# Near UV Spectroscopy and Electronic Structure of Dibenzo- $p$-dioxin, the Parent Compound of Highly Food-Polluting Agents 

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#### Abstract

Dibenzo- $p$-dioxin shows the first $\pi$-bond-order alternation observed when a six-membered ring is fused to a benzene moiety. This is particularly noticeable because the presence of phenolic oxygens in the molecule, and an increasing conjugation, should tend to quench alternation, when alternation is possible. Actually, oxygens tend to induce a quinodimethane-like structure. Alternation in dibenzo-$p$-dioxin is explained firstly on the basis of that the two phenolic oxygens have to share their $p_{\pi^{-}}$ electrons with two benzene moieties, which decreases their effects towards each other. This limits their quenching ability. Alternation is explained secondly on the basis of the fact that strain, which distorts the bridgehead bonds, inducing alternation, is increased compared to benzodioxan.

Intensity calculations using the Interaction Vector Model, and the above electron-structure calculations, lead to results that fit with experiment. This shows that electron-structure behaviour is understood.


Dibenzo-p-dioxin (Fig. 1A) is the parent compound of a series of widely encountered toxic substances, often issued from waste industries. As semivolatile substances they are found far from the regions where they have been produced. Being fat-soluble, they accumulate in higher animals. There is a tremendous amount of work done on these substances as well as concerns their occurrence in nature, the way they are introduced in animal or human food, and their effects on environment and human health. Actually, it is well known that small dioxin concentrations cause negative effects on health. As concerns only the year 2000, more than 250 scientific research papers have been issued, but very few bearing on physicochemical studies, and only two of them on spectroscopy $[1,2]$ or alike [3].

The present work is devoted to the intensity of the secondary transition of the UV spectrum of dibenzo-$p$-dioxin, in relation to its $\pi$-electronic structure. Actually, the secondary transition of the benzene chromophore is the most prominent feature in the near UV spectrum of benzene derivatives, being the longest wavelength transition. Furthermore, being an electronically forbidden transition, its intensity is very sensitive to the symmetry and the structure of the molecule, particularly its $\pi$-electronic one.

## THE SECONDARY TRANSITION OF DIBENZO-p-DIOXIN

The secondary transition of benzene is forbidden because of its $D_{6 h}$ symmetry. Its intensity is very weak (benzene: $\left\{\varepsilon_{\max }\right\}=220, \lambda_{\max }=255 \mathrm{~nm}$ ), but it increases all the more as the ring is distorted towards a new symmetry, provided this new symmetry allows the transition [4-8]. Long ago, Sklar and others [9-16] proposed a vector scheme (Fig. 3Aa) to understand intensity. The transition moment was assumed to be the vector addition of the individual contributions of the substituents. This approach was too much qualitative. The Interaction Vector Model [17, 18] (IVM) is more satisfactory. IVM has been used on more than one hundred molecules [18-26]. It is used also in this work. Experiment is given as $\varepsilon_{\mathrm{sm}}$, the maximum of the smoothed absorption curve (Ballester and Riera [27], calculated value: $\left\{\varepsilon_{\mathrm{sm}, \mathrm{calc}}\right\}$ ) (benzene: $\left\{\varepsilon_{\mathrm{sm}}=110\right\}$ ). As usual, the molar extinction coefficient, when it is written using the Greek letter $\varepsilon$, is given without units, it also has units of $1000 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$.

The maximum of the transition of dibenzo- $p$-dioxin lies at $289 \mathrm{~nm}\left(\varepsilon_{\max }=\varepsilon_{\mathrm{sm}}=3950\right.$; methanol, Fig. 2). As concerns 1,4-benzodioxan (Fig. 1B, Fig. 2) the 00 band of the subsystem B is still visible; intensity is
A

B


D

$E$

F

G

H



Fig. 1. Molecules or formulas appearing in this work. A. Dibenzo-p-dioxin. B. Benzodioxan. C. Catechol. D. Indane. E. 1,3Benzodioxole. F. Tetralin. G. Quinodimethane. H. Qinodimethane-like molecule with fused ring. I. The numbering of the bond lengths begins at the bridgehead bond, or at the bond between the two substituents.


