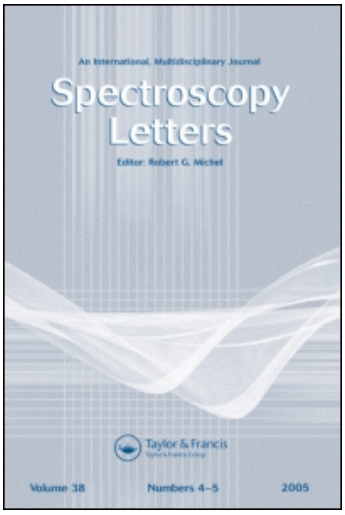


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# A Charge Transfer Transition in the Near U.V. Spectrum of 1,3-benzodioxole Derivatives

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# A CHARGE TRANSFER TRANSITION IN THE NEAR U.V. SPECTRUM OF 1,3-BENZODIOXOLE DERIVATIVES.

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1,3-benzodioxole derivatives [figure 1(A, B)] have been much studied for their biological activities.[1-12] Nevertheless, apart from our preceding papers[13,14] only few works have been done as concerns their spectroscopic behaviour and their electronic structures.[15,16] All the derivatives which have been studied in our recent works display a $-CH_2X$ group [Bzd-$CH_2X$] in para to one of the oxygens of the five membered oxygenated fused ring (X being -H, -OH, $-NH_2$, $-NH_3^+$, $-COCH_3$ etc...). We want to study here more strongly perturbating substituents with X directly linked to the benzene chromophore [figure 1(C)] [Bzd-X].

## I - A CHARGE TRANSFER TRANSITION IN THE NEAR U.V. SPECTRUM OF 1,3-BENZODIOXOLE

The secondary transition ($^1B_{2u} \leftarrow {}^1A_{1g}$ for the free benzene molecule) of 1,3-benzodioxole and of some of its Bzd-$CH_2X$ derivatives has

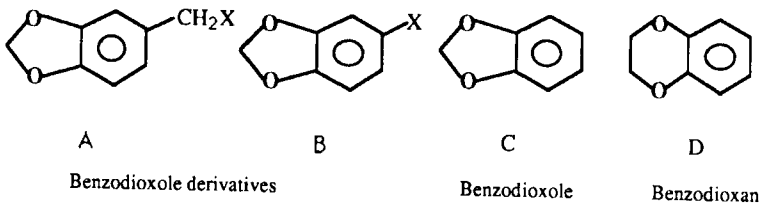
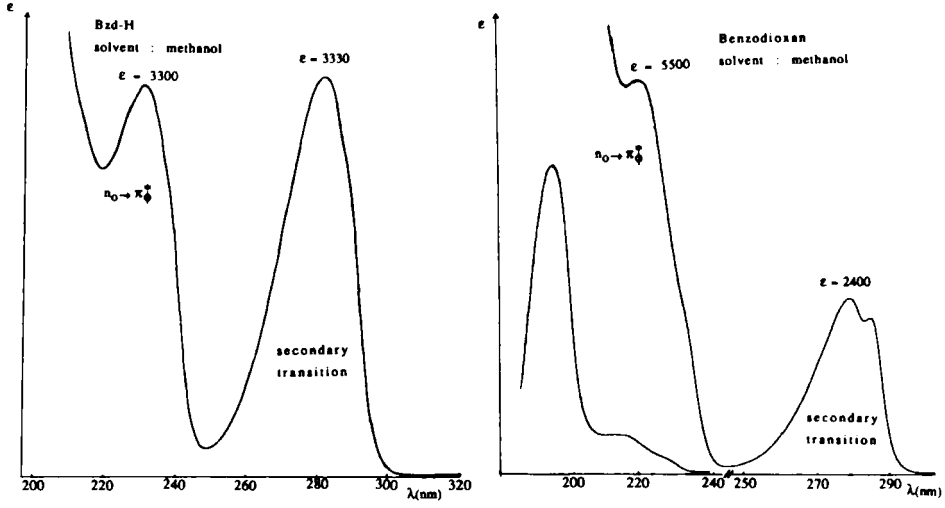



