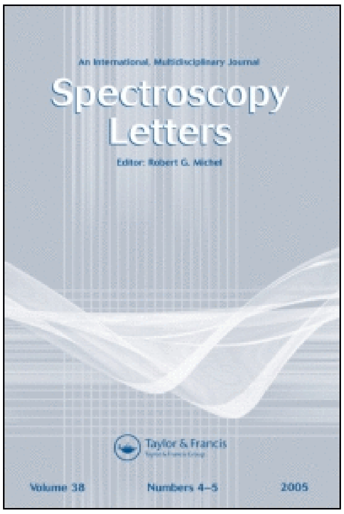

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Vardin, Josie and Vidal, Bernard(1990) 'UV Spectra of Some Derivatives of 1-3 Benzodioxole with Weakly Perturbating Substituents (-CH_2X). Study of a Constant Component of Intensity', Spectroscopy Letters, 23: 5, 611 — 626

To link to this Article: DOI: 10.1080/00387019008054443

URL: http://dx.doi.org/10.1080/00387019008054443

SPECTROSCOPY LETTERS, 23(5), 611-626 (1990)

UV SPECTRA OF SOME DERIVATIVES OF 1-3 BENZODIOXOLE WITH WEAKLY PERTURBATING SUBSTITUENTS (-CH_2X). STUDY OF A CONSTANT COMPONENT OF INTENSITY.

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INTRODUCTION

In a preceding work(1) we have studied the UV-Visible spectrum of pterocarpin, a natural product which is known, with many of its derivatives, for its antifungal properties.(2-6) The molecule of pterocarpin contains the benzodioxole moiety (figure I) whose presence could be a factor favourable to such properties. Furthermore, some of the benzodioxole derivatives are known as popular drug of abuse (ecstasy). (7-10) Among our studies on the benzodioxole derivatives substituted in para to one of the oxygen atoms, we present in that paper the results of our UV spectroscopic investigations. This work concerns molecules with substituents weakly interacting with the π system (i.e. substituents whose type is -CH_2X), since the spectra of these molecules display a basic phenomenon which has never been observed.

I- EFFECTS OF WEAKLY INTERACTING AUXOCHROMES (-CH_2X) ON THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE

The $^1B_{2u} \leftarrow ^1A_{1g}$ transition (secondary transition)(11-16) of the benzene chromophore is electronically forbidden because of the D_{6h} symmetry of the molecule. A progression called A appears with a very low intensity [$\varepsilon_{max}=220$ (medium : cyclohexane)] towards 250-260 nm. When a substituent is linked to the chromophore, its donating or withdrawing effect distort the

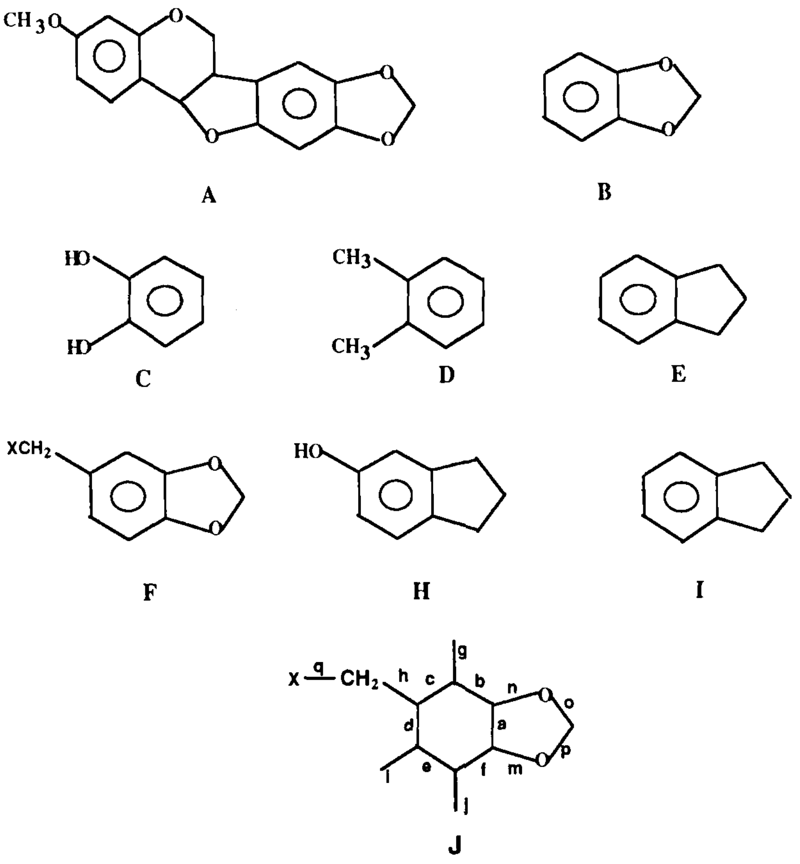


Figure I :