Fig. 2. Spectra of the secondary transition (medium methanol). Dibenzo-p-dioxin (upper spectrum), $\varepsilon_{\max }=3950$ (from unpublished work of Dr. B. Dutour, by permission). Benzodioxan (lower spectrum), $\varepsilon_{\max }=2450$.
$\varepsilon_{\max }=2450$ (methanol), which is also approximately $\varepsilon_{\mathrm{sm}}$, at 278 nm . The latter value is near to $\varepsilon_{\max }=2550$ ( 274 nm ; methanol) obtained for catechol (Fig. 2) and for the dimethoxy derivative. The dioxan-fused ring does not change much intensity. Actually, being almost without strain, it cannot perturb the bridgehead bond length, introducing no extra symmetry distortion in the ring.

Dibenzo- $p$-dioxin is shifted towards longer wavelengths, shorter frequencies, compared to benzodioxan. This shows that the two benzene moieties interact through the oxygens, using their $p_{\pi}$-nonbonding orbitals. Such a conjugation allows every $\pi$-electron a greater delocalization space. It is well known, using the simplest free-electron model, that an increase of the delocalization space decreases the energy gap between the electronic levels, and increases the wavelength necessary to promote electrons on higher levels.

More interesting is the intensity. Considering the benzene rings and the two oxygens, one could think that intensity could be near to that of two cate-
chol chromophores (or 1,4-benzodioxan ones). This would lead to: $\varepsilon_{\mathrm{sm}}=2500 \times 2=5000$, the value is much higher than that of the experiment (3950). Thus, dibenzo- $p$-dioxin displays a behaviour of its own, which needs some electronic data to be understood.

## THE $\pi$-ELECTRONIC STRUCTURE OF DIBENZO- $p$-DIOXIN

Perturbation on the $D_{6 h}$ symmetry depends on the $\pi$-donating power of the oxygens. In benzodioxan there are 1.8952 electrons in an oxygen $p_{\pi}$-orbital ( 0.1048 electron has been lost, being given to $\pi_{\phi}$ ), in dioxin this number is 1.8639 ( 0.1361 electron has been lost: 0.0313 electron more than in benzodioxan), as calculated by the MNDO method [28]. Thus, two benzene rings are only one third more efficient than only one (each oxygen is $68 \%$ as much efficient as an oxygen in the phenol molecule). Actually, electrons are much more difficult to withdraw from the oxygens as
much of them have already been withdrawn, owing to the positive charge they leave.
$N_{\pi}$, the number of $\pi$-electrons is 6.1858 in catechol, 6.1572 in benzodioxan. In one of the benzene rings of dioxin it is 6.1367 . In benzodioxan the $P_{\text {co }}$-bond order is 0.2717 ; it is only 0.2540 in dioxin. Bond order is not much decreased because of the greater extension of conjugation which smoothes $\pi$-bond orders differences as it does in the long polyene chains.

It is particularly interesting to notice the quite unusual fact that, although the $\pi$-system is extended, and although such a phenomenon is already observed only rarely for small $\pi$-systems [29], there is an alternation of the $\pi$-bond orders inside the benzene rings of dioxin. Starting from the bridgehead bond (bond $a$ (Fig. 1I) between the two substituents), the $\pi$-bond orders are: 0.5961 (bridgehead bond $a$ ), 0.6696 (bond $b), 0.6460$ (bond $c$ ), 0.6820 (bond $d$ ). Such a phenomenon is observed neither in benzodioxan: 0.6200, $0.6281,0.6788,0.6506$, nor in catechol: $0.5924,0.6505$, $0.6558,0.6723$. As concerns the benzodioxan bonds, as calculated by the MNDO method, still starting from the bridgehead bond, the values are: $1.427 \AA, 1.415 \AA$, $1.405 \AA, 1.406 \AA$, in dibenzo-p-dioxin: $1.433 \AA, 1.410$ $\AA, 1.409 \AA, 1.403 \AA$. The difference between the second and the third bond lengths is under the accuracy of the MNDO method. One could say that the bond length pattern is near to alternation. In fact, alternation of bond lengths and alternation of $\pi$-bond orders are related. A bond is lengthened if it is weakened, if its $\pi$-bond order decreases and vice versa. Alternation of bond lengths needs a strong alternation of $\pi$-bond orders, and the alternation of $\pi$-bond orders needs the lengthening or the shortening of the bridgehead bond.