**Figure 1**



been studied in preceding works.[13,14,17] In the spectra of these molecules another transition is observed. For 1,3-benzodioxole it lies at $\lambda$ = 231 nm(methanol), with $\varepsilon_{max}$ = 3300 [figure 2(A)]. This transition has never been studied. It appears also in pyrocatechol (1,2-dihydroxybenzene) [$\varepsilon_{max}$ = 6200; $\lambda_{max}$ = 218 nm (methanol)] as well as in phenol [$\varepsilon_{max}$ = 5200; $\lambda_{max}$ = 203 nm; (methanol)], in many phenol derivatives and in alkoxy benzene derivatives. In phenols, it has been assigned[18] to the $n_O \rightarrow \pi^*_\phi$ charge transfer transition of one of the non-bonding electrons of the oxygen atoms, towards an antibonding $\pi^*$ orbital of the benzene chromophore. In anisole ($\phi$-$OCH_3$) its intensity is : $\varepsilon$ = 8100 (methanol). The substitution of H by $CH_3$ does not quench the intensity. On the contrary, it enhances that latter and shifts it towards longer wavelengths because of the electron donating character of the methyl group. This is confirmed by the spectrum of 1,2-dimethoxybenzene whose intensity of the charge transfer transition is 11700, when it is 6200 for pyrocatechol. Thus, the decrease of intensity from pyrocatechol to 1,3-benzodioxole (where it is 3300) does not come from introducing an aliphatic substituent on the oxygen atoms. Furthermore, only a part of the difference could be related to the overlap of the charge transfer (C.T.) transition with another transition at lower $\lambda$, overlap which is stronger in phenol type molecules than in 1,3-benzodioxole.

The fused ring does not change much the number of electrons on the oxygens. Our MNDO calculations lead to the following results for the




A) Spectrum of benzodioxole; B) Spectrum of benzodioxan

**Figure 2**



number of electrons in the $p_\pi$ orbital of one of the oxygen atoms (orbital which will be denoted $n_O$ underneath):

| | Pyrocatechol | Benzodioxan | Benzodioxole |
|---|---|---|---|
| Electron density in $n_O$ | 1,9071 | 1,8978 | 1,8998 |

The strain red shifts the charge transfer transition since for benzodioxan [figure I(D)] that transition lies towards 220 nm when it lies at 230 nm for 1,3-benzodioxole. In benzodioxan its intensity is : $\varepsilon_{max}$ = 5500 (methanol) [figure 2(B)]. The transition is strongly overlaped 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, the intensity should be $\varepsilon_{max} \simeq$ 3500-4500. This value lies between the corresponding values for 1,3-benzodioxole (3300) and pyrocatechol (6200, or 4500-5500 when corrected from overlap).

We have shown[13,17] that the main effect of the fused ring - apart from the conjugation of the oxygens - is the strain imposed upon the $\phi$ moiety. Thus, the changes in the intensity of the charge transfer transition should be assigned to the strain of the fused ring. But, why should the strain decrease that intensity, when it has been proved that it increases the intensity of the secondary transition[17]? Strain increases the intensity of the secondary transition which is electronically forbidden (owing to the $D_{6h}$ symmetry of the benzene molecule), because it distorts symmetry. Strain decreases the intensity of the C.T. transition, because it decreases the $\pi$ bond orders between $n_O$ and the $p_\pi$ orbital of the carbon atom to which the oxygen is linked in the benzene ring. Our MNDO calculations give for that bond order (which will be written $BO_{CO}$ underneath):

| | Pyrocatechol | Benzodioxan | Benzodioxole |
|---|---|---|---|
| $BO_{CO}$ | 0,302 | 0,273 | 0,268 |
| Bond length (Å) ($C_\phi$-O) | 1.358 | 1.361 | 1.370 |

$BO_{CO}$ decreases because the strain increases the $C_\phi$-O bond length. The $C_\phi$-O bonds tend to lengthen to relieve a part of the strain. Such a behaviour is not specific of the $C_\phi$-O bonds since it has been shown[13] that the bridgehead bond increases also when increasing the strain (benzodioxan: 1.419 Å; benzodioxole: 1.438 Å).

