

Effects of Strongly Perturbing Substituents on the Near UV Spectra of 3,4-Methylenedioxybenzene Derivatives

J. VARDIN and B. VIDAL*

Laboratoire de Chimie Organique, Faculté des Sciences,
Université de La Réunion, 97489 Saint-Denis Cédex, La Réunion (France D.O.M.)

Received 27 September 1990

Accepted for publication 6 June 1991

The 3,4-methylenedioxybenzene derivatives with strongly perturbing substituents (OH, NH₂, NH₃⁺, COCH₃, CO₂H, CHO, CN, NO₂, etc.) display a charge-transfer $n_{O,p} \rightarrow \pi_{Ph}^*$ transition towards $\lambda = 230\text{--}290$ nm. The intensity of that transition is shown to depend on the electron density $d_{O,p}$ in $n_{O,p}$ orbital, the nonbonding p_x orbital of the oxygen of the fused membered ring being in *para* position to the substituent. It depends also on the value of the π bond order $BO_{CO,p}$ of the C_{Ph}—O_p bond.

As concerns the secondary transition, we have shown that the intensity arising from the π -donating effects of the *para* oxygen is quenched when substituent is strongly π -donor. Furthermore we explain why the intensity of the secondary transition (determined by ϵ_{sc}) roughly increases when the intensity of the charge-transfer transition ($\epsilon_{CT,o}$) increases.

Many benzodioxole derivatives are used for their biological activities. Several of them are known as popular drugs of abuse (ecstasy) [1–4], radioprotectors [5, 6] and some as synergistic activators of insecticides (for example they are used to enhance the efficiency of natural pyrethrins on the house fly) [7, 8]. Such a wide range of application makes them very valuable chemicals and shows that their potentials could be much more wider than what is already known. So their molecules should be studied from the fundamental point of view, in order to understand their basic behaviour. Their electronic structures, UV–VIS spectra, interactions of the substituents around the aromatic ring, and incidence of the five-membered fused oxygenated ring on all their properties are to be investigated. The present study is the introduction to other theoretical works relating the activities of the benzodioxole derivatives to quantum, structural or spectroscopic parameters.

Some of the benzodioxole derivatives, the general formula of which is A (Formulae 1), have been the subject of a recent spectroscopic study [9]. All these derivatives display a —CH₂X group with X being: H, OH, NH₂, NH₃⁺, COCH₃, etc. In such a study the effects of X on the benzene ring are buffered, smoothed, by the —CH₂— unit and they are transmitted towards the π_{Ph} system, through that unit, mainly by a hyperconjugative process (σ , π coupling). That preceding work [9] and some others [10, 11] devoted to structural calculations, have led us to a better understanding of the main factors

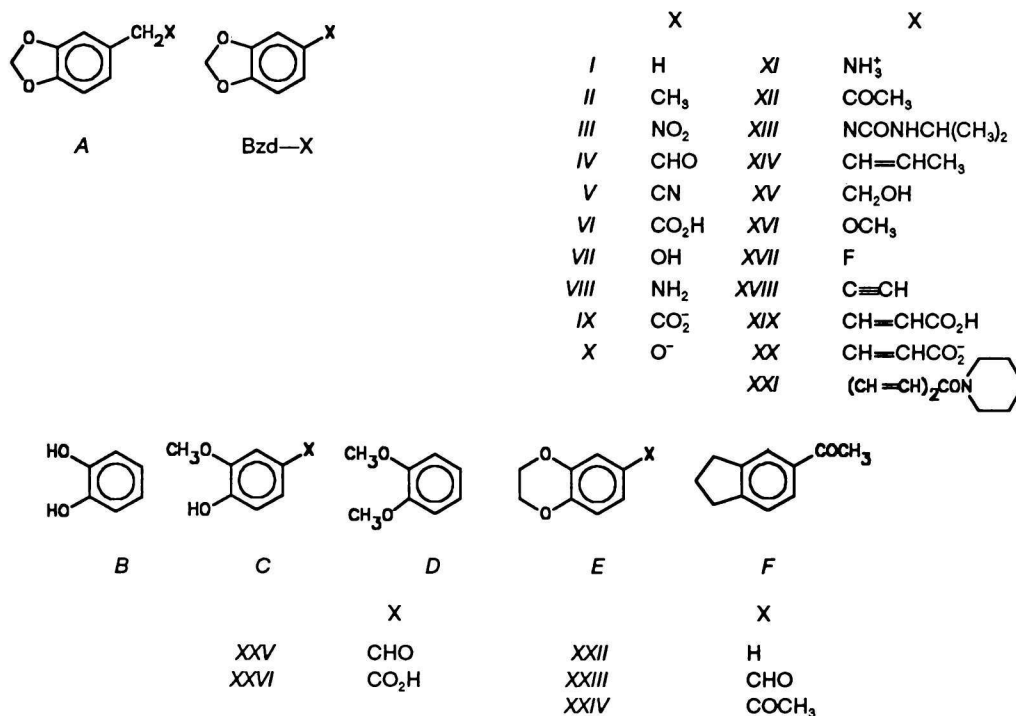
which influence the intensity of the secondary transition of these benzodioxole derivatives.

In the present work we shall study derivatives with much stronger perturbing substituents: those obtained when X is directly linked to the benzene moiety, without the buffer of the methylene group (Bzd derivatives I—XX). The spectroscopic behaviour of these molecules is very different from that of the molecules studied in our preceding paper. For example, we shall study, besides the secondary transition, a charge-transfer transition at lower wavelengths. Such a charge-transfer transition could not be studied in the molecules with —CH₂X as a substituent, since the intensity does not change enough when varying X.

UV SPECTRA OF BENZODIOXOLE, BENZODIOXANE, AND PYROCATECHOL

The secondary transition of the 1,3-benzodioxole (I) molecule (molar absorption coefficient $\epsilon_{max} = 3330$ dm³ mol⁻¹ cm⁻¹; $\lambda_{max} = 281$ nm (methanol)) proceeds from the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of the free benzene chromophore which is forbidden because of the D_{6h} symmetry ($\{\epsilon_{max}\} = 220$; $\{\lambda_{max}\} = 254$ (cyclohexane); only the numerical values of the mentioned quantities are given in the paper) [9]. The coupling of the nonbonding electrons of the oxygen atoms with the π_{Ph} system, and the steric strain imposed by the five-membered fused ring, distort the symmetry towards the C_{2v} one where the transition is allowed. Thus, the intensity of the transition is much stronger in 1,3-benzodioxole than

* The author to whom the correspondence should be addressed.



Formulae 1

in benzene. Intensity is stronger, too, than what is observed in pyrocatechol ($\{\epsilon_{\max}\} = 2650$ (methanol) in our paper) where there is no fused ring to distort the benzene ring. The strain distorts the symmetry not only by increasing the length of the bridgehead bond, but also by inducing alternating bond lengths towards a Kekulé-like structure [10, 11] (Mills—Nixon effect).

In 1,3-benzodioxole there is also another transition ($\{\epsilon_{\max}\} = 3300$; $\{\lambda\} = 230$ (methanol)) which has never been studied. This transition appears also in pyrocatechol ($\{\epsilon_{\max}\} = 6200$; $\{\lambda_{\max}\} = 218$ (methanol)) as well as in phenol ($\{\epsilon_{\max}\} = 5200$; $\{\lambda_{\max}\} = 203$ (methanol)), in many phenol derivatives and in alkoxybenzene derivatives. In phenols it has been assigned [12] to the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ charge-transfer transition of one of the nonbonding electrons of the oxygen atoms. For anisole ($\text{Ph}-\text{OCH}_3$) $\{\epsilon\} = 8100$; $\{\lambda\} = 210-220$ (methanol). The substitution of H by CH_3 enhances intensity and shifts the transition towards longer wavelengths because of the electron-donating character of the methyl group. This is confirmed by the spectrum of 1,2-dimethoxybenzene (veratrole D, $\{\epsilon\} = 11\,700$; $\{\lambda_{\max}\} = 225$). Thus, the decrease of intensity of transition from pyrocatechol (where $\{\epsilon\} = 6200$) to 1,3-benzodioxole ($\{\epsilon\} = 3300$) is not due to introducing an aliphatic substituent to the oxygen atoms. Only a part of the difference can be related to the overlap of the charge-transfer (CT) transition with another benzene transition at lower λ .

The fused ring does not change much the number of electrons on the oxygens. The MNDO electron

density in the p_x orbital (orbital denoted n_{O} below) of one of the oxygen atoms is 1.9071 for pyrocatechol (B), 1.8978 for benzodioxane (E, XXI), and 1.8998 for benzodioxole.

For benzodioxane the charge-transfer transition lies towards $\lambda = 220$ nm ($\{\epsilon_{\max}\} = 5500$ (methanol)) when it lies at 230 nm for 1,3-benzodioxole. Thus, strain red-shifts that transition. The transition is strongly overlapped by the transition appearing at 210 nm (${}^1B_{1u} \leftarrow {}^1A_{1g}$ for the free benzene molecule). Its actual intensity should be much lower than the observed one. Taking into account the overlap, its intensity may correspond to $\{\epsilon_{\max}\} \approx 3500-4500$. This value lies between the corresponding values for 1,3-benzodioxole (3300) and pyrocatechol (6200, or 4500—5500 when corrected from overlap).