A) Pterocarpin; B) Benzodioxole; C) Catechol; D) Xylene; E) Indan

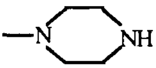
F) X = NH_2 Piperonylamine, X = OH Piperonyl alcohol;

X = $OCOCH(CH_3)_2$ Piperonylisobutyrate, X = N<>NH*1-piperonylpiperazine

X = $CH=CH_2$ Safrole, X = CN 3,4-(methylenedioxy)-phenylacetonitrile

G) Indan; H) Indanol-5; I) Indanol-4; J) Numbering and labelling of the bond lengths of the benzodioxole derivatives.

*N<>NH =



symmetry towards C_{2v}, a symmetry for which the transition is allowed. The transition becomes all the more allowed as the distortion towards C_{2v} is increased. A progression B, whose intensity is often evaluated by the values ε_{00} of its 00 band, characteristic of the perturbation, is superposed upon the progression A. The 00 band is very often clearly visible because of its position towards the long wavelength side of the transition.

When the substituent on the benzene chromophore is $-CH_2X$ (in the molecules ϕ-CH_2X), with X being a σ electron withdrawing group, the hyperconjugative π donating ability of the methylene (because of the σ, π coupling between π_ϕ and the σ pseudo π orbitals of $-CH_2-$) is all the more decreased as the σ electron withdrawing ability of X is increased. The D_{6h} symmetry tends to be restored, the perturbation decreases and ε_{00} decreases too. When the σ electron attracting power of X is high enough the π donating ability of $-CH_2-$ is cancelled, the D_{6h} symmetry of the π system is completely restored; the transition is forbidden and the 00 band disappears. Thus, the secondary transition is very near to what is observed for the benzene molecule itself (for example: ϕ-CH_2CO_2H).(13) For very σ attracting groups, not only the π donating effect of the methylene is cancelled, but also a π withdrawing effect through the σ, π hyperconjugative coupling of the $-CH_2-$, can be observed. The intensity of the progression B and that of its 00 band increases because once more the symmetry is distorted towards C_{2v}. Then, the intensity will increase all the more as the attracting ability of X increases. When ploting ε_{00} against a parameter Σ which takes into account the σ electron withdrawing character of X, a V-shaped curve is observed. This parameter has been defined by the spectroscopic efficiency of the substituent, compared to what happens in series whose type is ϕ-$(CH_2)_nX$.(11)(13)(17) In the present paper we have gathered for the first time all the data scattered in the literature (table I) ploting ε_{00} of the ϕ–CH_2X molecules against the Taft σ_I values of X (figure II). This latter parameter is easy to evaluate in a given series. The formula $\sigma_I(X)=0{,}161\sigma^*(X)$ (18) allows to turn the $\sigma^*(X)$ obtained in the literature into $\sigma_I(X)$. Furthermore, it is known that $\sigma_I(X)=0{,}45\sigma^*(CH_2X)$ (19) whence $\sigma_I(CH_2X)=0{,}358\sigma_I(X)$. Such a formula allows to generate the σ_I values of substituents $-(CH_2)_nX$ from the values of substituents $-(CH_2)_{n-1}X$. As shown in figure II the curve $\varepsilon_{00}=f(\sigma_I{}^X)$ is a parabola. The same intensity for ε_{00} is observed for two different σ_I, when the representative points are symmetric on the branches of the curve (mirror effect).(16)

The point corresponding to X = $COCH_3$ has been obtained from the spectrum of ϕ–CH_2COCH_3.(20)(21) In this molecule the intensity of the $n\rightarrow\pi^*$ transition of the carbonyl chromophore, is greatly increased by borrowing a part of its intensity from a charge transfer transition.(21) The $n\rightarrow\pi^*$ transition overlaps the secondary transition of the benzene chromophore. This latter transition should have to be corrected from that overlap. Fortunately, it is clearly visible that the 00 band does not appear.(21) Only the underlying continuum of the system A is observed, superimposed to the $n\rightarrow\pi^*$ transition. The intensity of the system A, in the place where the 00 band generally appears is $\varepsilon = 65$ approximately. This is the value