The decrease of $BO_{CO}$ shows that the $p_\pi$ atomic orbitals of the oxygens ($n_O$) are less and less coupled with $\pi_\phi$ when strain increases. That means that the interaction, the coupling of the two systems is weaker. Thus, this coupling is less efficient to allow a charge transfer.

Actually, a charge transfer needs a coupling between the $\pi$ system and the orbital bearing the non-bonding electrons ($n_O$). In order to be clear in studying the charge transfer, we shall use a C=C chromophore as in figure 3. The charge transfer is pictured by an arrow going from the n level to the $\pi^*$ one. The frequency for the $n \rightarrow \pi^*$ charge transfer transition will be higher or lower to that for the $\pi \rightarrow \pi^*$ transition according to the energy of the n level compared to that of the $\pi$ one. The case described in figure 3 is that of a n orbital lower than the $\pi$ one. Such a picture could wrongly lead to think that there is no condition imposed to the charge transfer, that latter being always allowed. It could

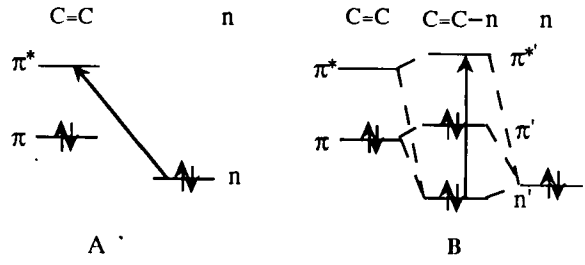



**Figure 3**

be observed whatever the relations between $\pi$ and n are. In fact, as shown in figure 3(B) the n orbital couples with the $\pi$ and $\pi^*$ ones to give three new levels n', $\pi'$, $\pi^{*\prime}$. The lowest one is mainly n (with a contribution from $\pi$ and a very small contribution from $\pi^*$), the second one mainly $\pi$ (with a contribution from n and a small contribution from $\pi^*$) and the third one mainly $\pi^*$ (with a small contribution from $\pi$ and a very small contribution from n). In figure 3(B) the two orbitals involved in the $n \rightarrow \pi^*$ transition are orbitals belonging to the whole molecule and the transition is in fact $n' \rightarrow \pi^{*\prime}$. The transition arises because n' and $\pi^{*\prime}$ belong to the same molecular orbital system. If there was no coupling between the $\pi$ system and n there would be no possibility at all to produce the orbitals n' and $\pi^{*\prime}$, and there would be no transition at all : the intensity of the charge transfer transition would be $\varepsilon = 0$. Thus, intensity depends on the amplitude of the coupling. This coupling can be evaluated by the bond order between n and the $p_\pi$ orbital of the nearest carbon atom of the $\pi$ system.

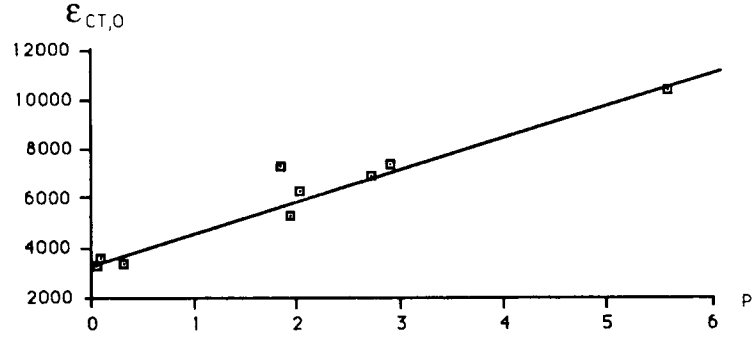
There is also another factor which has to be taken into account when the coupling between $\pi_\phi$ and n is weak. In that case the "non-bonding" electrons are only weakly delocalized on the $\pi$ system. They are mainly concentrated on the oxygens. The first step which has to occur, so that the charge transfer transition occurs also, involves - if we stay in a very simple scheme [figure 3(A)] - the collision between a photon and a non-bonding electron in n. This rather naive picture has been used successfully, for example in the spectroscopy of polyenes[20] and it is linked directly to the definition of the molar extinction

coefficient whose units are: 1000 $cm^2$/mole. Intensity of absorption will increase when the ultraviolet absorption cross section will increase, all other parameters being assumed constant, what is approximatly true only in very simple systems. In the present work, if we suppose that the coupling between $n_O$ and $\pi_\phi$ is very weak, the primary process to remove an electron from $n_O$, will be the "capture" of a photon inside $n_O$. It will be the collision of a photon and an electron in $n_O$. In other words, all other things being equal, the greatest will be the number of electrons in $n_O$, the highest will be the probability for a collision between an electron and a photon to occur, and the greatest will be the probability for the photon to be absorbed. The greatest will be the intensity of the C.T. transition.