The main effect of the fused ring is the strain imposed to the Ph moiety [10, 11]. Thus, the intensity changes for the charge-transfer transition should be assigned to the strain. Although the strain increases the intensity of the secondary transition (because it distorts the D_{6h} symmetry which makes it forbidden), it decreases the intensity of the CT transition. Actually, it decreases the π bond orders between the p_x orbitals of the oxygen atoms (n_{O}) and π_{Ph} . It decreases the π bond order because it lengthens the $\text{C}_{\text{Ph}}-\text{O}$ bonds (1.370 Å compared to 1.364 Å for phenol). Our MNDO calculations give for that bond order (which will be written BO_{CO} below): 0.302 for pyrocatechol, 0.273 for benzodioxane, and 0.268 for benzodioxole. Thus, the n_{O} atomic orbitals are less and less coupled with

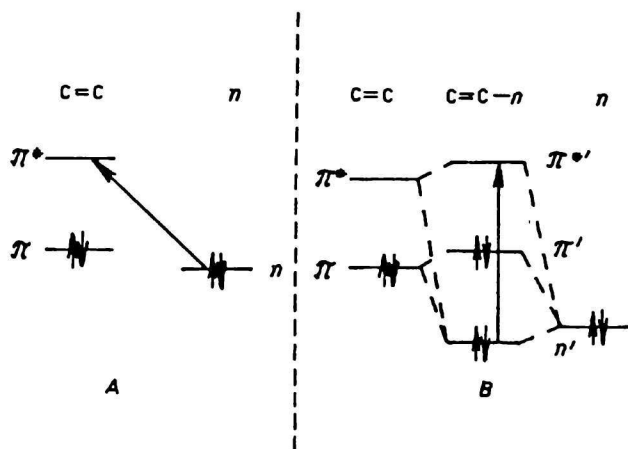


Fig. 1. Coupling and charge transfer.

Ph when the strain increases — the interaction is weaker, the charge transfer is less effective.

A coupling between the π system and n_O is necessary to allow interaction and to observe a charge transfer. The charge transfer involves a ground state with electrons in a molecular orbital which includes the π system and n_O , and which is centred on n_O (schematically: $a\pi + bn_O$ with $b \gg a$). In the excited state the electron involved in the transfer will be in an MO centred on π^* (schematically: $b'\pi^* - a'n_O$ with $b' \gg a'$) (Fig. 1). The case described in Fig. 1 is that of an n orbital lower than the π one. Fig. 1A emphasizes the angle "transfer of a charge". Fig. 1B is more appropriate: the two orbitals involved in the $n \rightarrow \pi^*$ transition belong to the whole molecule. The transition, in fact, is $n' \rightarrow \pi^*$. It arises because n' and π^* belong to the same molecular orbital system. If there were no coupling between the π system and n (as in Fig. 1A) there would be no possibility to produce the orbitals n' and π^* . There would be no "charge-transfer" transition, for which $\epsilon = 0$. Thus, intensity of transition depends on the amplitude of the coupling which can be evaluated by the bond order between n and the π system.

When the coupling between π_{Ph} and n is weak, the "nonbonding" electrons are mainly concentrated on the oxygens. The first step which has to occur is the collision between a photon and a nonbonding electron in n . This rather naive picture has been used successfully, for example for the spectroscopy of polyenes [13], and it is linked directly to the definition of the molar absorption coefficient the dimension of which is $1000 \text{ cm}^2 \text{ mol}^{-1}$. The intensity of absorption of photon increases when the ultraviolet absorption cross-section increases, all other parameters being assumed constant, which is approximately true only in very simple systems. In the present work, if we suppose that the coupling between n_O and π_{Ph} is very weak,

the primary process to remove an electron from n_O , will be the "capture" of a photon "inside" n_O . The greatest will be the number of electrons in n_O , the highest will be the collision probability and the photon absorption probability. The intensity of the CT transition will be the greatest. Here above, pyrocatechol, benzodioxane, and 1,3-benzodioxole have been compared to show that the bond order (BO_{CO}) between n_O and the p_x orbital of the adjacent carbon atom on the aromatic ring decreases when the strain increases. The decrease of the bond order causes the decrease of the intensity of the $n_O \rightarrow \pi_{Ph}^*$ charge-transfer transition. Furthermore, when going from pyrocatechol to 1,3-benzodioxole the number of electrons in n_O decreases from 1.9071 to 1.8998. This decrease induces also a decrease of the intensity of the CT transition. The fact that for benzodioxane this number is only 1.8978 is not very significant, since the six-membered fused ring is not planar and the number of nonbonding electrons on the oxygen atoms depends on the geometry obtained [11].

THE CHARGE-TRANSFER TRANSITION OF 3,4-METHYLENEDIOXYBENZENE DERIVATIVES

No correlation has been found between molar absorption coefficient of the CT transition $\epsilon_{CT,O}$ and parameters involving the oxygen atom in the *meta* position to X. There is a correlation between $\epsilon_{CT,O}$ and the bond order BO_{CO} (denoted $BO_{CO,p}$) or the electron density d_O (denoted $d_{O,p}$) when considering the oxygen atom in the *para* position to X. The oxygen atom in the *para* position to X constitutes with Ph and X some sort of a privileged group in the molecule. Literature has often emphasized mesomerism between substituents in *para* positions [14–16], although that phenomenon is not perfectly understood [16], contrary to what has been usually thought.

$\epsilon_{CT,O}$ has been plotted against a parameter $P = (0.263 - BO_{CO,p})(d_{O,p} - 1.901)$ in Fig. 2. P has been calculated against parameters which have been obtained by the MNDO method. The equation of the curve is

$$\epsilon_{CT,O} = 3295 + 0.1308 P$$

As P involves $BO_{CO,p}$, it is a measure of the sensitivity of the charge transfer to the conjugation of $n_{O,p}$ with π_{Ph} . As it involves also $d_{O,p}$ it is a measure of the ability of the nonbonding electrons in $n_{O,p}$ to capture a photon of the proper frequency. Our MNDO calculations show that $BO_{CO,p}$ and $d_{O,p}$ are not independent. When $BO_{CO,p}$ increases,

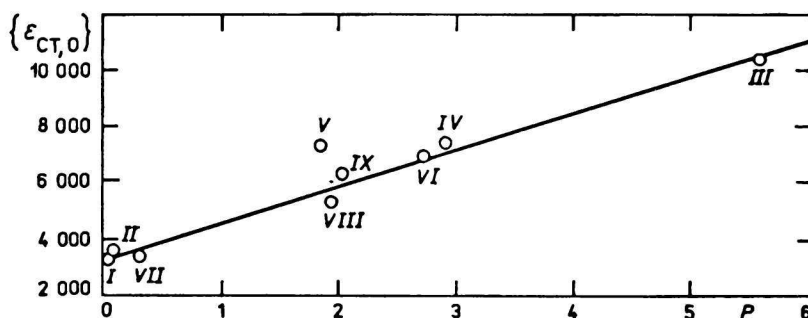


Fig. 2. Dependence of the molar absorption coefficient of the CT transition $\epsilon_{CT,0}$ on the parameter P (methanol).

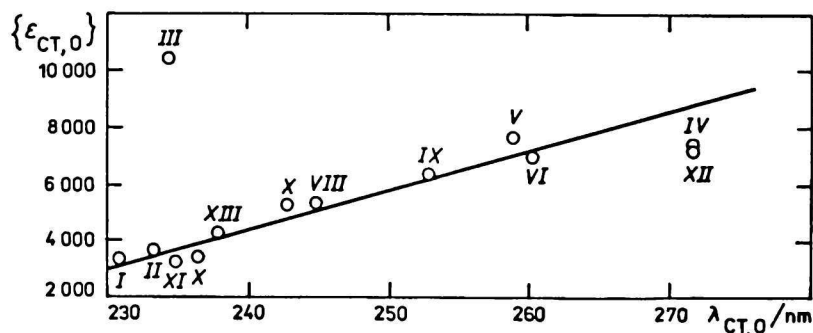


Fig. 3. Correlation of the wavelength of the CT transition $\lambda_{CT,0}$ with $\epsilon_{CT,0}$ of the Bzd—X derivatives (methanol).

$d_{O,p}$ decreases because the nonbonding electrons on the oxygen atom are partly used to strengthen the π , part of the $C_{Ph}-O$ bond.

P is canceled by the values $BO_{CO,p} = 0.263$ or $d_{O,p} = 1.901$. These values make $\epsilon_{CT,0}$ minimum. They roughly agree with those calculated for the parent compound — 1,3-benzodioxole (respectively: 0.268; 1.8998). The corresponding $\epsilon_{CT,0}$ value given by the above relationship is the same as the experimental one obtained for 1,3-benzodioxole. Thus, the intensity of the CT transition is always higher than what is observed for the parent compound. When X is a π -donating group it tends to increase the π electron densities in *ortho* and *para* positions to its position. Our MNDO calculations show that the increase of the π electron density in *para* position to X repels the π electrons of the *para* $C_{Ph}-O$ bond towards the oxygen atom and the $n_{O,p}$ orbital. Consequently, a π -donating group decreases the value of $BO_{CO,p}$ since the electrons used for conjugation now are located on the oxygen atom, where they become more nonbonding. Thus, an increase of the π -donating character of X will increase the probability for a photon to be captured by the nonbonding electrons. Although the efficiency of the coupling between π_{Ph} and $n_{O,p}$ decreases — phenomenon which is unfavourable to the charge-transfer transition — the intensity of transition increases because there is an increase of the probability of the capture of photon.

