p-dimethoxybenzene, o-methylhydroxybenzene. For p-dihydroxybenzene and pentamethylbenzene the discrepancy arises certainly from the fact that t_1 is too much taken into account in t for these two molecules.

The further step in our reseach will be to insert $-NH_2$ in the method, and to adapt that latter to the strain induced by rings fused to the benzene moiety. Actually, many natural products display such fused rings with oxygen or nitrogen bonded to the benzene moiety.

CALCULATIONS AND DATA

O stands for -OCH_3, o for -OH, c for -CH_3; C_i for another alkyl substituent identified at the end. Medium for phenols or anisole derivatives : methanol.

Positions on the benzene ring :

1	2	3	4	5	6		t_1	t_2	S	V	m	ε_{sm}
o		o		o		(1)	0	0		0.066	0.066	330
O	O	O				(2)	0.017	0.138	2.273	0.066	0.141	680
o	o	o				(3)	0.018	0.141	2.273	0.066	0.145	680
o	c	c	c	c	c	(4)	0.169	0.109	1.313	0.075	0.244	1200
O	c	c				(5)	0.156	0.175	1.337	0.066	0.272	1380
o		c		c		(6)	0.158	0.163	1.337	0.066	0.277	1430
o	c	c				(7)	0.163	0.162	1.337	0.066	0.280	1450
o						(8)	0.300	0.207	1	0.060	0.286	1450
O						(9)	0.302	0.215	1	0.060	0.291	1500
o		c				(10)	0.266	0.178	1.200	0.063	0.302	1500
O		c				(11)	0.260	0.191	1.200	0.063	0.309	1480
o		o		c		(12)	0.169	0.121	1.986	0.066	0.334	1550
o	c					(13)	0.273	0.188	1.200	0.063	0.311	1630
o		c	c			(14)	0.398	0.167	1.337	0.066	0.383	1850
o			c			(15)	0.461	0.196	1.200	0.063	0.385	1900
o	c		c			(16)	0.412	0.224	1.337	0.066	0.420	1950
O		O				(17)	0.312	0.118	1.786	0.063	0.400	2000
o		o				(18)	0.321	0.140	1.786	0.063	0.418	2000
o	o					(19)	0.302	0.237	1.786	0.063	0.502	2550
O	O					(20)	0.298	0.246	1.786	0.063	0.514	2550
o		o	C_1			(21)	0.419	0.149	1.986	0.066	0.539	2850
O	O		C_2			(22)	0.380	0.236	1.986	0.066	0.589	2900
o	o		c			(23)	0.397	0.226	1.986	0.066	0.586	3000
o	O		C_2			(24)	0.385	0.233	1.986	0.066	0.588	3000
O			O			(25)	0.576	0.298	1.786	0.063	0.680	3080
o			o			(26)	0.589	0.287	1.786	0.063	0.676	3100
O		C_3	O			(27)	0.521	0.276	1.986	0.066	0.704	3450
o	o		o			(28)	0.500	0.239	2.273	0.066	0.742	3650
benzene						(a)	0	0	0	0.018	0.018	110
c		c		c		(b)	0	0	0.455	0.027	0.027	170
c	c	c				(c)	0	0	0.455	0.027	0.027	170
c						(d)	0.135	0.0236	0.200	0.021	0.037	192
c	c	c	c	c	c	(e)	0	0		0.036	0.036	225
c	c					(f)	0.139	0.0296	0.357	0.024	0.055	234
c		c				(g)	0.148	0.0219	0.357	0.024	0.056	234
c	c	c	c	c		(h)	0.146	0.0167	0.510	0.033	0.077	260
c			c			(i)	0.270	0.0440	0.357	0.024	0.080	425
c		c	c			(j)	0.256	0.0337	0.455	0.027	0.094	440
c	c		c	c		(k)	0.295	0.0420	0.500	0.030	0.114	610

C_1 is n-hexyl for the intensity, and -CH_3 for calculation ; C_2 is -CH_2-$CH=CH_2$ with the C_ϕ-CH_2 bond in a plane orthogonal to the plane of the molecule ; C_3 : is -CH_3 for the calculation and an hydantoin substituent for intensity since in the literature the molecule with -CH_3 is given with a completely wrong value (ref.:[28]).

VI - INTENSITIES AND CALCULATIONS

For phenols and methoxybenzene derivatives we have done the calculation of ε_{sm} using the spectra of literature (for example : $^{35-36}$) (medium : methanol). One has to pay attention to the fact that many spectra found in the handbooks are sometimes completely wrong as concerns intensity, although they are published by authorities. Before using a spectrum it has to be confirmed from several sources. The values used in that work are those which have been obtained from these controls. We think that the worst values are faulty by less than ± 5%.

The ε_{sm} of the methylbenzenes are those which have been measured by BALLESTER and RIERA ^{34} on the API data ^{35}.

Our MNDO calculations have been done from La Réunion Island (France, Indian Ocean) on the Cyber 960 computer of the "Centre Interuniversitaire de l'Information" of Lille (France, Europe), *via* the TRANSPAC world satellite network.

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