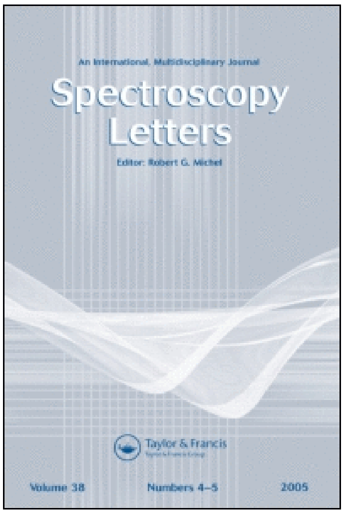

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Bernard Vidal[a]
[a] Laboratoire de Chimie Organique, Faculté des Sciences, Université de La Réunion, Saint Denis cédex, FRANCE (D.O.M.)

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THE INCIDENCE OF STRAIN ON THE QUENCHING OF THE VIBRATIONALLY INDUCED INTENSITY OF THE SECONDARY TRANSITION OF THE BENZENE CHROMOPHORE : A NEW EXPLANATION

Bernard VIDAL

Laboratoire de Chimie Organique, Faculté des Sciences
Université de La Réunion, 15 Avenue René Cassin
97489 - Saint Denis cédex, FRANCE (D.O.M.)

It has been assumed for a long time that strain, induced by rings fused to the benzene chromophore, limits the amplitude of vibrational motions, and then decreases the intensity of the vibrationally induced part of the secondary transition. That assumption has been grounded on the well known RAPOPORT and SMOLENSKY's work. [1-2]

Actually, the secondary transition of the free benzene molecule (towards 250-260 nm) is electronically forbidden because of the D_{6h} symmetry of that molecule. [3-7] Nevertheless, the coupling of electronic wavefunctions and vibrational ones, shows that a weak intensity is vibrationally induced. That vibrational component increases slightly with the number of substituents around the benzene ring (BALLESTER and RIERA [8]). This vibrational component is not to be confused with the increase of intensity observed when the chromophore looses its D_{6h} symmetry under substitution. Intensity is all the more increased as the substituents are more perturbating and the electronic symmetry much more distorted. [3-7]

The part of the RAPOPORT and SMOLENSKY's work wich is of concern to us is devoted to molecules I and II (Figure 1). The spectra of these molecules are well known, mainly from their appearance in the JAFFE and ORCHIN book. [2] In molecule I the vibrational fine structure is clearly visible with : $\varepsilon_{max} = 880$. In the spectrum of molecule II there is no fine structure at all and : $\varepsilon_{max} = 467$. This decrease has been assumed to originate in the strain which strongly reduces the vibrational amplitudes of the chromophore, thus the strain would quench the vibrationally induced intensity. In fact, we should like to show that this decrease is consistent with electronic symmetry considerations, and that

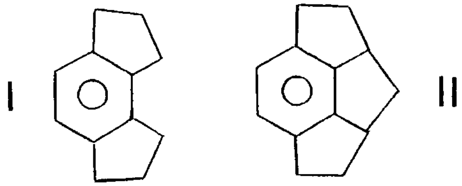

Figure 1. Molecules I and II displaying a strain effect

there is no reason to invoke such a small effect as the vibrational motion, or to explain the whole phenomenon on this only ground.

First of all, it is not possible to compare the two ε_{max} values. For the first molecule, ε_{max} is the molar extinction coefficient measured at the highest vibrational band of the secondary transition. For the second molecule, as there is no vibrational fine structure, ε_{max} is the maximum of the continuum of the transition. It would be best to use ε_{sm} which is the maximum of the smoothed absorption curve as defined by BALLESTER and RIERA. This parameter makes possible to compare the intensities of transitions showing different vibrational structures. ε_{sm} is more accurate and nearer to the integrated intensities. The value obtained for the molecule I, as measured by BALLESTER and RIERA, is : $\varepsilon_{sm} = 700$. The value for the molecule II is of course the same as ε_{max}, since there is no fine structure : $\varepsilon_{sm} = 467$. These values are closer than the preceding ones. It is possible to improve the measure of intensities in using the width at half height. This leads to : $\varepsilon_{sm} x \Delta\nu_{(1/2)} = 267x10^4$ and $201x10^4$, with $\Delta\nu_{(1/2)}$ in cm^{-1}. Although intensities are not so strongly different as it appears when comparing ε_{max} values, their difference deserves an explanation.

In order to show the electronic causes of the decrease of intensity when going from I to II, we shall use the simple Sklar vector model with the reference pattern of figure 2 for the transition moment vector components.