Table I

Values of the σ_I of X and of the intensity ε_{00} of the band 00 of Φ-CH_2X

X	ε_{00}	σ_I^X
CH_3	225[29]	-0,05[30]
$CH{=}CH_2$	161	0,09[30]
CH_2NH_2	145	0,08[30]
OH	86[29]	0,25[30]
$COCH_3$	72[b]	0,29[30]
CO_2H	72[29]	0,39[30]
Cl	126[29]	0,47[30]
$\overset{+}{N}H_3$	135[29]	0,6[30]
$H\overset{+}{N}Me_2$	235[29]	0,7[30]
NH_2	97[29]	0,12[30]
NMe_2	80[29]	0,05[31]
$\overset{+}{N}Me_3$	350[c]	0,86[31]
CH_2NH_2	145[30]	0,04[a]
$(CH_2)_2NH_2$	178[29]	0,01[a]
$(CH_2)_3NH_2$	186[29]	0,004[a]
$CH_2\overset{+}{N}H_3$	86[32]	0,215[a]
$(CH_2)_2\overset{+}{N}H_3$	135[29]	0,077[a]
$(CH_2)_3\overset{+}{N}H_3$	163	0,028[a]
CH_2CO_2H	125[33]	0,14[a]
$(CH_2)_2CO_2H$	167[33]	0,05[a]
CO_2^-	122	0,06[a]
$CH_2CO_2^-$	158	0,021[a]
$(CH_2)_2CO_2^-$	183	0,008[a]
CN	137	0,58[30]
NHMe	80	0,09

a) Calculated values; b) Reference 20; c) Personal communication from Dr. A. Darry-Henaut

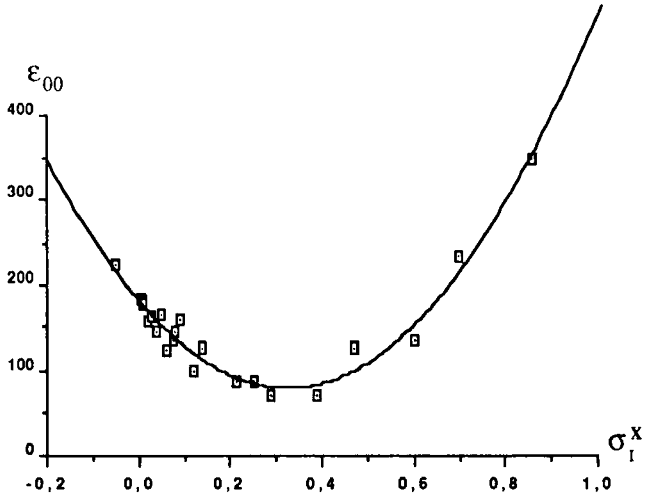


Figure II:

ε_{00} is the intensity of the band 00 of ϕ-CH_2X. σ_I^X is the Taft's value of X (see table I).

which has to be used for ε_{00} since none of the values of ε_{00} has been corrected of the underlying system A.

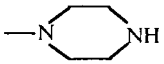
Anomalous behaviours have been observed for three molecules (which have not been used in the calculation of the polynomial regression in figure II) : ϕ-CH_2CN, ϕ-CH_2NHCH_3, ϕ-$CH_2N(CH_3)_2$. We cannot invoke experimental errors, neither as concerns the measures (the spectra are impurity free), nor as concerns the σ_I which are well known in the literature. It should be kept in mind that σ_I is not the only factor to take into account to explain the influence of the group X on the chromophore. Field effects through space could be invoked, with or without specific conformations favouring them. We observe that the non bonding electrons of the tertiary or secondary amines are very diffuse in space, owing to their basic characters. Furthermore, CN also is electron rich (with weakly bound electrons). The intensities of these molecules do not agree with the σ_I values of the corresponding X. It is possible to calculate with the V-shaped curve a theoretical value for ε_{00} of ϕ-CH_2CN using the σ_I value of CN. Such an intensity (ε_{00}= 137) will be used in later calculations for molecules where there is no anomalous behaviour, when we shall need a purely spectroscopic value, alternative to the use of σ_I, a non spectroscopic parameter. We have calculated also that the σ_I