When X is a π electron-withdrawing group, X tends to decrease the π electron densities in *ortho* and *para* position to its own one, favouring the positive charges. The nonbonding electrons of the $n_{O,p}$ orbital are attracted towards C_{Ph} , and $d_{O,p}$ decreases. These electrons are used to strengthen the $C_{Ph}-O$ bond. Thus, $BO_{CO,p}$ increases. The coupling between $n_{O,p}$ and π_{Ph} being more developed, the electrons of the *para* oxygen atom can participate more efficiently in a transition towards π_{Ph}^* , although the probability for the electrons of $n_{O,p}$ to capture a photon decreases. This transition is less and less a charge-transfer one as the coupling increases. It becomes more and more a $\pi \rightarrow \pi^*$ one. No two molecules have a transition with exactly the same identity. It is for 3,4-methylenedioxynitrobenzene (which we have denoted Bzd— NO_2 (III)) that the transition is the most $\pi \rightarrow \pi^*$, since the value of $BO_{CO,p}$ (0.302) is the highest one and that of $d_{O,p}$ (1.8867) is the lowest one. On the contrary, it is in the carboxylate derivative (the salt of piperonylic acid, Bzd— CO_2^- (IX)) that the transition is the most $n_{O,p} \rightarrow \pi_{Ph}^*$, since $BO_{CO,p}$ has the lowest value, and $d_{O,p}$ the highest one. It has been impossible to obtain realistic values of $BO_{CO,p}$ and $d_{O,p}$ for Bzd— O^- and Bzd— NH_3^+ . MNDO calculations put too much emphasis on the charges in these ions.

The wavelength of the charge-transfer transition ($\lambda_{CT,0}$) is correlated to $\epsilon_{CT,0}$ (Fig. 3). Actually,

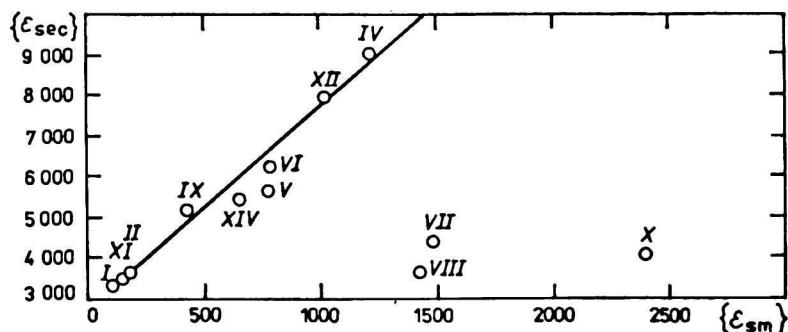


Fig. 4. Correlation of the molar absorption coefficient of the secondary transition of the Bzd—X (ϵ_{sec}) and Ph—X (ϵ_{sm}) derivatives (methanol).

$\epsilon_{\text{CT}, \text{O}}$ depends on $\text{BO}_{\text{CO}, \text{p}}$ and $d_{\text{O}, \text{p}}$. Furthermore, the frequency depends on the energy gap between $n_{\text{O}, \text{p}}$ and the π_{Ph}^* orbital. Thus, it can depend on the ionization potential of $n_{\text{O}, \text{p}}$, which depends on $d_{\text{O}, \text{p}}$. Nevertheless, the correlation between $\epsilon_{\text{CT}, \text{O}}$ and $\lambda_{\text{CT}, \text{O}}$ is complex, since the charge-transfer character changes all along the series studied here, becoming less $n_{\text{O}, \text{p}} \rightarrow \pi_{\text{Ph}}^*$ and more $\pi_{\text{Ph}} \rightarrow \pi_{\text{Ph}}^*$ when $\text{BO}_{\text{CO}, \text{p}}$ decreases.

As concerns Bzd—OH, there must be another CT transition involving the electrons of the non-bonding n_{OH} orbital. It should not be red-shifted since OH is not a part of the strained five-membered ring. It should appear near to the transition observed for phenol itself ($\{\lambda\} = 200\text{--}210$; $\{\epsilon_{\text{max}}\} = 5200$ (methanol)) (Table 1). Nevertheless, conjugation in Bzd—OH is more extended than in Ph—OH. It is well known that conjugation red-shifts the $\pi \rightarrow \pi^*$ transitions. Thus, the UV transitions of the benzene chromophore of Bzd—OH (VII) towards $\lambda = 180\text{--}220$ nm (${}^1E_{1u} \leftarrow {}^1A_{1g}$ and ${}^1B_{1u} \leftarrow {}^1A_{1g}$ for the free molecule) are red-shifted, overlapping the $n_{\text{OH}} \rightarrow \pi_{\text{Ph}}^*$ transition, preventing it to be clearly observed.

The electrons of the n_{O^-} orbital in Bzd—O⁻ (X) should be involved, too, in a charge-transfer transition. In order to compare Bzd—O⁻ to Bzd—OH we have first of all to compare Ph—O⁻ to Ph—OH. In Ph—O⁻ the intensity of the CT transition is increased ($\{\epsilon_{\text{max}}\} = 9000$; $\{\lambda_{\text{max}}\} = 222$ (methanol)) compared to what is observed for Ph—OH. That increase arises certainly because there is a greater interaction of n_{O^-} with π_{Ph} , *i.e.* a greater conjugation. It is increased also because there are more electrons in n_{O^-} than in n_{OH} . The probability to capture a photon is increased. The CT transition is red-shifted, too ($\{\lambda\} = 220$) (because the energy of n_{O^-} should be higher than that of n_{OH}). Nevertheless, it is overlapped by the $\pi \rightarrow \pi^*$ benzene transitions, which are also red-shifted because of the increase of conjugation.

When comparing Bzd—OH and Bzd—O⁻, the intensity of the CT transition from —OH or —O⁻ should be increased as it happens when comparing Ph—OH and Ph—O⁻. It should be shifted also towards longer wavelengths. We observe a shoulder towards 220 nm. It is difficult to evaluate

Table 1. UV Spectral Data (λ/nm , $\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$; methanol) of Bzd—X Derivatives

Compound	Secondary transition		$n_{\text{O}^-} \rightarrow \pi_{\text{Ph}}^*$		$\pi_{\text{Ph}} \rightarrow \pi_{\text{Ph}}^*$	
	$\{\lambda\}$	$\{\epsilon_{\text{sec}}\}$	$\{\lambda\}$	$\{\epsilon_{\text{CT}, \text{O}}\}$	$\{\lambda\}$	$\{\epsilon_{\text{CT}, \text{X}}\}$
Bzd—H (I)	281	3330	231	3290		
Benzodioxane (E, XXII)	279	2400	222	5500		
Bzd—OH (VII)	298.5	4400	236	3380	220	
Bzd—O ⁻ (X)	310.5	4100	242	5200	225	
Bzd—CH=CHCH ₃ (XIV)	302	5400				
Bzd—NH ₂ (VIII)	305.5	3640	241.5	5330		
Bzd—NH ₃ ⁺ (XI)	283.5	3480	235.5	3260		
Bzd—CHO (IV)	310.5	9030	271	7400	229.5	17100
Bzd—COCH ₃ (XII)	307	7940	271	7200	229.5	17800
Bzd—CO ₂ H (VI)	296	6240	260	6940	220	21150
Vanillin (C, XXV)	307	10220	276	10600	229.5	15280
Bzd—NO ₂ (III)	295	3450	237	10400	336	6780
Bzd—CO ₂ ⁻ (IX)	292	5200	256	6300	200	34500
1,4-Benzodioxane-6-carbaldehyde (E, XXIII)	309	7100	276	11450	232.5	17100
1,4-Benzodioxan-6-yl methyl ketone (E, XXIV)	305	5930	272.5	10730	230.5	17200

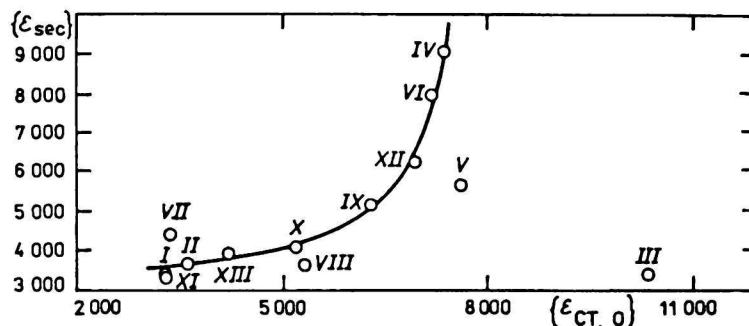


Fig. 5. Dependence of the ϵ_{sec} values of the secondary transition on the $\epsilon_{CT,0}$ values of the charge-transfer transition (methanol).

the intensity of the CT transition because of the strong overlap ($\{\epsilon\} = 15\ 000$ at 215 nm) with the benzene transitions. Nevertheless, we can be confident that the $n_{O^-} \rightarrow \pi_{Ph}^*$ transition cannot be confused with the $n_{O,p} \rightarrow \pi_{Ph}^*$ one at 240 nm, the wavelength of which is too much higher and intensity too much lower than what should be expected for the $n_{O^-} \rightarrow \pi_{Ph}^*$ transition.