Here above, pyrocatechol, benzodioxan and 1,3-benzodioxole have been compared to show that the bond order ($BO_{CO}$) between $n_O$ and the $p_\pi$ orbital of the adjacent carbon atom on the aromatic nucleus, decreases when the strain increases. The decrease of the bond order causes the decrease of the intensity of the $n_O \rightarrow \pi^*_\phi$ charge transfer transition (underneath noted $\varepsilon_{CT,O}$). But, there is the other parameter to take also into account : the number of electrons in the $n_O$ orbitals, on which depends the ultraviolet absorption cross section. When going from pyrocathecol to 1,3-benzodioxole that number decreases from 1.9071 to 1.8998. This decrease induces also a decrease of the intensity of the C.T. transition. The fact that for benzodioxan this number is 1.8978 (slightly lower than for 1,3-benzodioxole, when it should have to be higher) is not very significant since the geometry of benzodioxan is much more difficult to calculate. Actually, the six membered fused ring is not planar and the number of non-bonding electrons on the oxygen atoms is very sensitive to the geometry obtained.[14] Nevertheless, one sees that the differences of electron densities are small and the bond order ($BO_{CO}$) is certainly the determining factor.

## II - THE CHARGE TRANSFER TRANSITION IN THE 1,3-BENZODIOXOLE DERIVATIVES.

It has not been possible to correlate the intensity of the charge transfer transition ($\varepsilon_{CT,O}$) to the $\pi$ bond order between $C_\phi$ and the




$\varepsilon_{CT,O}$ is the intensity of the C.T. transition ($n_O \rightarrow \pi^*_\phi$) and
$P = (0.263\text{-}BO_{CO,p})(d_{O,p}\text{-}1.901)$.

**Figure 4**

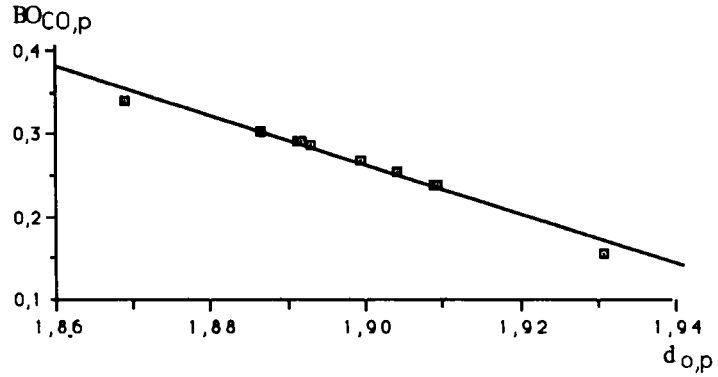


oxygen atom in the meta position to X, or to the electron density in the $n_O$ orbital of that oxygen. We shall note this bond order $BO_{CO,m}$, and the electronic density: $d_{O,m}$. On the contrary, there is a correlation between $\varepsilon_{CT,O}$, the bond order $BO_{CO}$, and the electron density $d_O$, when considering the oxygen atom in the para position to X (we shall note this bond order $BO_{CO,p}$ and this electron density $d_{O,p}$). This fact is not too much surprising since the literature has often emphasized mesomerism between substituents in para positions[21-23] although that phenomenon is very far to be perfectly understood[23] contrary to what is usually thought. Owing to this behaviour, the oxygen atom in para to X constitutes with $\phi$ and X some sort of a priviledged group in the molecule.