Table II

X	σ_I^X [a]	ε_{max} of Bzd-CH_2X [b]	$\lvert\mu\rvert$ [c]	ε_{max} calculated [d]	ε_{max} calculated [e]	ε_{00} [h]
CN	0,58	3790	1,3	3870	2705	137[g]
$\overset{+}{N}H_3$	0,6	3810	8,66	3775	2839	135
OH	0,25	3714	5,75	3733	3714	86
$CH{=}CH_2$	0,09	3850	7	3749	3681	161
NH_2	0,12	3750	6,78	3746	3667	97
N<>NH*		3900	6,71	3730	2917	73[29]
$\overset{+}{N}H{<>}\overset{+}{N}H_2$	(0,74)[g]	4100	12,12	3890	2720	256[29]
$OCOCH(CH_3)_2$		3880	6,56[29]	3738	2924	108[29]
$COCH_3$	0,29	3660[f]	8,92	3700	3244	72

a) Reference table I;
b) Intensities of the secondary transition (solvent: methanol)
c) Spectroscopic moments of -CH_2X in ϕ-CH_2X; d) Not using the Sklar's rule
e) Using the Sklar's rule; f) Reference 27b; g) Extrapolated value from the curve
ε_{00}= f(σ_I^X); h) Reference table I

* N<>NH =



value for -$NH^+{<>}NH_2^+$ (see table II, caption) which cannot be found in the literature is σ_I=0,74. We can have confidence in such a value, since generally all the ammoniums studied display a good correlation, as far as the V-shaped curve is concerned. We do not try to calculate the σ_I value for ϕ-CH_2X when X is an unprotonated amine, since some of these amines, whose σ_I are known, do not fit with the curve.

II - THE BENZODIOXOLE CHROMOPHORE.

In preceding papers(1)(22) we have shown that the secondary transition of the benzene chromophore of the benzodioxole molecule is very intense. In order to be able to compare

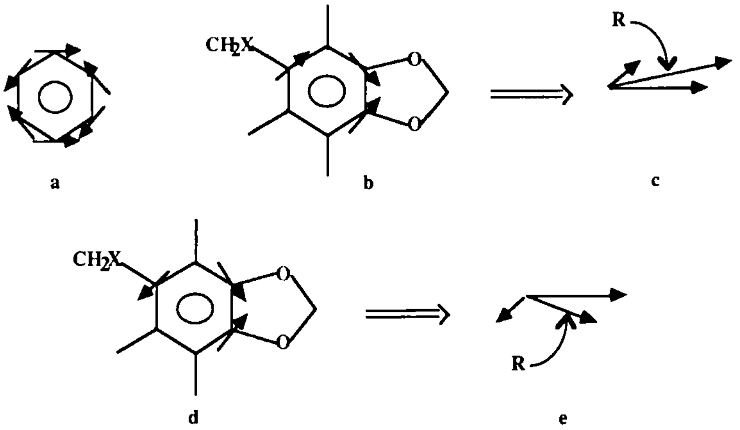


Figure III :

a) Transition moment vectors depending on the substitution scheme on a benzene nucleus
b) Benzodioxole derivatives with substituents in positions 1, 3, 4 with CH_2Xbeing a π donating subsituent. The Sklar-Platt's rule is supposed valid.
c) R: Resultant of the vector addition appearing in b (qualitative scheme).
d) Benzodioxole derivatives with substituents in positions 1, 3, 4 with CH_2X being a π attracting. subsituent. The Sklar-Platt's rule is supposed valid.
e) R: Resultant of the vector addition appearing in d (qualitative scheme).

transitions with different vibrationnal fine structures, the intensity of the secondary transition can be measured by ε_{sm}, the maximum of the smoothed curve (as defined by Ballester and Riera(23)).The value obtained is $\varepsilon_{sm} = 3330$ (medium : methanol) (here: $\varepsilon_{sm} = \varepsilon_{max}$) when ε_{sm} is only 2650 (medium : methanol) for catechol (figure I, C). Such a difference is caused by the cyclization of the substituents. The five membered fused ring, because of strain, lengthens the bridgehead bond, distorting the geometry of the chromophore towards C_{2v}. The selection rules of the D_{6h} group are less valid and the transition is less forbidden. Nevertheless, such an increase of the intensity of the secondary transition is weaker than what is observed when considering xylene (figure I, D) ($\varepsilon_{sm} = 235$; medium: cyclohexane) and indan (figure I, E) ($\varepsilon_{sm}= 1040$; cyclohexane). This phenomenon has been previously discussed.(1) It seems that the conjugation of the oxygen atoms cancels partly the effects of strain, on intensity. We have observed(1) that, although they are valid mainly for small perturbations, the Sklar-Platt's(24)(25) vector addition rules concerning the intensities of polysubstituted benzene chromophore, were still valid.