THE SECONDARY TRANSITION OF 3,4-METHYLENEDIOXYBENZENE DERIVATIVES

The intensity of the secondary transition of the 1,3-benzodioxole derivatives is determined by ϵ_{sec} , and ϵ_{sm} will be used for Ph—X derivatives (ϵ_{sm} is measured at the maximum of the smoothed curve, as defined by *Ballester and Riera* [17] in order to avoid problems related to the differences in vibrational structure from a species to another). We have tried to correlate the ϵ_{sec} values of the "secondary transition" of the 1,3-benzodioxole derivatives with the ϵ_{sm} values of the secondary transition of the corresponding Ph—X molecules. Such a correlation could be used to evaluate to what extent the benzene moiety in 1,3-benzodioxole is a chromophore perturbed by three substituents, or forms a new unit with the substituents. The correlation is not very good (Fig. 4). The point corresponding to X = CH=CH—CO₂H (XIX) cannot be used since in Ph—CH=CH—CO₂H there is no secondary transition clearly visible [18 a]. For X = (CH=CH)₂CONR₂ (piperine (XXI)) we have not found the spectrum corresponding to Ph—X. There is no point for X = NO₂ (III) since in the nitrobenzene spectrum the secondary transition is strongly overlapped by a much more intense charge-transfer transition ($\pi_{Ph} \rightarrow \pi_{NO_2}^*$) [19 a]. The fact that for X = NH₂ (VIII), OH (VII), and O⁻ (X) there is no correlation, shows that for these molecules the interactions of X with the 1,3-benzodioxole part are very different from what they are in Ph—X, between Ph and X. For the other molecules the interactions are certainly very different, too. Actually, not only X interacts with π_{Ph} , but it interacts

also with the "nonbonding" oxygen orbitals through the π_{Ph} system. It modulates their coupling with π_{Ph} . Thus, the linear relationship of Fig. 4 is due to the fact that these latter interactions can evolve regularly all along the series when ϵ_{sm} increases.

Molecules, the representative points of which do not fit with the curve, are those for which the X groups are the most π -donating ones. For these molecules our MNDO calculations show that $d_{O,p}$ is increased and $BO_{CO,p}$ decreased. Thus, the perturbation brought upon π_{Ph} , by the π -donating character of the *para* oxygen, decreases when X is a strong π -donor substituent. The perturbation induced by the oxygen atom tends to be replaced by that induced by X. Actually, as it has been already pointed out, when X is a strong π -donating substituent it tends to increase the π electron density on the *para* site and repels the nonbonding electrons in $n_{O,p}$. The coupling between $n_{O,p}$ and π_{Ph} is decreased. Thus, the perturbations on π_{Ph} arising from $n_{O,p}$ and from X, cancel each other when X is NH₂, OH, O⁻. Intensity of transition is lower than what it would be if the two perturbations would add.

In Fig. 5 ϵ_{sec} has been plotted against $\epsilon_{CT,0}$ (Bzd—CH=CHCH₃ (XIV) has not been used since the CT transition is not clearly defined). The intensity of the CT transition can be considered as roughly mirroring the perturbation of the benzene ring (as well in its ground state as in its excited state) since that intensity depends on the extent of the coupling between $n_{O,p}$, π_{Ph} , and X. Furthermore, it is well known that ϵ_{sec} for the benzene chromophore depends also on the perturbations imposed upon Ph, because these perturbations destroy the D_{6h} symmetry which makes the transition forbidden. Thus, it is consistent that ϵ_{sec} increases with the increasing $\epsilon_{CT,0}$. Bzd—NH₂, Bzd—OH, Bzd—O⁻ are no more exceptions. Actually, the interactions between the substituents are already taken into account in the experimental values of $\epsilon_{CT,0}$ while, of course, ϵ_{sm} in the Ph—X series (Fig. 4) did not involve these interactions. Fig. 5 shows that, for a given perturbation, ϵ_{sec} increases much more quickly than $\epsilon_{CT,0}$. This is

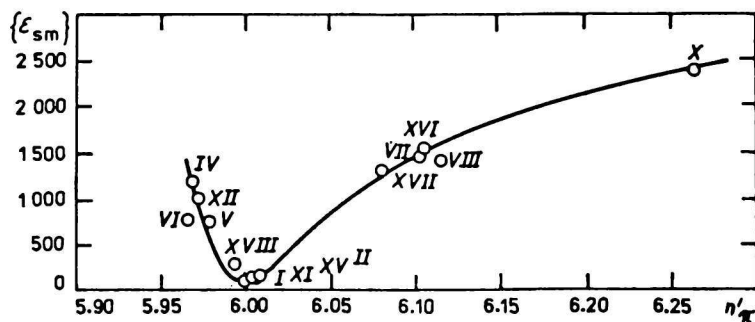


Fig. 6. Dependence of ϵ_{sm} on the number of π electrons of the π system (n'_π) of the Ph—X derivatives.

not very surprising since the secondary transition originates on Ph, to which X — the perturbing group — is linked, when the charge-transfer transition originates on n_o which is farther from X.

Bzd—NO₂ (III) is the only strong exception in Fig. 5. What arises for that molecule can be compared to what is observed for nitrobenzene [18 b]. The intensity of the secondary transition of nitrobenzene is weak and appears as shoulders or small peaks on the long-wavelength side of a strong charge-transfer transition $\pi_{Ph} \rightarrow \pi_{NO_2}^*$ ($\{\epsilon_{max}\} = 8270$; $\{\lambda_{max}\} = 260$ (methanol)). This intensity is difficult to evaluate. When using gas phase experiments we roughly obtain $\{\epsilon_{sm}\} \approx 150$ —300 corrected from the overlap. This is a very low value. We have no explanation, at this time, for such a value apart from the fact that NO₂ being a strongly perturbing group, the nature of the chromophore could also be strongly

One can see that the ϵ_{sm} increases as much as the $|n'_\pi - 6|$ value increases. Actually, D_{6h} symmetry is all the more distorted as that value is higher, whatever the direction of electron migration is, towards π_{Ph} or out of π_{Ph} . This is consistent with the results of our preceding paper [21] on Ph(CH₂)_nX. The correlation in Fig. 6 is sufficient to show roughly the evolution of ϵ_{sm} with n'_π . The slope of the V-shaped curve obtained is lower for high values of n'_π than for low values. Fig. 7 shows the same behaviour when the molecules Bzd—X are considered, using the n_π values from our MNDO calculations. But there is no more a well defined V-shaped curve since the branch for high n_π values is so flattened that it is almost a plateau. Furthermore, the number of π electrons in Bzd—CO₂⁻ (IX) and in Bzd—NO₂ (III) is very much surprising (Fig. 7). These numbers allow the two molecules

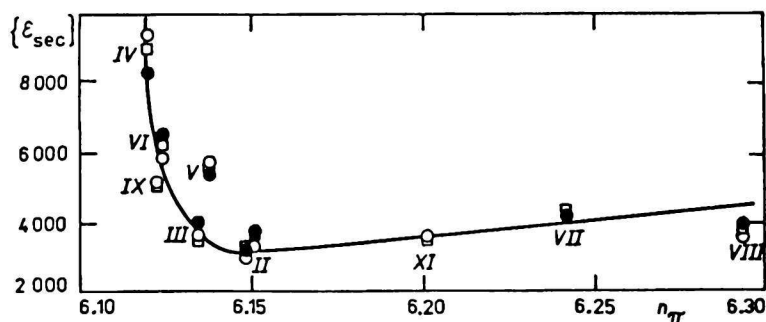


Fig. 7. Dependence of ϵ_{sec} on the number of π electrons of the π system (n_π) of the Bzd—X derivatives. The point corresponding to BzdO⁻ has not been taken into account because n_π is too high ($n_\pi = 6.571$). As it is a charged species, the MNDO method has probably overemphasized this value. ○ Water, □ methanol, ● cyclohexane.

changed. There is no explanation in the literature, since that transition being difficult to study has received little attention. We shall see later, when studying Bzd—NO₂, that its low intensity is linked to the number of π electrons in the π_{Ph} cloud and it could be the same for Ph—NO₂.

