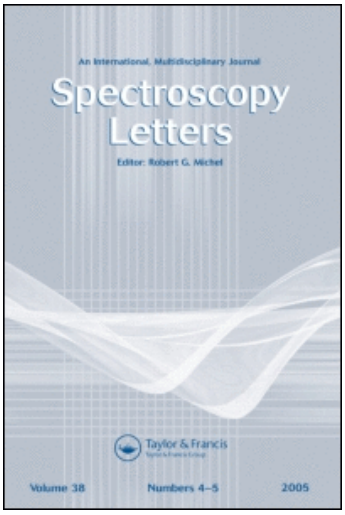

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SPECTROSCOPIC EVIDENCE IN φCXYZ MOLECULES FOR THE THREE GROUPS X,Y,Z ACTING AS A WHOLE,WHATEVER THE SYMMETRY MAY BE, IN THEIR LONG RANGE INTERACTIONS WITH THE CHROMOPHORE

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Long range interactions, in structures whose type is ϕCH_2X, between the aromatic chromophore and an auxochrome X, involve a σ,π coupling through the methylene C_α - H bonds. That hyperconjugative effect encountered with the hydrogen atoms linked to C_α, and the modulation of their effect by the auxochrome, allow to understand the spectroscopic behaviour of the secondary transition in many molecular systems[1-7].

We should like to produce in that paper some spectroscopic results showing that other bonds than C - H on C_α can also transmit interactions with a great efficiency. That experimental work will enable us to determine to what extent σ,π coupling is still possible when none of the symmetry conditions, which however seem to be required from the substituent for the coupling, is satisfied.

σ,π COUPLING THROUGH C_α - H BONDS

Because of its D_{6h} symmetry the benzene nucleus, when it is an isolated chromophore, has its secondary transition, in the near UV range, forbidden. The intensity is very sensitive to perturba-

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tions when the symmetry is distorted towards C_{2v} (for which the transition is allowed) by a mesomeric type effect. A σ,π coupling causes such an effect because it includes in the π system, orbitals which are outside of the ring. If X is a sufficiently electron attracting group it can cancel out the mesomeric electron donating tendency of the methylene to which it is attached. D_{6h} symmetry is restored in the π cloud. The transition is forbidden as it is in benzene and the 00 band does not appear. On the contrary, when the electron attracting power is not sufficient C_α- H bonds can exert their mesomeric effect on the chromophore and alter its symmetry. The transition being allowed the 00 band has a definite intensity. When X is a very strong electron attracting group not only it can cancel out the electron donating power of the methylene but it can also, through the σ,π coupling, exert on the π cloud some perturbation of an attracting type. It modifies the symmetry and increases the intensity all the more as it is attracting, exactly as in the case when there is from the whole substituent a donating tendency.

The σ,π coupling between a methylene and an unsaturated system proceeds from the C_{3v} symmetry of the methyl group which allows combinations of orbitals which have the symmetry of the π cloud[8a]. A tertiobutyl group has the same symmetry. Hence it can give rise to the same coupling as a methyl. The coupling induces an intensity of ε_{oo}=265 for the 00 band of toluene. That intensity is still 115 for ϕtBut. The coupling has a lower but definite efficiency.

The C_{3v} symmetry does not exist in $-CH_2X$ group. There is still a C_s symmetry allowing an antisymmetric combination of the hydrogens orbitals. That combination has the symmetry of the π system. The same combination is possible with two X when the $-CHX_2$ group is involved. However that treatment by means of symmetry considerations presumes that the coupling is highly dependent on the rotation around C_ϕ- C_α . The coupling involved should cancel out when the pseudo-π orbitals and the π system are orthogonal. It seems that there is no experimental evidence showing such a drastic dependency for the σ,π coupling in these structures.For example in benzylalkylketones the 00 band is weak and retains a constant value

whatever the conformation may be [14]. On the contrary it is well known that many other "through space" or "through bond" interactions[9-13] need well defined conformations to be studied.

SPECTRA OF SOME $\phi CRR'CO_2H$ AND $-CO_2^-$ SPECIES

Phenylacetic acid shows a 00 band which is very weak (ε_{oo}= 70 in water + HCl) if we take into consideration the fact that the overlap with the other parts of the secondary transition is at that wavelength approximately of 60-65. Using the simple scheme described in the foregoing part such an intensity shows that $-CO_2H$, which is an electron attracting group, cancels out almost completely the perturbation produced by the methylene on the benzene chromophore. The symmetry being D_{6h} the transition is forbidden. A $-CO_2^-$ group is a weaker electron attracting group. It cannot cancel out the perturbation, so that the symmetry is not D_{6h}. The transition is not completely forbidden (ε_{oo}=120), and there is during the protonation a change in the intensity ($\Delta\varepsilon$=50) in the intensity.