Thus, we should expect, for the present derivatives of benzodioxole (figure I, F), a decrease of the intensity of the secondary transition, when the withdrawing effect of X increases (nevertheless still keeping -CH_2X as a π donating group). Actually, since there are π donating substituents in position : 1, 3, 4 the vector addition of the individual transition moments according to the Sklar-Platt's rules(24)(25), should lead, as shown in figure III, to a resultant transition moment greater than what is observed for the benzodioxole molecule itself. The modulus of the transition moment vector for -CH_2X, decreases (the π donating effect of -CH_2X decreases), with the increase of the σ electron withdrawing character of X. Thus, for weak σ withdrawing X intensity should begin to decrease when the σ withdrawing character of X increases. Intensities should remain higher than the intensity of benzodioxole when -CH_2X remains a π donating group. The σ electron withdrawing character of X can increase to the point where it cancels the π donating effect of the -CH_2- group, and induces by inverse hyperconjugation a π-attracting effect on π_{ϕ}. The vector addition rule should lead to what is drawn in figure III, D. The resulting transition moment should be smaller than what is observed in benzodioxole. The contrary is observed. All the coumpounds which have been studied display an intensity higher than $\varepsilon = 3330$ for the secondary transition (table II) . The case of Bzd-$CH_2NH_3^+$ and Bzd-CH_2NH^+<>NH_2^+ (Bzd stands for benzodioxole) is particularly striking since -$CH_2NH_3^+$ and -CH_2NH^+<>NH_2^+ are strong π electron attracting substituents. In the frame of the Sklar-Platt's rules they should display a much lower intensity than benzodioxole, even if the Sklar-Platt's rules do not hold quantitatively.

As concerns Bzd-$CH_2NH_3^+$, not only intensity is higher than that observed for benzodioxole itself, but also one observes that the protonation of Bzd-CH_2NH_2 - to give the ammonium - leads to an increase of intensity (ε_{max}: 3750→3810). The same thing is observed when protonating Bzd-CH_2N<>NH (ε_{max}: 3900→4100) contrary to what was expected. Everything seems to behave as if the intensity was still a V-shaped function of the σ_I character of X, as it has been established in the ϕ-CH_2X series (figure II). In that assumption Bzd-$CH_2NH_3^+$ and Bzd-CH_2NH_2 should be placed on positions almost symmetric on the two branches of the curve. The same should happen for Bzd-CH_2N<>NH and Bzd-CH_2NH^+<>NH_2^+. However, we cannot use Bzd-CH_2N<>NH to draw a curve, nor Bzd-CH_2OCOR since we do not know the σ_I value of OCOR and that of -N<>NH. The curve of figure IV has been drawn using the other points. We notice that the representative point of -CH_2CN is perfectly correlated with the others points of the curve contrary to what has been observed in the series ϕ-CH_2X (figure II). That point is on the right branch of the curve; i.e. on the side where the -CH_2X groups are π electron withdrawing.

The behaviour of Bzd-CH_2CN is quite normal. The phenomenon observed when ϕ-CH_2CN was involved (the representative point of this latter species do not correlate with the other points in figure II) no more exists in the Benzodioxole derivatives.

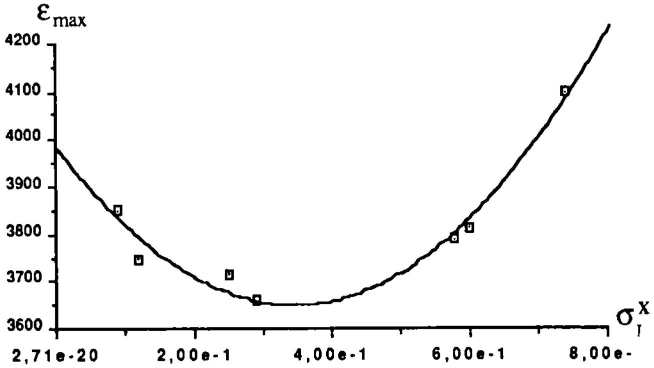


Figure IV :

ε_{max} is the intensity of the secondary transition of Bzd-CH_2X and $\sigma_I X$, the Taft's value.

The Sklar-Platt's rule is no more valid since the intensity varies as a V-shaped function of σ_I. It is always higher than the intensity of the parent compound of the series. Such a phenomenon can be compared to what has been observed when studying the anilinium ions.(26) Because of the frame of the study restricted to these ions, we had not been able to produce a definite explanation. Now, such a phenomenon is observed with molecules whose type is very different from the aniliniums ions. That fact shows that we are facing a fundamental behaviour of benzene derivatives. Such a behaviour has not been previously pointed out and deserves to be studied.