Bond lengths alternation can arise when there is a ring fused to the benzene chromophore. If this fused ring imposes a strain on the bridgehead bond, as it is observed when the fused ring is a five-membered one, lengthening or shortening that bond, it destroys the $D_{6 h}$ symmetry of the chromophore, towards a $C_{2 v}$ one. The $C_{2}$ axis is lying in the middle of two opposed bonds, one of them being a bridgehead bond. It is the $D_{6 h}$ symmetry which makes all the six bond spaces, between the carbon atoms, electronically equivalent. When this symmetry is strongly distorted, $\pi$-bond lengths alternate, as they do in linear conjugated chains. The bridgehead bond would be lengthened to an almost infinite length, this bond would be almost broken and one would obtain an alternation similar to that observed in the hexatriene molecule.

The lengthening of the conjugated system in dioxin compared to benzodioxan, should smooth the bondorder differences and the bond-order alternation, as occurs when the lengths of polyenes are increased. The contrary is observed, particularly for the bridgehead bond. Actually, in dibenzo-p-dioxin the increase of conjugation shortens the fused ring, as explained underneath. This increases the strain on the bridge-
head bond, lengthening it to release the strain, distorting the $D_{6 h}$ symmetry, inducing the $\pi$-bond-order alternation.

Bond length alternation imposes some specific reactivity to the benzene ring. This has been known for a long time in some aliphatic-type fused rings as the Mills-Nixon effect [28].

Alternation arises in indane (Fig. 1D), in 1,3benzodioxole (Fig. 1E), and in some other fivemembered fused rings $[6,7]$, too. No alternation has ever been observed when the fused ring is a sixmembered one, such as in tetralin (Fig. 1F), benzodioxan (Fig. 1B), etc. Dibenzo-p-dioxin is the first case being observed. When bond lengths alternate, bond orders do too, since bond length depends on the strength of the bond, i.e. on the value of the $\pi$ bond order. But, when $\pi$-bond orders alternate, bond lengths do not alternate necessarily. Alternation of bond orders has to be strong enough to impose bond lengths alternation. In dioxin there is no bond length alternation, but only a $\pi$-bond order one. This alternation is quite surprising since, at first glance, the fused ring in dioxin should not impose on a bridgehead bond a strain greater than in benzodioxan. In fact, it is possible to evaluate strain. As given above, the calculated bridgehead bond length in dioxin is $1.4326 \AA$, longer, thus under a greater strain, than in benzodioxan: $1.4269 \AA$. Actually, the perimeter of the fused ring is shorter in dibenzo- $p$-dioxin than in benzodioxan: $7.088 \AA$ in benzodioxan, excluding the bridgehead bond and $6.917 \AA$ in dioxin, excluding one of the bridgehead bonds (the other is part of the fused ring). Actually, the aliphatic $\mathrm{C}-\mathrm{C}$ bond is replaced by a shorter benzene bond. Furthermore, conjugation establishes all along the fused ring, increasing the $\pi$-bonding character. This shortening increases the strain imposed on the bridgehead bond; it increases its length to release the strain, thus decreasing its $\pi$-bond order. Such a perturbation can cause the $\pi$-bond-order alternation but it is not strong enough to cause bond lengths alternation.

What MOs are responsible for such a $\pi$-bond-order alternation? In fact, calculation shows that the $\pi$ -bond-order alternation involves the contribution of all the $\pi$-MOs. It has not been possible to find in dibenzo-$p$-dioxin one or several MOs more involved. Nevertheless, this molecule being complex it is easier to find the key MOs on lighter molecules.