The correlation between $\varepsilon_{CT,O}$, $BO_{CO,p}$ and $d_{O,p}$ is illustrated in figure 4. $\varepsilon_{CT,O}$ has been plotted against a parameter:
$P = (0.263\text{-}BO_{CO,p})(d_{O,p}\text{-}1.901)$ and the equation of the curve is:

$$\varepsilon_{CT,O} = 3295 + 1308 \cdot 10^4 P$$

As P involves $BO_{CO,p}$, it is a measure of the sensitivity of the charge tranfer to the conjugation of $n_{O,p}$ with $\pi_\phi$. As it involves also $d_{O,p}$ it is a measure of the ability of the non-bonding electrons in $n_{O,p}$ to capture a photon of the proper frequency.




$BO_{CO,p}$ is the π bond order of the $C_\phi$-O bond in para to X and $d_{o,p}$ the electronic density of this oxygen for the Bzd-X molecules.

**Figure 5**



In fact, our MNDO calculations show that $BO_{CO,p}$ and $d_{o,p}$ are not independant [figure 5]. Actually, when $BO_{CO,p}$ increases, $d_{o,p}$ decreases because the non-bonding electrons on the oxygen atom become less non-bonding. They are partly used to strengthen the π part of the $C_\phi$-O bond [figure 7].

The definition of P shows that P is canceled by the values $BO_{CO,p}$ = 0.263 or $d_{o,p}$ = 1.901. These values makes $\varepsilon_{CT,O}$ minimum ($\varepsilon_{CT,O(minimum)}$ = 3295). They roughly agree with those calculated for the parent compound: 1,3-benzodioxole (respectively: 0.268; 1.8998). Moreover the corresponding $\varepsilon_{CT,O(minimum)}$ value given by the above relationship, is the same as the experimental one obtained for 1,3-benzodioxole ($\varepsilon_{CT,O}$ = 3300). In other words, the intensity of the C.T. transition is always higher than what is observed for 1,3-benzodioxole [Table 1]. Actually, when X is a π-donating group it tends to increase the π densities in ortho and para to its position (which is well known in monosubstituted benzenes). Our MNDO calculations show that the increase of the π electron density in para to X repels the π electrons of the para $C_\phi$-O bond towards the oxygen atom, and the $n_{o,p}$ orbital [figure 5, figure 7]. Consequently, a π-donating group decreases the value of $BO_{CO,p}$, since the electrons used for

**Table 1**

| X | $\lambda_{CT,O}$(nm) | $\varepsilon_{CT,O}$ |
|---|---|---|
| H | 231 | 3300 |
| OH | 236 | 3380 |
| $O^-$ | 242.5 | 5200 |
| $NH_2$ | 244.5 | 5330 |
| $NH_3^+$ | 234.5 | 3260 |
| CHO | 271.5 | 17100 |
| $COCH_3$ | 271.5 | 17760 |
| $CO_2H$ | 260 | 6940 |
| $CO_2^-$ | 252.5 | 6280 |
| $NO_2$ | 234 | 10400 |



conjugation, now are located on the oxygen atom, where they become more non-bonding. Thus, an increase of the $\pi$-donating character of X will increase the probability for a photon to be captured by the non-bonding electrons. Although the efficiency of the coupling between $\pi_\phi$ and $n_{o,p}$ decreases - phenomenon which is unfavourable to the charge transfer transition - the intensity increases because there is an increase of the capture probability.

MNDO calculations show that when X is a $\pi$ electron withdrawing group, X tends to decrease the $\pi$ densities in ortho and para to its own position, favouring the positive charges, phenomenon which is well known. But above all, the non-bonding electrons of the $n_{o,p}$ orbital are attracted towards $C_\phi$, and $d_{o,p}$ decreases. These electrons are used to strengthen the $C_\phi$-O bond. Thus, $BO_{CO,p}$ increases. The coupling between $n_{o,p}$ and $\pi_\phi$ being more developped, the electrons of the para oxygen atom can participate more efficiently to a transition towards $\pi_\phi^*$, though 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. In fact no two molecules have a transition with exactly the same identity. It is for 3,4-methylenedioxynitrobenzene (underneath noted Bzd-$NO_2$) that the transition is the most $\pi \rightarrow \pi^*$, since its value of $BO_{CO,p}$ (0.302) is the