Hehre, Radom, and Pople [20] have carried out calculations on benzene monoderivatives with an *ab initio* method. Among these calculations, we have used those on the π electron population values (n'_π) to draw the curve of Fig. 6: $\epsilon_{sm} = f(n'_\pi)$.

to be correlated to the other ones, showing that the value ϵ_{sec} for Bzd—NO₂, although it is a very small one, is in accordance with the number of π electrons on the Ph moiety. Here, we have the answer to the question concerning the low value of the intensity of the secondary transition of Bzd—NO₂ (and perhaps for that of Ph—NO₂). The intensity is low because the number of π electrons in π_{Ph} is near to 6.148 which is the number of π electrons of benzodioxole. This behaviour seems to be contrary to the fact that NO₂ appears as a

strong electron-withdrawing substituent [22] when reactivity is considered. Nevertheless, in this latter case, the action on the σ electron frame as well as on the π cloud is involved and no comparison should be done with the present case. The number of π electrons in Bzd—CO₂⁻ fits with the value of ϵ_{sec} , but this value is very high compared to the other π -donating species. In fact, —CO₂⁻ appears as an overall π -attracting species, since it is less π -donating than the two oxygen atoms of 1,3-benzodioxole. We have seen here above that CO₂⁻ acts as a π -donating substituent as concerns the distribution of the electrons between C_{Ph} in the *para* site and the *para* oxygen, repelling the electrons on that oxygen. Thus, it appears as an overall π -attracting species because in fact it quenches the π -donating tendency of the oxygen nonbonding electrons. It induces the oxygen atoms to give less electrons to π_{Ph} . The number of π electrons for Bzd—NH₃⁺ (XI) and Bzd—O⁻ (X) is very high ($n_{\pi} = 6.202$ and 6.571 , respectively). This is certainly an artefact of the MNDO method [21]. Furthermore, the fact that the number of π electrons for Bzd—NH₃⁺ is greater than for 1,3-benzodioxole is not surprising since it has been proved many times that ammonium groups although they are σ -withdrawing substituents are weak π -donating ones [23–26]. Only the too high number of π electrons given by the MNDO methods is questionable. Considering the complexity of the nature of the ammonium groups, their behaviour is very difficult to explain. Sometimes, contradictory results could be obtained. The behaviour of O⁻ substituent is easier to understand since, besides its field effects, it is a very strong π -donor and it is certainly neutral as concerns the σ effects [27].

The value for the minimum of the V-shaped curve $\epsilon_{\text{sec}} = f(n_{\pi})$ is not zero. It should be zero for a complete restoration of the D_{6h} symmetry, *i.e.* when the substituent is neither a π -attracting one, nor a π -donating one. In fact, there is a vibrational component to the intensity [17], which depends on the substituents and on their interactions. Thus, the value for the minimum of curve should change from one series of molecules to another as we have shown when studying the anilinium ions [28]. Furthermore, we have already observed [9] in the series Bzd—CH₂X that the minimum of the V-shaped curve, obtained when varying X, corresponds to the ϵ value of the 1,3-benzodioxole molecule and not to that of the benzene one. Actually, when X is an electron-attracting group which exactly cancels the π -donating effect of —CH₂—, the ϵ value has to be the same as that observed for Bzd itself. But an increasing electron-attracting character — if the vector Sklar-Platt's [29] rules could apply — should decrease the value

of ϵ under the value observed for 1,3-benzodioxole. The Sklar-Platt's rules do not apply here because the spectroscopic moment for a given substituent is not a constant (it depends on interactions with the other substituents) and because there is a component of the intensity which is analogous to the "vibrational component", and makes the 1,3-benzodioxole group the actual chromophore of the series.

Figs. 6 and 7 are similar. The slope of the curve is flatter for $n'_{\pi} > 6$ than for $n'_{\pi} < 6$ (Ph—X series) and for $n_{\pi} > 6.148$ than for $n_{\pi} < 6.148$ (Bzd—X series). The difference lies in the value of the slope of the right part of the V-shaped curve. For the Bzd—X series it has been observed that the right part of the curve is almost a plateau. Actually, in the Bzd—X series the π -donating effects of the oxygens and that of X quench each others. It is the reason why when n_{π} increases beyond $n_{\pi} = 6.148$, ϵ_{sec} does not change much. That quenching is consistent with the behaviour of Bzd—NH₂, Bzd—OH, and Bzd—O⁻ in Fig. 4, when we have already noted that the strong π -donating tendency of —NH₂, —OH, —O⁻ quenches the intensity of transition.

IDENTIFICATION OF SOME TRANSITIONS

Transitions of the Bzd—COR Derivatives (R = H (IV), CH₃ (XII), OH (VI))

The spectra of the derivatives Bzd—CHO, Bzd—COCH₃, Bzd—CO₂H display more complex features than the others. This could be linked to the spectroscopic behaviour of Ph—CHO, Ph—COCH₃, and Ph—CO₂H. As concerns Ph—CHO, its near UV spectrum displays near to the secondary transition ($\{\epsilon_{\text{max}}\} \approx \{\epsilon_{\text{sm}}\} = 1210$; $\{\lambda\} = 278.5$ (methanol)) another transition much more intense ($\{\epsilon_{\text{max}}\} \approx \{\epsilon_{\text{sm}}\} = 15200$; $\{\lambda\} = 241$ (methanol)) [18 b]. That transition is considered as a CT one from π_{Ph} to π_{CO}^* ($\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$) [30]. In fact, as there is no pure charge-transfer transition, it should be mixed with a $\pi_{\text{Ph}} \rightarrow \pi_{\text{Ph}}^*$ one (certainly the primary transition).

When comparing the spectra of Bzd—CHO, Bzd—COCH₃, and Bzd—CO₂H to those of their homologous species such as Bzd—NH₂ (VIII), Bzd—OH (sesamol (VII)), *etc.* the transition towards $\lambda = 310$ nm can be identified as the secondary transition. That transition would be only slightly shifted towards longer wavelengths because of the lengthening of the π system, because of the increase of conjugation (the LUMO and the HOMO are drawn energetically closer). Furthermore, it has been observed before that the transition towards 310 nm behaves as the other secondary transitions.

For the same reasons (lowering of the π_{Ph}^* orbitals), the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition should be shifted towards longer wavelengths compared to 1,3-benzodioxole, to Bzd—OH, etc. The only transition other than the secondary one, which appears at wavelengths longer than 230–240 nm, lies near to 271 nm. Thus, that transition is the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ one. Furthermore, when studying it, here above, we have seen that it behaves as the other $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transitions. Consequently, the transition lying at 230 nm is the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ charge-transfer one. Its intensity is very sensitive to solvent effects, although it remains roughly at the same wavelength. That transition, the molar absorption coefficient of which will be denoted $\epsilon_{\text{CT}, \lambda}$ displays the following values for Bzd—CHO: in water $\{\epsilon_{\text{CT}, \lambda}\} = 15\,340$; in methanol, $\{\epsilon_{\text{CT}, \lambda}\} = 17\,090$ and in cyclohexane $\epsilon_{\text{CT}, \lambda} = 21\,460$. The molar absorption coefficient is higher than for Ph—CHO (15 200 (cyclohexane)). As the transition is structured, and narrower ($\tilde{\nu} = 3240\text{ cm}^{-1}$ at half-height) than in Ph—CHO (3985 cm^{-1}), and its value we have calculated multiplying the ϵ_{max} of the smoothed curve with the width at half-height. The ratio of values for the two molecules is 1.075 showing that the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition is only slightly higher for Bzd—CHO than for Ph—CHO: it is 8 % higher.

The interpretation grounded on two distinct charge transfers ($n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ and $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$) is a very rough one. In fact, when an electron is promoted from π_{Ph} to π_{CO}^* some of the electrons from the oxygen atoms are drawn towards π_{Ph} . Thus, that charge transfer involves also the nonbonding electrons of the oxygens of the five-membered fused ring. The same should be true for the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition which should have a $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ character. This is consistent also with the fact that the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition has a growing $\pi_{\text{Ph}} \rightarrow \pi_{\text{Ph}}^*$ character when X is a π -attracting substituent, as it has been discussed here above (the second section).

The importance of the contribution of the 1,3-benzodioxole oxygens to the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition, can be enlightened by the spectrum of 5-indanyl methyl ketone (formula F) [18 c] in which there is no oxygen atom in the fused ring. For that molecule the intensity of the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition ($\{\lambda\} = 258$) is determined by $\epsilon = 12\,400$ (methanol) when $\epsilon = 14\,300$ for Ph—COCH₃ (methanol) [18 d]. Taking into account the width of the transition, the ratio of the given values is in fact 0.80 (the value for the indanyl methyl ketone being the lowest one). That ratio when Bzd—CHO and Ph—CHO are involved is 1.075. If the oxygen atoms of the fused ring in Bzd—CHO have no influence on the intensity of the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ charge-transfer transition, this intensity should be lower than the corresponding intensity in Ph—CHO, as it is when comparing 5-indanyl methyl ketone to Ph—COCH₃. As in fact, this

intensity is higher for Bzd—CHO than for Ph—CHO we have to assume that a part originates from the oxygen atoms. It can be argued that it is the strain induced by the oxygens in the Ph moiety which is the actual origin of the intensity, and not the pure electronic effects of the nonbonding electrons of the oxygens. In fact, the strain should not be too much involved since the transition takes place, for a part, outside of the benzene ring and outside of the fused ring. One more proof that the conjugative effect of the oxygens — and not the strain — has to be involved to explain the intensity of the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition is given by the spectrum of 1,4-benzodioxane-6-carbaldehyde (formula E, XXIII) and that of the vanillin molecule (formula C, XXV) (Table 1). The strain induced by the six-membered fused ring of the first molecule is very weak, and the strain does not exist in vanillin (apart from some possible steric interaction between —OCH₃ and —OH). For all that, the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition still exists in these two molecules with roughly the same intensities as in Bzd—CHO (vanillin: $\{\epsilon_{\text{max}}\} = 15\,275$; $\{\lambda\} = 276.5$; 1,4-benzodioxane-6-carbaldehyde: $\{\epsilon_{\text{max}}\} = 18\,840$, and for Bzd—CHO $\{\epsilon_{\text{max}}\} = 17\,090$ (methanol)).