One of the bonds of a free benzene ring has been lengthened to $1.4326 \AA$, the length of the bridgehead bond in dibenzo- $p$-dioxin. Alternation of the bond lengths ( $1.433 \AA, 1.400 \AA, 1.412 \AA, 1.401 \AA$ ) as well as a strong alternation of $\pi$-bond orders ( $0.6309,0.6996$, $0.6358,0.6952$, to be compared to 0.6667 in the benzene molecule) is obtained. The lowest $\pi_{\phi}$-MO in the free benzene molecule (the combination without node of the six $p_{\pi}$-atomic orbitals) leads to the same contribution to the six $\pi$-bond orders. In the distorted
benzene the corresponding orbital displays the next partial $\pi$-bond orders: $0.3219,0.3290,0.3391,0.3418$. This $\pi$-MO is not involved in the alternation: its partial $\pi$-bond order decreases for the lengthened bridgehead bond and increases for the opposed one. Actually, lengthening a bridgehead bond drives slightly the $\pi_{\phi}$-system towards hexatriene. In this latter molecule alternation does not involve the lowest $\pi$-MO since this MO displays any node. In the free electron model the maximum electron density lies in the middle of the $\pi$-space, decreasing towards each end of the molecule. It is the reason why, here, the highest partial $\pi$-bond order corresponds to the bond opposed to the lengthened bridgehead one. Furthermore, none of the two upper $\pi$-MOs displays an alternation of its $\pi$-bond orders. The highest are: $0.4930,0.0212,-0.0214,0.5059$; the other: $-0.1840,0.3494,0.3181,-0.1522$. Nevertheless, the sum of their partial $\pi$-bond orders leads to the alternation: $0.3090,0.3706,0.2968,0.3534$. Thus, alternation arises when adding the effects of the two HOMOs which are degenerate in the free benzene molecule (degeneracy is removed in the distorted benzene molecule).

As concerns the $\pi$-bond orders in the distorted catechol molecule ( $1.4326 \AA$ for the bridgehead bond length), these values are obtained: $0.5964,0.6474$, $0.6588,0.6697$. No alternation is produced by the lengthening of the bridgehead bond. This means that introducing two oxygen atoms quenches the $\pi$-bondorder alternation effect. One of the reasons lies in the fact that the $\pi$-donating effect of the oxygens increases the $\pi$-density within the benzene ring. This overwhelms the weaker electronic effects due to the strain. Lengthening more the bridgehead bond should increase the strain effect and perhaps lead to an alternation of $\pi$-bond orders. Increasing slightly the bridgehead bond length to $1.4400 \AA$ produces the $\pi$-bondorder alternation: $0.5848,0.6584,0.6475,0.6804$. Increasing it much more, to $1.5500 \AA$, leads to: 0.4576 , $0.7553,0.5374,0.7719$, and to the next bond lengths alternation: $1.5500 \AA, 1.3923 \AA, 1.4231 \AA, 1.3857 \AA$. This confirms the fact that the $\pi$-bond-order alternation is easier to obtain than the bond length alternation. It is only when the $\pi$-bond orders alternate strongly that the bond lengths are imposed to alternate.

The second reason explaining the tendency of the phenolic oxygens to quench the alternation of the $\pi$ bond orders lies in the fact that the oxygens increase the $\pi$-bond orders of the phenolic bonds: $\mathrm{O}-\phi$. This phenomenon is more important than the increase of the $\pi$-electron number in the benzene moiety as observed here above. Actually, the oxygens in catechol (thus in dibenzo-p-dioxin, too) play the part of two more centres to be included in the $\pi$-system with their $p_{\pi}$-orbitals, and establishing a nonzero $\pi$-bond order with the $\pi_{\phi}$-system. Thus, the catechol molecule has to be compared to the quinodimethane model
(Fig. 1G). In this model, calculations show that conjugation is weak. The bond orders of strong $\pi$-bonds are near to 1 , and the others display only much smaller $\pi$-contributions: 0.929 for the exocyclic $\pi$-bonds, and 0.244 for the bond $a, 0.269$ for $b, 0.920$ for $c, 0.313$ for $d$. The exocyclic bonds are almost completely $\pi$-ones, which imposes the three bonds adjacent to the substituents (the bond $a$ and the two $b$ ones) to have only little $\pi$-character. Thus, inside the "benzene" ring, the presence of three adjacent bonds displaying only a small $\pi$-character (the bond between the substituent and the adjacent ones) is able to destroy any alternation which could be induced by fused rings. Of course, in catechol, the $\pi_{\phi-\mathrm{O}}$-bond order is much weaker than a $\mathrm{C}=\mathrm{C}$ exocyclic bond in this quinodimethane-like molecule, thus the oxygens are less efficient to quench alternation. Thus, in dibenzo- $p$-dioxin their $\pi_{\phi-O}$-bond order is decreasing compared to benzodioxan, their quenching effect decreases, too, and the alternation of $\pi$-bond orders is observed.