As far as the aniliniums ions are concerned, V-shaped curves are observed when considering ε_{00} ploted against the σ_I value of the substituent Y which is linked to the nitrogen atom (type: ϕ-NH_2^+Y).(21) The values observed for the minima of the curves are different for each series (ϕ-NH^+CH_3Y; ϕ-NH_2^+Y). Furthermore, these minima are different from the intensity of ϕ–NH_3^+ for which the interaction between -NH_3^+ and ϕ leads only to a very weak 00 band. Actually, according to the general scheme of the perturbation of the benzene chromophore, which has been explained in the beginning of that paper (part I), one should observe the quenching of the 00 band when the effects of the substituent Y cancel those of NH_2^+ or -NH^+CH_3. On the contrary the points corresponding to ϕ–$NH_2^+CH_3$ and ϕ–$NH^+(CH_3)_2$ - the parent compounds of the two series - lie at the bottom of the V shaped curves. The differences between the hyperconjugative σ, π coupling schemes in these series have been invoked. Inside a given series, the σ, π coupling should have a given efficiency.

Thus, this coupling should induce a perturbation which should be almost constant in the series, and should not be cancelled by Y.

When going back to the spectroscopy of benzene itself, one reminds that although the symmetry is D_{6h}, the progression A is observed because of the coupling of electronic motion and vibrations. When there are substituents on the benzene chromophore, the intensity of the progression A depends on the number of these subsituents.(23) The value of this intensity is a constant to add to the intensity calculated from the vector addition of the transition moments of the substituents. Thus, although the Sklar-Platt's rules are obeyed there is a constant value of the intensity to be taken into account. This intensity in ϕ-CH_2X remains when the effects of -CH_2- are cancelled by those of X. For example, in ϕ-CH_2CO_2H the 00 band and the whole B system are almost completely cancelled, and the system A, with its remaining intensity, still exists.(13) It could be the same every time that the chromophore and some substituent, inducing a definite perturbation inside the chromophore, constitute a moiety with its own identity strongly marked, and irreducible to the simple benzene chromophore. The perturbations induced by a substituent are not limited to the π attracting or π donating effects. These effects when weak enough can be taken into account to calculate the transition moments by means of a vector addition as it is done with the Sklar-Platt's rules. The distorsion of the aromatic moiety has an influence too on the intensity, since it modifies the symmetry of the π system. The distorsion can be caused by a steric strain imposed by the substituents (such as in the benzodioxole derivatives, where the five membered fused ring lentghens the bridgehead bond, and impose alternating bond lengths within the benzene moiety). In fact, it is not necessary that the benzene ring be submitted to a steric, mechanical, strain to be distorted. The distorsion can be caused also, by the electronic effects induced by the substituents in the σ frame or in the π cloud. These effects can change σ and/or π densities. Furthermore, when there is no geometric distorsion, changes in σ densities induced by the subtituents can modify the core potentials in which the π electrons are moving. It is difficult to take these changes into account by the Sklar-Platt's vector addition, because the σ inductive effects do not obey to the same scheme as the π effects, and because the Sklar's rules take mainly into account the π electrons behaviour. Some of these above effects could induce a constant perturbation within the ϕ moiety in a given series. The perturbation could be unaffected by the simple π electron withdrawing or π electron donating effects of a substituent. For example, as concerns the benzodioxole derivatives studied in that work, the π donating effects of the oxygens of the five membered fused ring are only a part of the effects induced by these oxygens. The σ withdrawing character of these oxygens can modify the core potentials near to their sites of substitution. Such a perturbation in the σ frame (and the subsequent σ, π interaction) will not be cancelled by the influence of X which is far from these sites, although X can modify the whole π cloud through the hyperconjugative coupling.

There is also the steric strain imposed on the benzene nucleus by the five membered fused ring. We have shown that the Mills-Nixon structural effects could be extended to the