The spectra of vanillin and of 1,4-benzodioxane-6-carbaldehyde are quite interesting (Tables 1 and 2). They confirm the assumption which has been made in the beginning of that work, concerning the influence of strain on the decrease of the intensity of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ charge-transfer transition. The intensity of that transition is almost the same for the two molecules (vanillin: $\{\epsilon_{\text{max}}\} = 10\,600$; $\{\lambda\} = 276.5$; 1,4-benzodioxane-6-carbaldehyde: $\{\epsilon_{\text{max}}\} = 11\,450$; $\{\lambda\} = 276.5$) while it is much lower for Bzd—CHO ($\{\epsilon\} = 7380$; $\{\lambda\} = 272$) where there is strain.

The spectrum of vanillic acid [18 e] (formula C, XXVI) leads to the same conclusion. The intensity of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ charge-transfer transition ($\{\epsilon_{\text{max}}\} = 11\,900$; $\{\lambda\} = 259$ (methanol)) decreases when the oxygens are in a fused five-membered ring such as in piperonylic acid (VI) ($\{\epsilon_{\text{max}}\} = 6940$; $\{\lambda\} = 260$ (methanol)) (Tables 1 and 2). The secondary transition of vanillic acid ($\{\epsilon\} = 6210$; $\{\lambda\} = 290$ (methanol)) [18 e] is weaker than the secondary transition of vanillin ($\{\epsilon\} = 12\,220$; $\{\lambda\} = 306.5$ (methanol)) since, as concerns the secondary transition, CO₂H is a less perturbing substituent than CHO. Actually, in benzoic acid the secondary transition (ϵ_{sm} corrected from overlap is 780 ($\{\epsilon_{\text{max}}\} = 895$; $\{\lambda\} = 272$ (methanol)) is lower than in benzaldehyde ($\{\epsilon_{\text{max}}\} \approx \{\epsilon_{\text{sm}}\} = 1210$; $\{\lambda\} = 278.5$ (methanol)).

Another point concerning these species is worthy of notice. In vanillic acid the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}_2\text{H}}^*$ CT transition ($\{\epsilon_{\text{max}}\} = 22\,900$; $\{\lambda\} = 217$ (methanol)) and the secondary one do not change much when

Table 2 UV Spectral Data (λ/nm , $\epsilon/(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$; cyclohexane) of Bzd—X Derivatives

Compound	Secondary transition		$n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$		$\pi_{\text{Ph}} \rightarrow \pi_{\text{X}}^*$	
	$\{\lambda\}$	$\{\epsilon_{\text{sec}}\}$	$\{\lambda\}$	$\{\epsilon_{\text{CT, o}}\}$	$\{\lambda\}$	$\{\epsilon_{\text{CT, X}}\}$
Bzd—CH=CHCH ₃ (XIV)	300.5	5200				
Bzd—CHO (IV)	303	8500	271	8850	229.5	21500
Bzd—COCH ₃ (XII)	300	7000	271	7950	229.5	19800
Bzd—CO ₂ H (VI)	296	7300	260	6700	221.5	23600
Vanillin (C, XXV)	307	8200	276	14600	223	29900
Bzd—NO ₂ (III)	290	4030	235.5	12000	324	7000
1,4-Benzodioxane-6-carbaldehyde (E, XXIII)	301.5	5700	272.5	12900	233	20400
1,4-Benzodioxan-6-yl methyl ketone (E, XXIV)	297.5	4850	270.5	12100	230.5	22250

compared to the cyclized compound (piperonylic acid (VI)). The same is true for vanillin (XXV) when compared to piperonal (IV). This phenomenon is not surprising as concerns the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CHO}}^*$ transition which involves a part of the molecule which is far from the OR substituents or from the fused ring. But we have observed, in the beginning of that work, an increase of the intensity of the secondary transition when going from pyrocatechol (B) ($\{\epsilon\} = 2650$) to benzodioxane (E) ($\{\epsilon\} = 2390$) and 1,3-benzodioxole (I) ($\{\epsilon\} = 3330$) because of the distortion of the D_{6h} symmetry of the chromophore. In a preceding work [29] we have shown that such an increase was low compared to what is observed when there is no oxygen atom in the five-membered fused ring (*o*-xylene: $\{\epsilon\} = 254$; $\{\lambda\} = 260$ (methanol) [18 f]; indan: $\{\epsilon\} = 1030$; $\{\lambda\} = 266$ (methanol) [18 g]). We have explained that such a phenomenon is due to the conjugation of π_{Ph} with the oxygen atoms. The conjugation quenches for a part the increase of intensity. In vanillin and piperonal on one hand, vanillic acid and piperonylic acid on the other, conjugation is greater than in 1,3-benzodioxole since there is another conjugated substituent. Thus, the increase of intensity of transition when cyclization occurs is more quenched.

The $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition displays two peaks in cyclohexane which is a less solvating medium than methanol or water, and more structure can be seen. These two peaks belong to the same transition, since both of them display always the same behaviour as concerns their intensities as well as their energy difference. (In vanillin (XXV): $\Delta\tilde{\nu} = 1210 \text{ cm}^{-1}$, the ratio of molar absorption coefficients $r = 1.01$; in 1,4-benzodioxane-6-carbaldehyde (E, XXIII): $\Delta\tilde{\nu} = 1210 \text{ cm}^{-1}$; $r = 1.07$, in Bzd—CHO (piperonal (IV)): $\Delta\tilde{\nu} = 1250 \text{ cm}^{-1}$, $r = 1.07$.) Thus, these peaks belong to the vibrational structure of the transition. The values of 1200—1300 cm^{-1} are typical wavenumbers of vibrations. Furthermore, this is near to $\tilde{\nu} = 1180 \text{ cm}^{-1}$, which corresponds to $\pi^2 n \pi^*$ excited state of the carbonyl group [28]. When considering

the same transition in 1,4-benzodioxan-6-yl methyl ketone (E, XXIV): $\Delta\tilde{\nu} = 1100 \text{ cm}^{-1}$ ($r = 1.07$). In Bzd—COCH₃ (XII) and Bzd—CO₂H (VI) the peaks are almost smoothed out and their overlap prevents to measure their frequency differences.

The intensity of the transition arising at 200—210 nm for Bzd—CHO is determined by $\{\epsilon\} \approx 16\,000$. This value is in good agreement with a primary band (${}^1B_{1u} \leftarrow {}^1A_{1g}$ for benzene itself) the chromophore of which is perturbed by several substituents.

The Spectrum of Bzd—CH=CHCH₃ (XIV)

The spectrum of Bzd—CH=CHCH₃ is very different from the spectra of the derivatives with a C=O double bond instead of the C=C one. In styrene itself (Ph—CH=CH₂), besides a transition towards 280—290 nm ($\{\epsilon_{\text{max}}\} = 930$; $\{\epsilon_{\text{sm}}\} = 650$) [18 h] which proceeds from the secondary one, there is another very intense transition ($\{\epsilon\} = 15\,200$; $\{\lambda_{\text{max}}\} = 245$). It has been sometimes named "conjugation band" [19 a]. In fact, it is similar to the charge-transfer transition $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ of Ph—CHO. Actually, in Ph—CHO the CT transition is partly a $\pi_{\text{Ph}} \rightarrow \pi_{\text{Ph}}^*$ one by coupling with the primary transition. In styrene, this "conjugation band" proceeds also from the primary transition of the benzene chromophore, and from the $\pi_{\text{C=C}} \rightarrow \pi_{\text{C=C}}^*$ transition. The term charge-transfer transition is not used in styrene but the couplings are almost the same. In other words, the CT transition ($\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$) in Ph—CHO and the "conjugation band" in styrene are (partly) primary transitions shifted towards higher wavelengths, because of the conjugative couplings with the unsaturated substituent. The same arises in Bzd—CH=CHCH₃ when comparing this molecule to Bzd—CHO (IV), Bzd—COCH₃ (XII), and Bzd—CO₂H (VI).

The conjugation band in styrene lies at higher wavelengths than the CT $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition in benzaldehyde. Thus, the transition in Bzd—

$\text{CH}=\text{CHCH}_3$ which corresponds to the conjugation band in styrene, should be nearer to the secondary transition appearing at higher wavelength, than is the $\pi_{\text{Ph}} \rightarrow \pi_{\text{CO}}^*$ transition in $\text{Bzd}-\text{CHO}$. Thus in $\text{Bzd}-\text{CH}=\text{CHCH}_3$ the CT $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition involving the oxygen atoms of the five-membered fused ring is buried under the "conjugation band". It is the reason why the intensity of the CT $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition has not been used in Figs. 3 and 5. Furthermore, this is consistent with the fact that the band observed at $\lambda = 260$ nm in $\text{Bzd}-\text{CH}=\text{CHCH}_3$ is strongly affected by the *cis-trans* isomerism of the methyl group [31]. (In the *trans* isomer which is studied in that work the band consists of two peaks, when there is one for the *cis* isomer.) That band cannot be the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ one since the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition involves parts of the molecule far from the methyl group.