Using the quinodimethane model one can introduce the two substituents in a five-membered fused ring as in Fig. 1H. Although in indane the bond lengths and the bond orders display a strong alternation pattern, alternation is completely quenched in this model, confirming the quenching role of the exocyclic $\pi$-system: 0.899 for the exocyclic $\pi$-bonds, and 0.277 for the bond $a, 0.297$ for $b, 0.909$ for $c, 0.328$ for $d$. Although it is not strong enough to induce a $\pi$ bond alternation, the five-membered fused ring tends to oppose the effects of the exocyclic $\pi$-system and tends to restore, although quite weakly, the balance between strong and weak $\pi$-bond orders, which is the first step before bond length equalization and then alternation.

Thus, in dibenzo- $p$-dioxin, the strain imposed on the bridgehead bond by the fused ring is greater than in benzodioxan and the distortion leads to an alternation of the $\pi$-bond orders. For a given lengthening of the bridgehead bond, the $\pi$-donating effect of the oxygen atoms tends to quench the alternation of $\pi$-bond orders and bond lengths, because they tend to impose a quinodimethane structure. In dibenzo-pdioxin, compared to benzodioxan, the $\pi$-donating effect of the two oxygens does not quench completely the $\pi$-bond-order alternation induced by strain. This arises from the fact that this $\pi$-bond-order alternation is induced by a greater strain, and by the fact that the $\pi$-donating effect of the oxygen atoms towards each one of the two benzene rings is decreased compared to the pure phenolic oxygens of benzodioxan. Actually, the $\pi$-donating effect of the oxygens has to be shared with the two benzene rings, and these oxygens are less efficient to quench bond-order alternation. Nevertheless, the $\pi$-donating effect of the oxygens is still too strong to allow alternation of bond lengths.

Calculations show that the two oxygen atoms of dibenzo- $p$-dioxin, sharing their $\pi$-donating effects to-









Fig. 3. A. Direction of the basis vectors. All the directions are relating to each other. a) First drawing: the Sklar's basis virtual vectors pattern. b) Other drawings: the basis vectors corresponding to the positions of the substituents. The interaction vectors have been drawn inside the benzene ring. B. Strain vectors corresponding to the fused ring. The strain vectors bisect the angle between the two basis vectors of the two substituents corresponding to the fused ring. The basis vectors at the positions of substitutions have also been drawn, since the direction of a given strain vector depends on the direction chosen for the basis vector pattern. Three examples are given.
wards two benzene moieties instead of one in catechol, are less efficient, thus less perturbating as concerns the $D_{6 h}$ symmetry of the chromophore. Thus it should be possible to use the IVM with parameters for the substituents adapting these parameters to mirror the lack of efficiency.

## INTENSITY OF THE SECONDARY TRANSITION OF DIBENZO- $p$-DIOXIN

## The Interaction Vector Model

Although the IVM uses the Sklar's vector scheme (Fig. 3A $a$ ), three new concepts have been introduced. They strongly change the approach: the interaction vector (Fig. 3Ab) takes into account interactions of substituents. The strain vector (Fig. 3B) arises from the strain imposed by fused rings (symmetry distortion). A component related to a photonic crosssection has been used, too. It increases as much as the substituents coupled to the $\pi$-system enlarge this $\pi$-system, increasing its efficiency to capture photons.