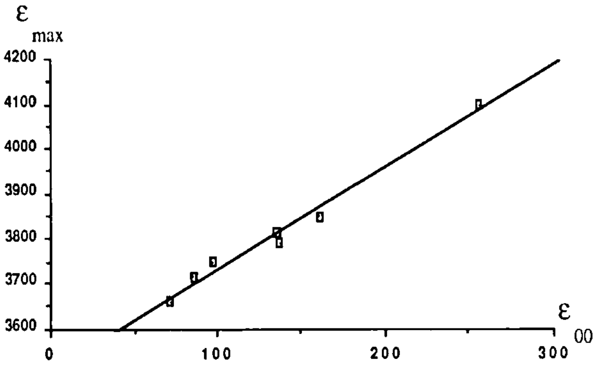


Figure V : ε_{00} is the intensity of the 00 band of ϕ-CH_2X

benzodioxole molecule.(1)(22) There is an alternation of the bond lengths and of the π bond orders of the ϕ moiety. In other words : there is a tendency, weak but definite, towards a kekulé like structure. Such an alternation - which is a distorsion from the D_{6h} symmetry - is very stable. Actually, we have found that it is also present in several other molecules (indanone-1, phtalide and benzofuran) with five membered fused rings although there is conjugation in these molecules. One can assume that such a stable distorsion, induced by the steric strain of the five membered fused ring, cannot be cancelled by the weak π donating or π withdrawing effects of -CH_2X. These latter effects are different in nature. Thus, owing to the complexity of the phenomena superimposed on the pure π donating or π withdrawing effects of -CH_2X, the vector addition rule cannot be used.

σ_I is not a spectroscopic parameter. Furthermore, some of the σ_I values are missing. Thus, we have used ε_{00} of the molecules ϕ-CH_2X, to correlate the ε_{max} values of the benzodioxole derivatives. Actually, ε_{00} is a measure of the efficiency of -CH_2X when it distorts the symmetry of the benzene chromophore and modifies intensities. In figure V we have ploted these ε_{max} values of the benzodioxole derivatives against the ε_{00} values of the corresponding ϕ-CH_2X molecules. Two points excepted, the correlation is quite good. The ε_{00} used for -CH_2CN is 137, a value obtained above from the curve $\varepsilon_{00}=f(\sigma_I^X)$. Such a correlation leads to the law :

$$\varepsilon_{max}=3450 + k'\varepsilon_{00};$$

$$k'=2,79$$

That result confirms the fact that the Sklar-Platt's rule - as it has already been shown by the V-shaped variation of ε_{max} versus σ_I - is not valid in the present case. Intensity obeys to a simpler law, grounded on the addition of an intensity arising from the presence of the substituent $-CH_2X$, and a constant intensity from the benzodioxole moiety. The value of the constant intensity (3450)is slightly higher than that of benzodioxole itself ($\varepsilon_{max} = 3330$). Actually, that latter molecule does not belong to the series studied here since it bears no substituent. Changing an hydrogen atom by a $-CH_2-$ group should modify at least repulsive interactions between bonds and should be responsible for a great part of the difference observed between 3330 and 3450.

We can also study the origin of intensities with another parameter such as ε_{sm} (the maximum of the smoothed curve as it has been defined by Ballester and Riera(23)) using with ε_{sm} the individual transition moments of the substituents. We consider too that the intensities arising from the perturbations add, and not the moment vectors. That is to say: the perturbations are completely independant. Each of them acting by itself alone on the chromophore, inducing a given component of the intensity.

The spectroscopic moments are given in table II. There is a constant component of the intensity called ε_v to take into account, which depends on the number of substituents linked to ϕ (170 for two aliphatic substituents, 175 for three(23)). Nevertheless, as the number of substituents is constant all along the series studied in that paper, and as the substituents are not aliphatic as in Ballester and Riera's work, an emperical value of 120 has been added to all calculations. The results are in table IV. In that table we give also the results of the calculations, assuming that the Sklar-Platt's rules hold. The agreement with experiment is far better when considering the results obtained from separate perturbations. Actually, when the five membered fused ring is less perturbative than a dioxolo ring, such as in indan, the Sklar's rules hold at least qualitatively. For example experiment gives for indanol-5 (figure I) ε_{sm}=2950 when it is 750 for indanol-4.(27a) The calculation using vector addition of transition moments lead to: 3450 and 500, illustrating the specificity of the perturbations in the positions 4 and 5. If we should assume an additivity of intensities we should obtain 2200 for both of them which is a very bad assumption. Thus, we do not want to say that the Sklar's rule do not hold for every benzodioxole derivative, but that in our present work, with small perturbations coming from $-CH_2X$ in position 4, the benzodioxole moiety retains a great part of its identity all along the series acting as a given chromophore. The underneath part will support such an assumption. Nevertheless, for several other substitutions, in different sites the vector rule could be still valid, such it has been shown for the spectrum of pterocarpin.(1)

III - MNDO CALCULATIONS ON SOME DERIVATIVES OF BENZODIOXOLE.