When considering orthoxylene (Figure 3a and 3b) one sees that the resulting transition moment vector is bissecting the angle of the two substituents. The same happens, of course, for indane (Figure 3c and 3d) – since the symmetry is the same –, apart from the fact that strain strongly distorts the chromophore, increasing the allowed electronic part of intensity from $\varepsilon_{sm} = 234$ (orthoxylene) [8] to $\varepsilon_{sm} = 1040$ (indane) [8]. The resulting transition moment vector would be oriented in the opposite direction if we had choosen the opposite directions for the reference vector pattern of figure 3a. One can say that the transition moment vector induced by the fused ring in indane is as shown in figure 3d. For molecule I the vector components are given in figure 3e and 3f. The angle between the two vectors being 120° in figure 3f, their resultant is the same as in indane. Intensity in fact is lower because of a possible interaction between the effects of the two rings, each one being partly quenched by the other.

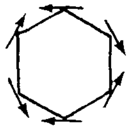

Figure 2. The Sklar's vector pattern

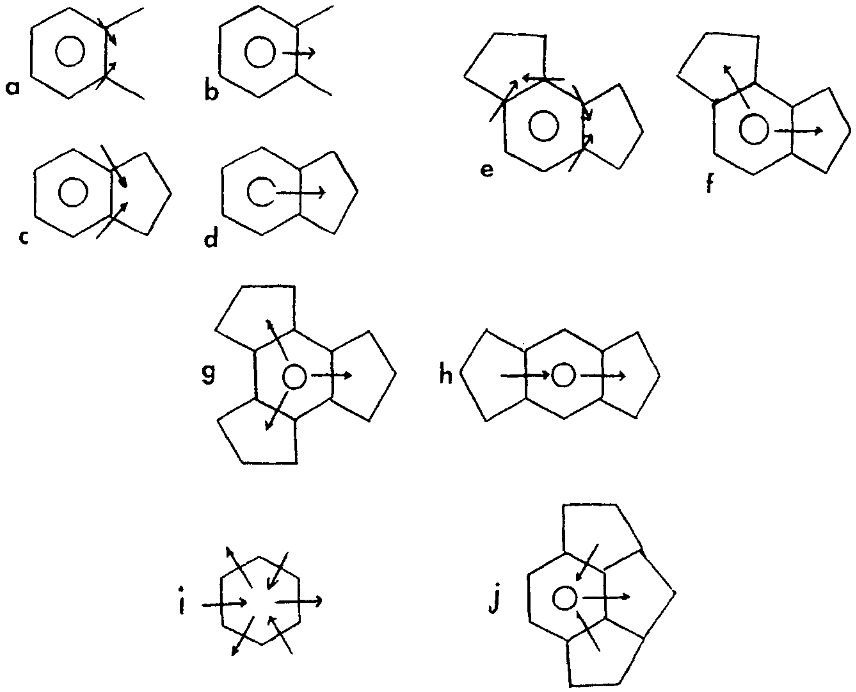

Figure 3. (See the text)

When using a third fused ring, as shown in figure 3g, intensity has to be strongly quenched. It has to be reduced to its vibrationaly induced component since the resulting transition moment vector is zero. Actually, intensity is very low : ε_{sm} = 230. That value is very near to what is observed when there are six methyl substituents around the benzene chromophore (ε_{sm} = 225). Furthermore, when considering the molecule of figure 3h one sees that the two component vectors are colinear and their addition leads to a transition moment vector with a modulus which is twice the modulus of what is observed in indane. Actually : ε_{sm} = 3700.[8] Thus, we can draw the vector pattern of figure 3i for the contribution of fused rings around the benzene chromophore. This is only an adaptation of the original vector pattern to fused ring substituents.

When considering the pattern of figure 3i (Figure 3j), introducing a bridge ($-CH_2-$) in molecule I between the two already existing five membered fused rings creates a new fused ring between them. One sees that its contribution to the transition moment vector opposes the resulting contribution of the two other rings. The new length of the transition moment vector is zero. Intensity should be reduced to the vibrational contribution, about : ε_{sm} = 200-250. In fact intensity is reduced only to ε_{sm} = 467, because the third ring is far from being equivalent to the two preceding ones. It is sandwiched between them. Its vector component is not equal to the others and the resulting vector is not zero. Furthermore, distorting the two preceding fused rings the new ring changes their contributions. In other words : distorsion is not suppressed ; it is not the same as that observed in molecule I, but it still displays a strong C_{2v} symmetry, which causes an increase of intensity which adds to the pure vibrationnally induced one.

One sees that symmetry considerations are sufficient enough to explain the intensity differences observed when comparing molecule I and molecule II, without being obliged to invoke a lack of vibrational facilities in II, or an increase of vibrational facilities in I compared to II. What is noteworthy is not the decrease of intensity from I to II, but the fact that the intensity of the molecule II is so great. The explanation of that phenomenon lies in the extra strain imposed by the third fused ring. The lack of vibrational facilities, which is not the cause – or the main cause – of that decrease, can be clearly observed in the lost of the vibrational fine structure in molecule II.

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