The modulus of the basis vector (Fig. $3 \mathrm{~A} a$ ) for the -OR substituents has been calculated as: $n_{\mathrm{O}}$ $=0.3900$, for a methyl substituent $n_{\mathrm{C}}=0.0980$ (no such substituent here) $[17,18]$. The interaction vector length for two ortho, then meta, then para - OR substituents is: $n_{\mathrm{O}, o}=0.1330, n_{\mathrm{O}, m}=0.0450, n_{\mathrm{O}, p}=$ -0.1800 . An interaction vector lies on the line bisecting the angle of the two basis vectors involved in the interaction (Fig. 3Ab). $\boldsymbol{n}$ (length $n$ ) is the vector sum of the basis vectors and all the interaction vectors.
$n_{\mathrm{C}}$ is the number of alkyl substituents (no such substituents here), $n_{\mathrm{O}}$ the number of -OR ones. $V$ is a weak vibrational component. $S$ and $\sigma\left(\sigma=S^{1 / 2}\right)$ are functions of the number and of the nature of substituents

$$
V=0.0180+0.0390 K+0.0030\left(n_{\mathrm{C}}+n_{\mathrm{O}}\right),
$$

$$
\begin{aligned}
& \text { if } n_{\mathrm{O}}=0 K=0, \text { if } n_{\mathrm{O}} \neq 0 K=1 \\
& S=\left(5 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)\right)+n_{\mathrm{C}} /\left(4.8+0.2 n_{\mathrm{C}}^{\left(2+0.5 n_{\mathrm{O}}\right)}\right)
\end{aligned}
$$

$\boldsymbol{S}$ and $\boldsymbol{n}$ display the same direction. $a=n^{1.5} \sigma^{0.5}, b=$ $n(n+\sigma) / 2$. Then $p=(a+k b) /(1+k)$ with $k=d^{6}$, and $d=|n-\sigma|$.
$\boldsymbol{R}$, related to the fused ring effect, is the sum of all the $\boldsymbol{R}_{\mathrm{i}}$ around the benzene moiety. Calculation is done for the corresponding parent molecule with $-\mathrm{CH}_{3}$ (for an alkyl substituent) and -OR..., and no fused ring. This leads to $S, \sigma, n, p, V$. Strain is taken into account as a vector $\boldsymbol{R}$, then as $\boldsymbol{S}^{\prime}$ : $\boldsymbol{S}^{\prime}=\boldsymbol{S}+\boldsymbol{R}$. Here, only one fused ring imposes strain on the chromophores. The direction of a given $\boldsymbol{R}_{\mathrm{i}}$ proceeds from the basis vector pattern (Fig. 3B). $R$ is given the next values in the IVM: +1.92 for an aliphatic five-membered fused ring, +0.55 for an aliphatic six-membered one, +0.55 for a benzodioxoletype one (methylenedioxy fused rings), and -0.1 for a benzodioxan-type one.

A general relationship has been obtained: $\varepsilon_{\mathrm{sm}, \text { calc }}=$ $4905\left[1.025 p\left(S^{\prime} / S\right)+V\right]$.

## Constants

Basis parameters have been established using several molecules $[17,18]$. Here, assuming that the conjugation behaviour should be similar in dioxin as in diphenyl ether derivatives, neglecting the conformation differences, and using the spectra of diphenyl ether-type molecules as a basis, one finds that $S=$ 0.6795 for the monosubstituted compound with - $\mathrm{O} \phi$, instead of 1 for an -OR phenolic group (which imposes $S=3.6014 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$ for the relationship concerning - $\mathrm{O} \phi$, with $n_{\mathrm{O}}$ being the number of $-\mathrm{O} \phi$ substituents), $n=0.2858, V=0.0392$. Assuming too, on an empirical basis, that the interaction vectors are those for -OR multiplied by 1.118, thus in case of $\phi-\mathrm{Oc}-\phi \varepsilon_{\mathrm{sm}, \exp }=1750, \varepsilon_{\mathrm{sm}, \text { calc }}=1785 ; \mathrm{MeO}-\phi-$
$\mathrm{O}-\phi-\mathrm{OMe}: \varepsilon_{\mathrm{sm}, \exp }=4150, \varepsilon_{\mathrm{sm}, \mathrm{calc}}=4365 ; \phi-\mathrm{O}-$ $\phi-\mathrm{O}-\phi: \varepsilon_{\mathrm{sm}, \exp }=3270, \varepsilon_{\mathrm{sm}, \mathrm{calc}}=3205$.