As concerns the geometry of the benzodioxole derivatives, the part of the molecule involved in the five membered fused ring is only weakly changed from what is calculated for

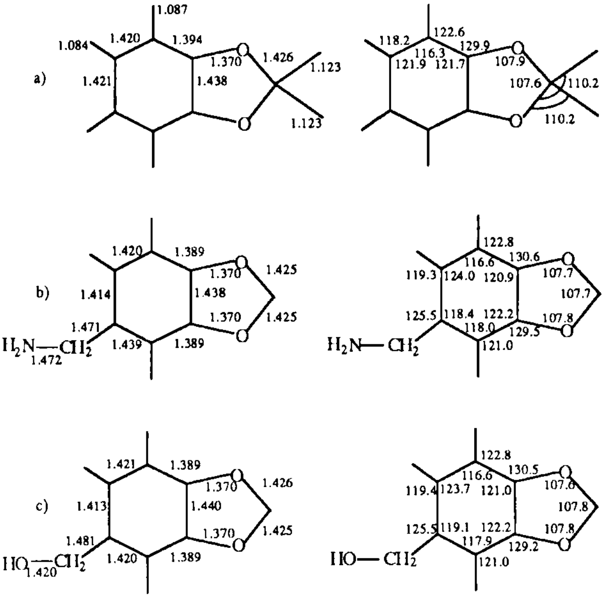


Figure VI :
a)Benzodioxole geometry; b) Piperonylamine geometry
c) Piperonyl alcohol geometry

benzodioxole. In figure VI we give the geometries calculated in that work for piperonyl alcohol, piperonylamine and benzodioxole. The geometries have been also calculated for X=-CN, -CH=CH_2,-NH_3^+. We do not give these latter geometries since there is no main difference compared to X = OH and X = NH_2. Comparing to benzodioxle some changes can be observed: an opening of the two angles near to the site of substituent inside the benzene ring, a decrease of the angle at the site of substitution, a lengthening of the two C_ϕ-C_ϕ bonds on the site of substitution. Nevertheless, the main point to notice is that the most characteristic feature of the geometry and of the electronic structure of benzodioxole is preserved: in all the molecules studied, there is an alternation of bond lengths and π bond orders within the benzene moiety (table III). The distorsion from a D_{6h} symmetry is an important factor to which intensity obeys. This distorsion is increased in the derivatives of benzodioxole compared to benzodioxole itself and the intensity too is increased. A measure of the distorsion towards a Kekulé structure is given by $A_\pi = 100(\Pi\text{-}\pi)/\Pi$. Π is the average of the three greatest π_ϕ bond orders and π the average of the three smallest ones (another index could be

Table III

Bzd-X	a	b	c	d	e	f
H	0,561	0,698	0,615	0,711	0,698	0,615
CH_2OH	0,545	0,707	0,605	0,714	0,588	0,716
CH_2NH_2	0,548	0,705	0,607	0,712	0,591	0,714
CH_2CN	0,552	0,699	0,613	0,709	0,594	0,709
$CH_2CH{=}CH_2$	0,555	0,699	0,613	0,709	0,599	0,707
CH_2NH_3	0,537	0,675	0,639	0,675	0,577	0,712

π bond orders of the benzene bond in the benzodioxole derivatives (figure I, J).

built with the bond lengths instead of the bond orders). A_π is the percentage of distorsion towards a pure Kekulé structure for which A_π=100. The values calculated are 14,9% for benzodioxole, 18,1% for Bzd-CH_2NH_2, 18,7% for Bzd-CH_2OH, 16,5% for Bzd-$CH_2CH{=}CH_2$, 15,0 % for Bzd-$CH_2NH_3^+$ and 17,0 % for Bzd-CH_2CN. A great part of the distorsion is already present in the benzodioxole molecule itself and could account for a part of the constant component of the intensity.

IV - MNDO CALCULATIONS

Benzodioxole is planar.(28) It has been completely optimized (C-H bond lengths and angles included) with several steps until the values of the parameters to be optimized do not change. Actually, the MNDO methods does not allow to optimize in a single calculation an indefinite number of parameters. As the C-H bond lengths around the benzene moiety are very near to standard values (1.084 and 1.089 Å) we have kept them constant in the calculations for the other molecules.

In the derivatives of benzodioxole the optimizations have been performed for all the parameters whose values are given in figure VI. As concerns -CH_2OH, standard values have been used for the C-H bond lengths (1.107 Å) and the O-H bond length (0.96 Å). The angle HCH has been taken 109.5°. In the NH_2 derivative standard values have been used for the N-H bond length (1.008 Å), and the HNC angle (107°), the HCH angle inside CH_2 has been taken 109.5°. For all the derivatives, only the conformation where C-X is in the plane of the molecule has been studied.

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Date Received: 01/09/90
Date Accepted: 02/14/90