The Spectrum of $\text{Bzd}-\text{NO}_2$ (III)

The spectrum of $\text{Bzd}-\text{NO}_2$ displays an unexpected feature (Tables 1 and 2). The long wavelength transition lies at 324 nm in cyclohexane, 337 nm in methanol and 351 nm in water. Such a large shift has already been noted for the spectrum of nitrobenzene, where the charge-transfer $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ transition lies at 240 nm in gas phase, 252 nm in heptane, 260 nm in methanol and 268 nm in water [19 b]. That bathochromic shift is caused by a greater polarization of the excited state of the transition. This induces a greater solvation of that state, and a decrease of its energy, when going from a nonsolvating medium to a very solvating one.

Thus, the long-wavelength transition should be in $\text{Bzd}-\text{NO}_2$ a $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ charge-transfer transition since it behaves, as concerns the solvent effect, as the $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ transition in $\text{Ph}-\text{NO}_2$. Its bathochromic shift is greater than what is observed in nitrobenzene: at 27 nm for $\text{Bzd}-\text{NO}_2$ when going from cyclohexane to water, 16 nm for $\text{Ph}-\text{NO}_2$. Actually, the excited state of $\text{Bzd}-\text{NO}_2$ should be more polar than the same in $\text{Ph}-\text{NO}_2$, since in the benzodioxole derivative in *para* position to NO_2 there is an oxygen which is a π -donating group, while NO_2 is a π -attracting one.

In nitrobenzene, the secondary transition (or what proceeds from the secondary transition) lies on the long-wavelength side of the $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ transition. In $\text{Bzd}-\text{NO}_2$ on the contrary, owing to the great shift of the $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ transition, the secondary one lies on the lower-wavelength side (still partly overlapping with the $\pi_{\text{Ph}} \rightarrow \pi_{\text{NO}_2}^*$ one). Furthermore, the secondary transition in $\text{Bzd}-\text{NO}_2$ has been shifted towards long wavelengths (283 nm), when compar-

ing to $\text{Ph}-\text{NO}_2$, because of the conjugation of the nonbonding electrons of the oxygens with the π system of the benzene moiety.

The wavelength of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition in $\text{Bzd}-\text{NO}_2$ is surprisingly low ($\{\lambda\} = 237$ (methanol)). Its intensity correlates perfectly with the other $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transitions (Fig. 2) (the n_{O} orbital of the *para* oxygen is strongly coupled with π_{Ph} ; $\text{BO}_{\text{CO}, p} = 0.302$). The low wavelength of that transition could be explained by the fact that the number of electrons in n_{O} (1.8867) is lower than for $\text{Bzd}-\text{CHO}$ (1.8913) and for $\text{Bzd}-\text{CO}_2\text{H}$ (1.8917). These electrons are more tightly bound to the nucleus of the *para* oxygen atom, increasing the energy gap with the excited state.

The Spectrum of $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$ (XIX), $\text{Bzd}-(\text{CH}=\text{CH})_2\text{CONR}_2$ (Piperine (XXI))

Intensity of transitions increases in the given series with the increasing conjugation. Actually the lengthening of the π system increases the probability for a photon of the proper energy to be captured. It is well known that the long-wavelength transition should also shift towards longer wavelength (free electron model). This is what is observed when comparing the two long-wavelength transitions of the following molecules: $\text{Bzd}-\text{CO}_2\text{H}$ (VI) ($\{\lambda\} = 260$ and 296; $\{\epsilon\} = 6940$ and 6420) or $\text{Bzd}-\text{CH}=\text{CHCH}_3$ (isosafrole (XIV)) ($\{\lambda\} = 262$ and 302; $\{\epsilon\} = 11\,920$ and 5410) to $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$ ($\{\lambda\} = 288$ and 323; $\{\epsilon\} = 12\,220$ and 16\,500) and to $\text{Bzd}-(\text{CH}=\text{CH})_2\text{CONR}_2$ ($\{\lambda\} = 308$ and 338; $\{\epsilon\} = 23\,900$ and 35\,500) (all values in methanol).

The molecules $\text{Bzd}-\text{CH}=\text{CHCH}_3$, $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$, and piperine are big molecules. Interpreting their spectra becomes somewhat more difficult than for the others (Fig. 8). Our study will be limited to some features and we will propose only interpretation elements. We have used again in Fig. 9 the data used in Fig. 3, $\epsilon_{\text{CT}, \text{O}} = f(\lambda_{\text{CT}, \text{O}})$, adding the points of all the other derivatives which have been studied, even if no MNDO calculation has been made.

In the spectrum of $\text{Bzd}-\text{CH}=\text{CHCH}_3$ $\epsilon = 11\,920$ at the wavelength where the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition occurs. This value is much greater than what is expected when considering the other $\text{Bzd}-\text{X}$ derivatives. From Fig. 8 we should expect for a molecule the intensity of which for the secondary transition is determined by $\epsilon = 5400$, a value of 6700, and not 11\,900, for the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition. Thus, there is an increase of 5200. In fact, that increase is certainly not an increase of the intensity of the CT transition. We cannot see where that increase would come from. It is rather another

transition overlapping the CT one. This new transition could be perhaps related to the so-called "conjugation band" [19] which appears in styrene and which has been discussed above. Its intensity would be very low for some structural reason specific for the benzodioxole chromophore. But, as we have no evidence that it is the conjugation band it will be named below unidentified band

(UIB), although it is linked to the presence of a C=C double bond, fixed on the benzene moiety, which lengthens the π system. This new transition (UIB) should be shifted towards longer wavelength, and its intensity should increase, when increasing conjugation, as it is well known for the absorption band of polyenes or phenyl polyenes. There is another transition — proceeding from the secondary

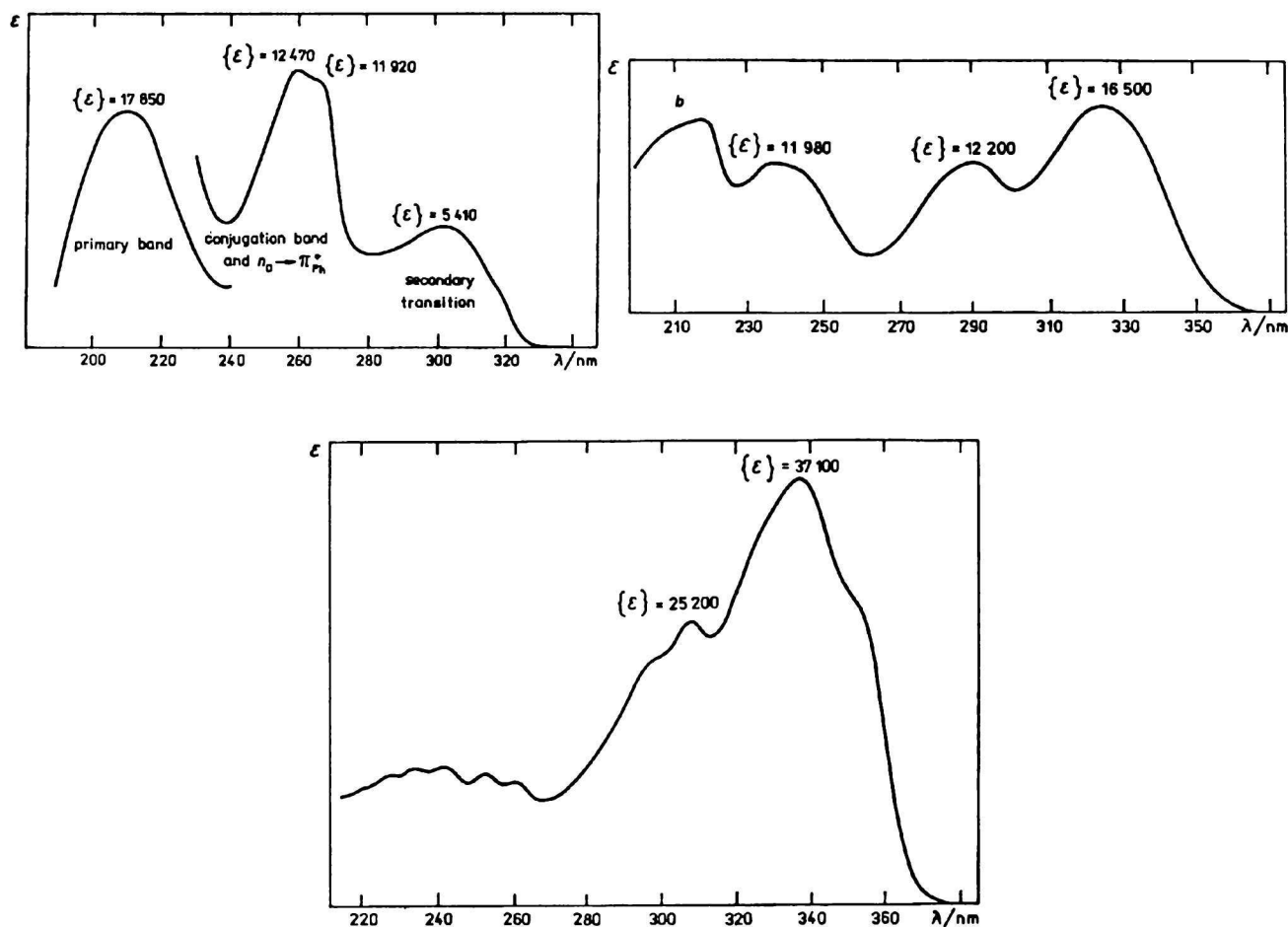


Fig. 8. UV spectra of: a) Bzd—CH=CHCH₃ (in methanol), b) Bzd—CH=CHCO₂H (in methanol), c) Bzd—(CH=CH)₂CONR₂ (in cyclohexane with dioxane).