## Calculations

When only -OR substituents are present $S=$ $5 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$. Thus, when there is only one -OR substituent $n_{\mathrm{O}}=1$, and the value of $S$ is $S=1$. For - $\mathrm{O} \phi$ one has obtained here above the next value $S_{\mathrm{O}-\phi}=0.6795$. This means that, if one considers - $\mathrm{O} \phi$ as a sort of -OR substituent, one will use the relationship $S=5 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$. And to obtain $S=0.6795$ from that relationship one has to assume that $n_{\mathrm{O} \phi}=0.6643$. As concerns $S$, the oxygen in diphenyl ether would be similar to the 0.6643 part of an OR oxygen. Thus, instead of using $S=3.6014 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$ for $-\mathrm{O} \phi$ it is possible to use the relationship obtained for the -OR phenolic substituent: $S=5 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$, with the number of - O $\phi$ substituents multiplied by 0.6643 (notice that this is near to 0.68 , the value which has been calculated for the comparison of $\pi$-donating effects). If there are - $\mathrm{O} \phi$ and -OMe substituents on the same benzene ring, the number $n_{\mathrm{O}}$ to take into account is $n_{\mathrm{O}}=n_{\mathrm{OR}}+0.6643 n_{\mathrm{O} \phi}$.

The dibenzo- $p$-dioxin molecule displays a fused ring separating the two benzenes. The effect of strain on intensity should be weak since for an aliphatic sixmembered fused ring (such as in tetralin) $R=+0.55$, and when there are two oxygen atoms in the $\alpha$ position, such as in benzodioxan, $R$ is reduced to -0.10 . The difference is 0.65 . In benzodioxan the two oxygen atoms cause $R$ to decrease in comparison with tetralin by a quantity 0.65 . An - $\mathrm{O} \phi$ substituent is worth 0.6643 times an -OR one as concerns $S$. In the IVM the strain is considered as modifying $S$ ( $S^{\prime}=S+R$ ), i.e. as the same nature as $S$. Thus it is possible to do a proportion and $R=0.1182$. One is aware that this is a rough estimate. Nevertheless, this is a small value which has not to be known with great accuracy since it will be involved only in addition on a much greater value, more than ten times (see below).

As the substituents lie in ortho positions, the two basis vectors display a $120^{\circ}$ angle and the length of their sum is equal to the length of one of them. Thus their sum is $n=0.2858$. The interaction vector is directed to the same direction as the basis vectors sum. As the interaction vector length for ortho -OR groups is $n_{\mathrm{O}, o}=0.1330$, and using the empirical correction obtained above, for two ortho - $\mathrm{O} \phi$ substituents $0.1330 \times 0.118=0.1487$. The new value for $n$, taking into account interaction is $n=0.2858+$ $0.1487=0.4345$.

As concerns $S, S=3.6014 n_{\mathrm{O}} /\left(4.8+0.2 n_{\mathrm{O}}^{2}\right)$ $=1.2862$; thus $\sigma=1.1341$. Considering that $a=$ $n^{1.5} \sigma^{0.5}=0.2864 \times 0.06494=0.30501, b=n(n+$ $\sigma) / 2=0.3408$, and $k=0.0000$, thus $p=a=0.3050$. As $R=0.1182, S^{\prime}=S+R=1.2862+0.1182=$
1.4044 and $S^{\prime} / S=1.0919$. The strain imposed by the fused ring causes a change of $9 \%$ in the intensity of the secondary transition. As concerns $V$, to the basic value used for one - $\mathrm{O} \phi$ substituent, 0.003 has to be added for the second one: $V=0.0392+0.003$ $=0.042$. Thus $\varepsilon_{\mathrm{sm}}=4905(1.025 \times 0.305 \times 0.0919$ $+0.042)=1880$. The secondary transition for the dibenzo-p-dioxin molecule itself is $1880 \times 2=3760$, when the experiment gives 3960 . Difference is only 5 $\%$. In preceding works, calculations have been considered as satisfactory when differing less than $10 \%$ from experiment.