highest one of all those which have been obtained in this work, and since $d_{O,p}$ (1.8867) is the lowest value. On the contrary, it is in the carboxylate derivative (the salt of piperonylic acid, underneath noted Bzd-$CO_2^-$) that the transition is the most $n_{O,p} \rightarrow \pi_\phi^*$, since $BO_{CO,p}$ has the lowest value, and $d_{O,p}$ the highest one. Unfortunatly, it has been impossible to obtain from our MNDO calculations realistic values for $BO_{CO,p}$ and $d_{O,p}$ as concerns Bzd-$O^-$ and Bzd-$NH_3^+$. It is well known that, sometimes, when there are charged species, MNDO calculations put too much emphasis on these charges.[26] Perhaps, in these two latter cases, the charges are too much near to the aromatic ring. Furthermore, only molecules whose C.T. transition can be identified without any ambiguity have been studied.

In Bzd-OH, there must be another C.T. transition involving the electrons of the non-bonding $n_{OH}$ orbital. In that molecule, the -OH oxygen is not part of the fused ring, in which there is strain. As it has been observed here above, strain red shifts the C.T. transitions of the oxygen of the fused ring. Thus, contrary to what happens for these oxygens, the charge transfer transition from $n_{OH}$ should not be red shifted. It should appear near to the transition observed for phenol itself [$\lambda$ = 200-210 nm; $\varepsilon_{max}$ = 5200 (methanol)]. Nevertheless, conjugation in Bzd-OH is much more extended than in $\phi$-OH. Conjugation red shifts the $\pi \rightarrow \pi^*$ transitions. Thus, the U.V. transitions of the benzene chromophore of Bzd-OH towards 180-220 nm ($^1E_{1u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1a_{1g}$ for the free benzene molecule) are red shifted, overlapping the $n_{OH} \rightarrow \pi_\phi^*$ transition, preventing it to be observed. There is only a very small fluctuation on the long wavelength side of the benzenic absorptions.

In Bzd-$O^-$ too, the electrons of the $n_{O^-}$ orbital should be involved in a charge transfer transition. In order to be able to compare Bzd-$O^-$ to Bzd-OH we have first of all to compare $\phi-O^-$ to $\phi-OH$.

In $\phi-O^-$ the intensity of the C.T. transition is increased [$\varepsilon_{max}$ = 9000; $\lambda_{max}$ = 222 nm (methanol)] compared to what is observed for $\phi-OH$. That increase arises certainly because there is a greater interaction of $n_{O^-}$ with $\pi_\phi$; that is to say a greater conjugation, a better coupling between $n_{O^-}$ and $\pi_\phi$. 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