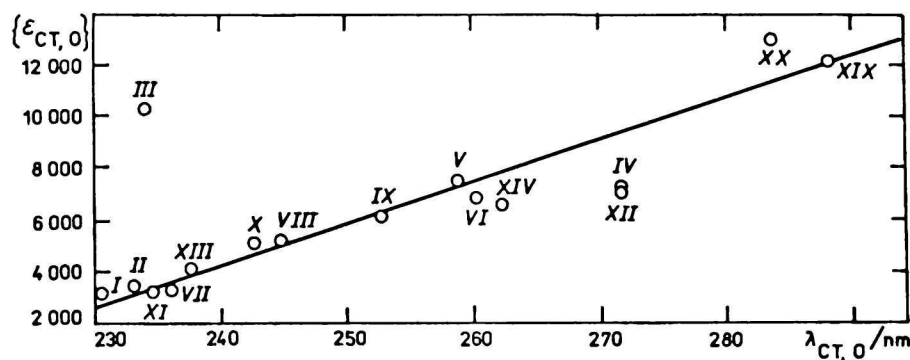
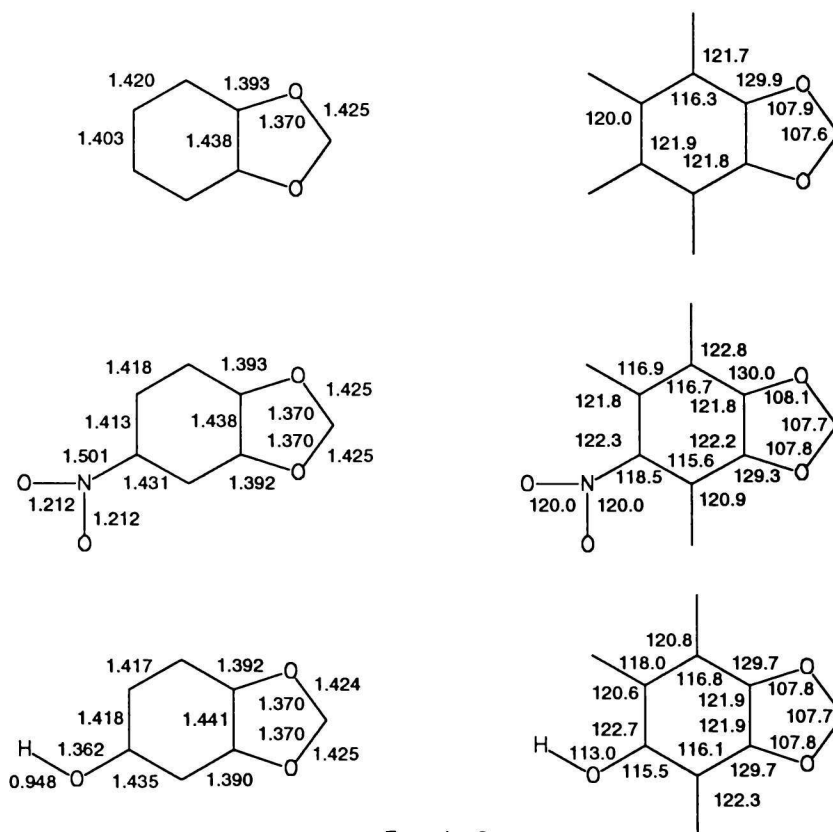


Fig. 9. Dependence $\epsilon_{CT,0} = f(\lambda_{CT,0})$ of the Bzd—X derivatives.

one — at higher wavelength ($\{\lambda\} = 302$; $\{\epsilon\} = 5400$). When increasing the conjugated system we should observe the overlap of the UIB with the secondary transition (and no more with the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ one). Thus, in $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$ — taking this only point into account — we should observe a decrease of the ϵ value at the wavelength where the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition appears, and a great increase at the wavelength where the secondary one appears. In fact, the decrease of ϵ value at the wavelength of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition cannot be observed since when increasing conjugation, the intensity of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition increases by itself. We observe for that transition $\{\epsilon\} = 12\,220$ which is only slightly higher than ϵ value observed at the wavelength of the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition in isosafrole (XIV), but higher than the value corrected from the UIB (6700).

As concerns the secondary transition, one band only is observed in methanol for $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$ with $\{\epsilon\} = 16\,500$ ($\{\lambda\} = 325$). In cyclohexane (Fig. 8), a less solvating medium, the two transitions are visible but their intensities are difficult to evaluate. In fact, the spectrum has been taken in the medium cyclohexane—dioxane ($\varphi_r = 99 : 1$) to obtain dissolution, and concentration is not perfectly known. It is the comparison between the spectrum measured in methanol and that in cyclohexane with dioxane which allows to deduce

the corresponding values: $\{\epsilon\} = 16\,500$ for the transition at 320 nm in cyclohexane, and 12 900 for the transition at 333 nm. The UIB would be at 320 nm and the secondary transition at 333 nm (values have not been corrected from the overlap since there are several overlaps, and some of them, already present in the other molecules, have not been corrected). The UIB displays a great shift, when going from isosafrole to $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$, but it still does not overwhelm the secondary transition. When going from $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$ to piperine, a $\text{C}=\text{C}$ double bond is added instead of a $\text{C}=\text{O}$ one. The UIB is shifted but no more than the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition and the secondary one. Actually, we assume that there should be a continuity in the spectra when increasing conjugation. The distance between the $n_{\text{O}} \rightarrow \pi_{\text{Ph}}^*$ transition and the secondary one is roughly 5290 cm^{-1} in $\text{Bzd}-\text{CH}=\text{CHCH}_3$, 4670 cm^{-1} in $\text{Bzd}-\text{CH}=\text{CHCO}_2\text{H}$. If the “secondary transition” in piperine is the transition at 340 nm the difference should be 3000 cm^{-1} , which is not enough. On the contrary, if the secondary transition is that appearing at 353 nm, the difference is 4080 cm^{-1} , the value which fits with the others. As the overlap is greater in that molecule than in the others, it is difficult to correct these values. The actual values should be considerably lower than what is measured. For that reason the piperine



Formulae 2

Geometry of some $\text{Bzd}-\text{X}$ molecules. The bond lengths are in the left part of the figure and the bond angles are in the right part.

values have not been used in the figures of the first, second, and third section. In methanol, owing to solvation, the two transitions (UIB at 338 nm and secondary transition at 353 nm) cannot be distinguished. As concerns Bzd—CH=CHCO₂⁻ (XX) the spectrum cannot be obtained in cyclohexane. Thus, it is not possible to separate the UIB from the secondary transition. Nevertheless, comparison with the spectrum of Bzd—CH=CHCO₂H in methanol and cyclohexane, shows that the maximum of the curve at 324 nm for Bzd—CH=CHCO₂⁻ roughly corresponds to the UIB with {ε} = 14 400 (Fig. 8). The same comparison leads to a secondary transition with {ε} = 11 300. Nevertheless the molecules Bzd—CH=CHY seem to display a specific behaviour when compared to the others, and too tight comparisons should not be attempted.

EXPERIMENTAL

All the spectra studied — unless otherwise specified in the text — have been recorded in our own laboratory using a Philips PU 8820 UV—VIS spectrophotometer. Spectrophotometric grade solvents have been used (methanol: C. Erba; cyclohexane: Merck and Aldrich).

All the products are commercially available (Aldrich, Merck). To purify them, we have used distillation under vacuum (safrole, 3,4-methylenedioxytoluene), recrystallization in a cyclohexane medium (piperonal, sesamol, Bzd—COCH₃, Bzd—NO₂, and Bzd—CH=CHCO₂H).

MNDO calculations [32, 33] have been done on the Honeywell Bull computer (DPS8/70M bi-processor) of the "Centre Interuniversitaire de Traitement de l'Information de Lille" (C.I.T.I., France) to which we are connected from La Réunion Island (Indian Ocean) via the world TRANSPAC satellite network.

All the geometries used have been obtained in this work using MNDO optimization. The substituents do not strongly modify the geometry of the benzodioxole group. Thus, we give in Formulae 2 only some example results.

As concerns the benzodioxole group, all the molecules have been assumed planar, since it has been shown on an infrared spectroscopic ground that it was the case for benzodioxole itself [34].

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