We explained the coupling in ϕCH_2X on the ground of a C_s symmetry. That symmetry disappears when an hydrogen atom is replaced by a methyl. We should expect a lowering of the coupling. The chromophore and $-CO_2H$, or $-CO_2^-$, should no longer interact : the intensity should be very weak and identical for the protonated and the unprotonated species. On the contrary we measured : ε_{oo}= 75 for $\phi CH(CH_3)CO_2H$ and ε_{oo}= 115 for $\phi CH(CH_3)CO_2^-$ ($\Delta\varepsilon$=40). These values are similar to those obtained with ϕCH_2CO_2H,$-CO_2^-$. Coupling and "through bond" interaction maintain their efficiency.

When all the hydrogen atoms are removed we obtain : ε_{oo}=70 for $\phi C(CH_3)_2CO_2H$ and ε_{oo}= 105 for $\phi C(CH_3)_2CO_2^-$ ($\Delta\varepsilon$=35) . The general behaviour is the same as previously. If C_α - H bonds were essential to the interaction between ϕ and X, intensities should be identical and very weak for the latter two species. If symmetry conditions were essential, intensity of $\phi C(CH_3)_2CO_2^-$ for example (easier to compare with its homologues, than protonated species which have too low intensities) should be comprised within the va-

lues obtained for $\phi CH_2CO_2^-$ and $\phi CH(CH_3)CO_2^-$. As for $\phi CH_2CO_2^-$, $\phi CH(CH_3)\ CO_2^-$ has the right symmetry but achieved with C-C bonds which are less π donors than C - H ones. Now intensity is outside of that range and slightly weaker than the weakest one ($\phi CH(CH_3)CO_2^-$). Thus, in spite of the symmetry, the coupling efficiency is slightly weaker than in the ion where however the symmetry conditions are not satisfied.

We deduce from these results that C_α - C bonds allow a σ,π coupling and a ϕ - X interaction almost as much as C_α - H bonds do, whatever the symmetry of the substituent is.

From the point of view of intensity the protonated species should behave in the same way as the unprotonated do. But we lack of precision to compare these protonated species to each other. The intensities seem to be much alike because they are weak. The OO band is only a shoulder and its measure is difficult. The electron attracting power of $-CO_2H$ is near the point where it could cancel out the π electron donating power of CH_2, $CHCH_3$ or $C(CH_3)_2$. It was necessary to study some molecules where the OO bands are more intense in order to compare them. We studied Cl-ϕ-C-CO_2H (para)(ε_{oo}=180) and Cl-ϕ-C-CO_2^- (ε_{oo}= 270) on the one hand and Cl-ϕ-CH_2CO_2H (ε_{oo}= 200) and Cl-ϕ-$CH_2CO_2^-$ (ε_{oo}=290) on the other hand (all these values are in methanol). Although it has a σ attracting power a chlorine atom is a π donor by its non bonding electrons[8b]. It induces a spectroscopic moment which added to that of $-CH_2CO_2H$ or $-CH_2CO_2^-$ (because the two substituents are in para positions) increases the intensity. The OO band intensity of Cl-ϕ-C-CO_2^- is only slightly weaker than that of Cl-ϕ-$CH_2CO_2^-$ as it was expected from our above results. That of Cl-ϕ-C-CO_2H is also weaker, and only slightly weaker than that of Cl-ϕ-CH_2CO_2H, $\Delta\varepsilon$=90 is the same when protonation is achieved, results that had to be ascertained. We have checked that introducing a cyclopentane ring instead of two aliphatic substituents on C_α did not produce a specific behaviour: ϕ-C-CO_2H and $-CO_2^-$ have intensities very similar to that measured for $\phi C(CH_3)_2CO_2H$ and $-CO_2^-$, respectively : ε_{oo}=75 and 110.

An OH group has an electron attracting power which goes between those of $-CO_2H$ and $-CO_2^-$: ε_{oo}= 85 for ϕCH_2OH (in methanol), ε_{oo}= 70 for ϕCH_2CO_2H and 120 for $\phi CH_2CO_2^-$. Introducing a methyl destroys the C_s symmetry on C_α but, as previously encountered with $\phi CH(CH_3)CO_2H$ and $-CO_2^-$, alters the intensity only slightly : ε_{oo}= 80 for $\phi CH(CH_3)OH$ (in methanol).

If C_α - CH_3 and C_α- H bonds which are different in length and electron donating power, allow the same σ,π type coupling, we cannot privilege in the constitution of the coupling these bonds against those involving the auxochromes C_α - CO_2^-, C_α - CO_2H, C_α-OH.