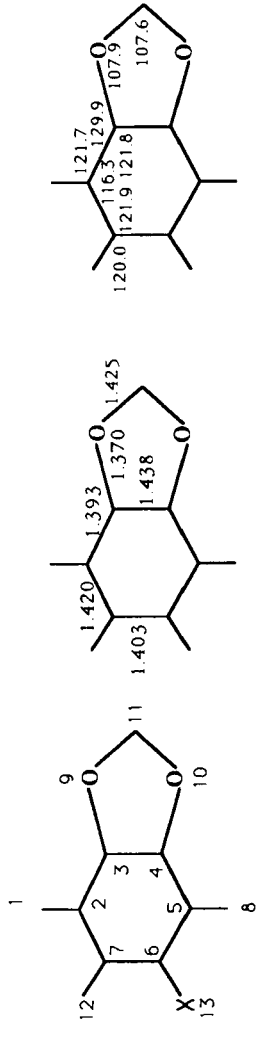
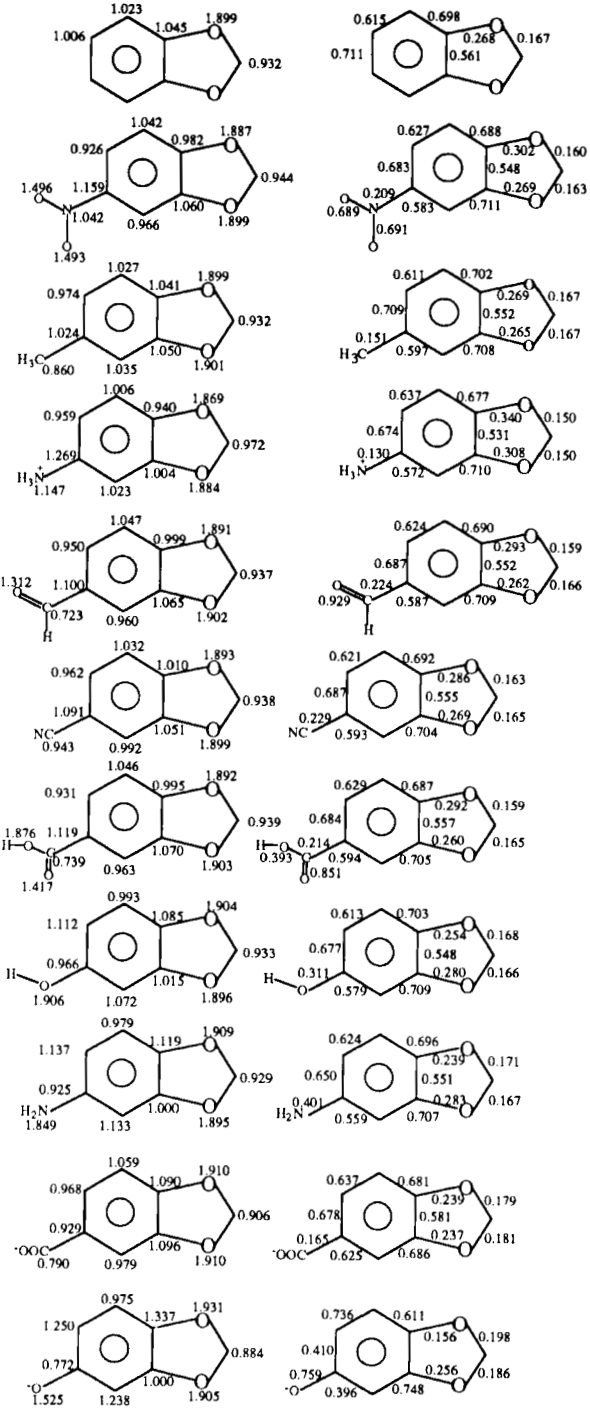



Figure 6



wavelength increases too ($\lambda$ = 220nm) because the energy of $n_{O^-}$ should be higher than that of $n_{OH}$.

Although the C.T. transition in $\phi$-$O^-$ is shifted to longer wavelength it is still overlapped by the $\pi \rightarrow \pi^*$ benzenic transitions. Actually, these transitions are also red shifted because of the increase of conjugation.

When comparing Bzd-OH and Bzd-$O^-$, the C.T. transition from the -OH group is changed in a C.T. transition originating on -$O^-$. Its intensity should be increased as it happens when comparing $\phi$-OH and $\phi$-$O^-$. It should be shifted also towards longer wavalengths. Actually, we observe that the above fluctuation is more visible, and it is shifted towards 220 nm. Intensity is difficult to evaluate because of the strong overlap ($\varepsilon$ = 15000 at 215 nm) with the benzenic transitions appearing to lower wavelengths. Nevertheless, we can be confident that the $n_{O^-} \rightarrow \pi^*_\phi$ transition cannot be confused with the $n_{O,p} \rightarrow \pi^*_\phi$ one and that we have not been wrong in our above identification of that latter transition which is clearly visible at 240 nm. The wavelength is too much higher and the intensity too much lower than what is expected for the $n_{O^-} \rightarrow \pi^*_\phi$ transition.

## III - MNDO CALCULATIONS ON 1,3-BENZODIOXOLE DERIVATIVES

In order to obtain accurate electron densities in the non-bonding orbitals of the oxygen atoms, ($n_O$, $d_{O,p}$, $d_{O,m}$), as well as accurate $\pi$ bond orders ($BO_{CO,m}$ and $BO_{CO,p}$) we have had to MNDO optimize the geometry of the 1,3-benzodioxole derivatives. Some of these geometries are given in figure 6 and table 2. We give also the geometry of 1,3-benzodioxole which has already been published[13] in order to allow comparison, and because in our preceding paper the value for the shortest bond of the

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Figure 7

On the left part of the figure, the electronic density of the p orbital of the atoms in the Bzd-X molecules; on the rigth part, the $\pi$ bond order of the differents bonds.