One could be interested in calculations grounded on the assumption that the oxygen atoms are the same as in classic phenolic -OR substituents. Using 0.3900 as the basic vector length for the -OR group and 0.1330 as ortho interaction value $n=0.39$ $+0.133=0.523, S=1.7857, \sigma=1.3363, \sigma^{0.5}=$ 1.1560. Thus $a=0.4372, b=0.4862$, and $k=0.2894$, leading to $p=0.5165$. As $R=-0.1$ as indicated above, a dioxan-type fused ring decreases slightly intensity, while a dioxin-type one increases it slightly. Thus $S^{\prime}=S+R=1.787-0.1=1.687$. $S^{\prime} / S=$ $1.6857 / 1.7857=0.9440, V=0.063$. This gives $\varepsilon_{\mathrm{sm}}=$ 2760 and for the two benzene moieties 5520. Interaction between the two benzene moieties, through the two "nonbonding" orbitals of the oxygens and their electrons, decreases intensity from 5520 to 3960 . This is a strong effect. A part of the strain effect of the fused ring is quenched, but less than - OR groups would do.

Using the IVM, one is able to find the correct value, as concerns the intensity of the secondary transition of dibenzo- $p$-dioxin, on the ground that the strain imposed on the benzene moieties is stronger than in benzodioxan, and that the $p_{\pi}$-AOs of the oxygen atoms are less coupled with the $\pi$-system, thus less able to quench the strain effect. This confirms MNDO calculations.

## CONCLUSION

As intensity calculations show, the different factors (strain, oxygen quenching of alternation) which cause the unusual $\pi$-bond-orders alternation in dibenzo- $p$ dioxin are correctly taken into account, and the behaviour of the $\pi$-system of the molecule is understood. Particularly, the tendency towards a quinodimethanelike structure which quenches alternation has been brought out.

## REFERENCES

1. Klimenko, V. G., Nurmukhametov, R. N., Gastilovich, E. A., and Lebedev, S. A., Opt. Spektrosk. 88, 379 (2000).
2. Gastilovich, E. A., Serov, S. A., Korol'kova, N. V., and Klimenko, V. G., J. Mol. Struct. 553, 243 (2000).
3. Klimenko, V. G., Nurmukhametov, R. N., Gastilovich,
E. A., and Lebedev, S. A., Opt. Spektrosk. 88, 385 (2000).
4. Vidal, B., Bastaert, G., and Brocard, J., Spectrochim. Acta 35A, 1043 (1979).
5. Denis-Courtois, D. and Vidal, B., Spectrochim. Acta 39A, 735 (1983).
6. Vidal, B., Conan, J.-Y., and Lamaty, G., Aust. J. Chem. 41, 1107 (1988).
7. Vidal, B., Vardin, J., and Darry-Henaut, A., Chem. Pap. 44, 603 (1990).
8. Vardin, J. and Vidal, B., Chem. Pap. 46, 301 (1992).
9. Sklar, A. L., J. Chem. Phys. 10, 135 (1942).
10. Sklar, A. L., Rev. Mod. Phys. 14, 232 (1942).
11. Förster, Th., Z. Naturforsch. 2a, 149 (1947).
12. Platt, J. R., J. Chem. Phys. 19, 263 (1951).
13. Petruska, J., J. Chem. Phys. 34, 1111 (1961).
14. Petruska, J., J. Chem. Phys. 34, 1120 (1961).
15. Stevenson, P. E., J. Chem. Educ. 41, 234 (1964).
16. Stevenson, P. E., Ph.D. Thesis, Part I. University of Chicago, 1964.
17. Vidal, B., Spectrosc. Lett. 27, 41 (1994).
18. Vidal, B., Spectrosc. Lett. 27, 709 (1994).
19. Vidal, B., Chem. Pap. 55, 7 (2001).
20. Vidal, B., Spectrosc. Lett. 33, 681 (2000).
21. Vidal, B., Spectrosc. Lett. 28, 191 (1995).
22. Vidal, B., Spectrosc. Lett. 29, 379 (1996).
23. Vidal, B., Spectrosc. Lett. 29, 1259 (1996).
24. Vidal, B., Spectrosc. Lett. 31, 111 (1998).
25. Vidal, B., Spectrosc. Lett. 31, 717 (1998).
26. Vidal, B. and Wong Pin, F., Spectrosc. Lett. 30, 1301 (1997).
27. Ballester, M. and Riera, J., Tetrahedron 20, 2217 (1964).
28. Dewar, M. J. S. and Thiel, W., J. Amer. Chem. Soc. 99, 4899 (1977).
29. Mills, W. H. and Nixon, I. G., J. Chem. Soc. 132, 2519 (1930).