In the molecules : $\phi CH(OCH_3)CO_2H$ (ε_{oo}=125) and $\phi CH(OCH_3)CO_2^-$ (ε_{oo}=95) ($\Delta\varepsilon$ =30) the ion has a weaker intensity than the protonated species unlike what was previously observed in phenylacetic acid and its methylated derivatives.There are two electron attracting groups. The donating effect of C_α - H is completely canceled out. The attracting power is high enough to exert on π_ϕ a perturbation of an attracting type. Thus intensity is for these species all the more strong as the attracting power is high.

The C_α - O bond can pass for assuming, with C_α - H, the σ,π coupling, and thus constituting the"bridge" conveying the influence of $-CO_2H$ or $-CO_2^-$, although in benzyl alcohol the oxygen atom was part of the auxochrome. On the contrary the bonds C_α - CO_2H, or C_α - CO_2^-, and C_α- H may be considered as assuming the coupling and OCH_3 be considered as the auxochrome. In other words which is the auxochrome perturbing the π system and what bonds are those constituting the σ,π coupling? We are bound to assume from our spectroscopic results that all the substituents linked to C_α occur as a whole. The classical description using symmetry properties conceals this point and leads to fallacy. It has to be revisited.

A REVISITED COUPLING SCHEME

Let be x,y,z three orbitals belonging to X,Y,Z groups attached to C_α , and taking part in the bonds with C_α . In the classical method we could isolate the set of these three orbitals from the rest of the substituent . We should have to consider how they transform under the symmetry operations of the group to which they

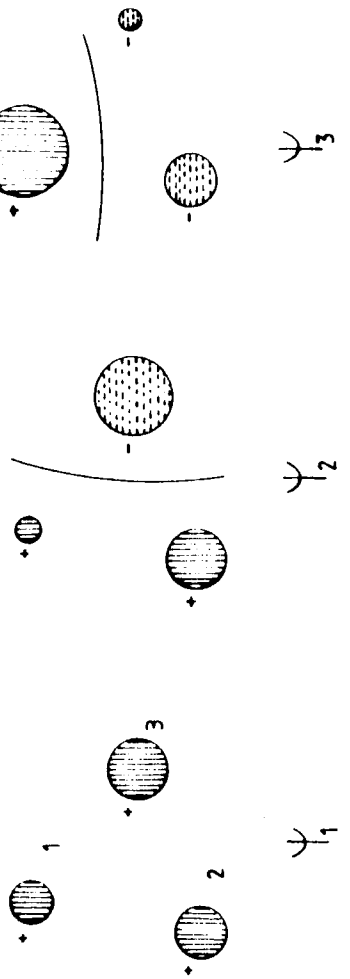

FIGURE 1

belong and by this way we should obtain a linear combination of these orbitals. But assuming that x,y,z are all different there is no symmetry property in connection with an axis going through the $C_\phi - C_\alpha$ bond. We cannot use the group theory to build up combinations. Nevertheless we retain the fact that it is possible, in a first step, to isolate them from the rest of the substituent. Although there is no symmetry they form a basis set and they may be coupled in the simplest way allowed by the MO theory. We obtain of course three functions, two of them having nodal surfaces allowing a coupling with a π system. To clear up that point let us suppose that x has a potential α , y : α+ 0,5β and z : $\alpha+\beta$ to make them different (α and β are the classical parameters). The combinations are : ψ_1=0,48x+0,56y+0,67z , ψ_2=0,23x+0,66y-0,72z , ψ_3=0,85x-0,50y-0,19z. These functions have been drawn in the figure. Nodal surfaces between positive and negative lobes of ψ_2 and ψ_3 allow a coupling with $2p_x$ and $2p_y$ orbitals belonging to C_α. Two orthogonal pseudo-π systems may be built on the substituent -CXYZ. Each of these systems couples with the p atomic orbitals constituting the π_ϕ cloud. As these two pseudo-π systems are orthogonal to each other, when one of them is in the maximum overlap with π_ϕ, the other does not overlap. When one of these overlaps increases during rotation around $C_\phi - C_\alpha$ the other decreases and vice versa. Thus the incidence of rotation on the coupling efficiency is minimized.

The ψ_1 orbital, which has no nodal surface, couples with 2s and 2pz (that one is directed along the $C_\phi - C_\alpha$ bond) of C_α and belongs to the σ system.

This treatment should obviously produce, when there is a C_{3v} or C_s symmetry, exactly the same analytical functions than those obtained with the symmetry considerations.

CONCLUSION

From that spectroscopic work it arises, that substituents on C_α occur as a whole in their interaction with π_ϕ. The σ,π coupling is described as a coupling between the whole group of the substi-

tuents on C_α, and π_ϕ, through the $2p_x$ and $2p_y$ orbitals belonging to C_α. Neither a group, nor a given symmetry are to be privileged.

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