**Table 2**

| X | Bond 2-3 | Bond 4-3 | Bond 5-4 | Bond 6-5 | Bond 7-6 | Bond 2-7 | Bond 9-11 |
|---|---|---|---|---|---|---|---|
| -H | 1.393 | 1.438 | 1.393 | 1.420 | 1.403 | 1.420 | 1.426 |
| $-NH_2$ | 1.392 | 1.441 | 1.390 | 1.438 | 1.421 | 1.416 | 1.424 |
| -OH | 1.392 | 1.441 | 1.390 | 1.435 | 1.418 | 1.416 | 1.424 |
| $-NO_2$ | 1.393 | 1.438 | 1.392 | 1.431 | 1.413 | 1.418 | 1.428 |
| $-CO_2H$ | 1.394 | 1.435 | 1.393 | 1.432 | 1.417 | 1.418 | 1.426 |

Bond length (Å) of the $C_\phi$-$C_\phi$ bond i-j for the Bzd-X molecules.

| X | 3.2.1 | 4.3.2. | 5.4.3 | 6.5.4 | 7.6.5 | 6.7.2 | 7.2.3 | 9.3.4 | 10.4.3 | 8.5.4 | 13.6.5 | 12.7.6 | 11.9.13 | 12.7.6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -H | 121.7 | 121.8 | 121.8 | 116.3 | 121.9 | 121.9 | 116.3 | 108.4 | 108.4 | 121.7 | 118.1 | 120.0 | 107.7 | 107.7 |
| $-NH_2$ | 122.4 | 121.9 | 121.9 | 116.4 | 121.2 | 121.7 | 116.8 | 108.3 | 108.3 | 121.7 | 118.9 | 120.6 | 107.8 | 107.7 |
| -OH | 122.4 | 121.9 | 121.9 | 116.1 | 121.8 | 121.4 | 116.9 | 108.3 | 108.3 | 122.3 | 115.5 | 120.6 | 107.8 | 107.7 |
| $-NO_2$ | 122.8 | 121.8 | 122.2 | 115.6 | 122.3 | 121.3 | 116.7 | 108.2 | 108.5 | 120.9 | 118.5 | 121.8 | 107.9 | 107.6 |
| $-CO_2H$ | 122.8 | 121.4 | 122.3 | 116.9 | 120.0 | 122.9 | 116.4 | 108.4 | 108.6 | 120.9 | 121.4 | 120.4 | 107.6 | 107.8 |

Bond angle (°) around the benzene moiety for the Bzd-X molecules. Numbering of the atoms is in figure 6

The values which are not given have been kept constant using the values obtained when optimizing the 1.3-benzodioxole molecule (figure 6).

benzene moiety, owing to a typing mistake, was written 1.421 Å instead of the correct value: 1.403 Å. One sees that bond length alternation towards a hexatriene like structure within the benzene moiety, as well as the π bond orders which have been discussed for 1,3-benzodioxole[14] are preserved in Bzd-OH, Bzd-$CH_3$, Bzd-$CO_2^-$, Bzd-$CO_2H$ (but two bonds have almost the same value), Bzd-$NO_2$; in Bzd-$O^-$ and in Bzd-$NH_3^+$ the bond alternation is not preserved, but the first benzodioxole derivative has not been fully optimized and both of them are ions and the MNDO methods is not always reliable for charged species. In Bzd-CHO, alternation of bond length is not preserved, nor in Bzd-$NH_2$, although alternation of π bond orders still exists. These differences of alternation originates in the new π electron distribution on the ϕ moiety induced by the substituent, and because of the repulsion of the substituent bonds with the vicinal bonds of the benzene moiety. For example in Bzd-CHO rotating the -CHO group around the $C_\phi$-CHO bond by 180° to reach the other planar isomer could have increase the bond length n° 5-6 instead of 6-7 because of the repulsive interaction, thus increasing the alternation instead of decreasing it. Alternation of bond length is not quenched by the substituent, but shrouded up by their additive effects [Table 2].



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