Theoret. Chim. Acta (Berl.) 38, 199—210 (1975)

PCILO Method for Excited States

IV. Localized Character of the $n \rightarrow \pi^*$ Excitation of Polyenic Aldehydes

Jacqueline Langlet

Institut de Biologie Physico-Chimique, Laboratoire de Biochimie Théorique, Paris

Received October 18, 1974

This present paper deals with the localized character of the $n\pi^*$ excited state of the polyenic aldehydes. A comparison of the localized and delocalized descriptions shows that 1) the localized description gives directly a localized $n\pi^*_{C=O}$ excited state, the delocalization of the hole and particle over the neighbouring bonds may be considered as a perturbation; 2) In the delocalized description the π^*MO is delocalized over the whole π system and a realistic description of the $n\pi^*$ excited state requires the relocalization of the particle through the CI of singly excited states.

Many contributions from higher excitations are also analyzed in terms of local phenomena.

Key word: Aldehydes, polyenic, $n\pi^*$ excited state of ~

1. Introduction

In the lowest members of the series of polyenic aldehydes (formaldehyde, crotonaldehyde), one band of rather low intensity appears in the region 270–290 mμ. McMurry and Mulliken [1] have claimed that this band is due to the transition of one electron from the lone pair localized on oxygen, to the antibonding π^* orbital and this band has been called the $n \rightarrow \pi^*$ band by Kasha [2]. This low intensity band (which is forbidden by symmetry, but can be observed because of vibrational interactions) is overrun, and swamped by the high intensity $\pi \rightarrow \pi^*$ band, as the length of the conjugated system increases [3]. The $n \rightarrow \pi^*$ band of small conjugated aldehydes have been the object of very intensive study, both experimentally [4–18] and theoretically (by semi-empirical [19–31] and *ab initio* [31–36] methods). But all these calculations have been made using delocalized molecular orbitals. It is clear that the use of symmetry delocalized Molecular Orbitals allows in general a single determinantal rather satisfactory representation of the delocalized spectroscopic phenomena. But the excited state may be also represented, from a set of localized Molecular Orbitals using then multideterminantal wave functions: this is the excitonic model of excited states [37–41]. We have recently compared the two descriptions on a very simple model case, the case of linear homogeneous polyenes [42]. In that case, the delocalized π and π^* MO's are completely different from the π and π^* bond MO's. We have demonstrated that 1) the Canonical Orbital model overestimates the delocalization of the excitation especially the long range delocalization effects; 2) the delocalized model used with Configuration Interaction (CI) between the singly excited determinants is equivalent to the excitonic treatment using localized Molecular Orbitals. So the excitonic treatment gives an interpretation of the physical effect of the Configuration Interaction of the singly excited states. The CI relocalize the excitation with respect to the Virtual Orbital (VO) approximation.

The present paper shows an analogous and even clearer phenomenon on the $n\pi^*$ transition of polyenic aldehydes. The localized description gives directly a localized $n\pi^*_{C=O}$ excited state, the delocalization of the hole and particle on the neighbour bonds being small it may be considered as a perturbation. In the delocalized model the π^* MO is delocalized on the whole π system and a realistic description of the $n\pi^*$ excited state requires the relocalization of the particle through the CI of singly excited states.

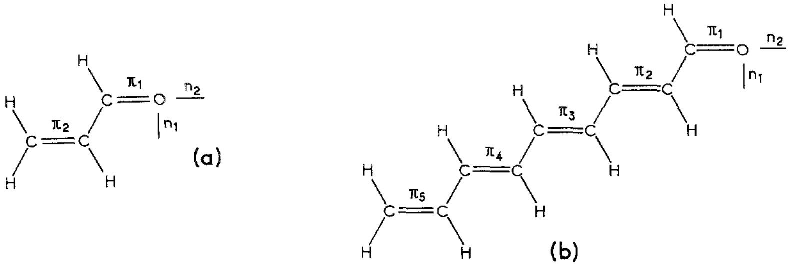


Fig. 1a and b. The acrolein molecule (a) and a polyenic aldehyde with $4\pi_{C=C}$ bonds (b) with the numbering of the π bonds

Contributions from higher excitations are also analyzed in terms of local phenomena; the main contribution to the transition energy from the doubly excited states comes from the repolarization of the bonds of the CO region in the polar $\pi\pi^*$ excited state.

This work has been made with the help of the PCILO method for excited states [41] within the CNDO/2 parametrization [43].

The zeroth order transition energies result from the diagonalization of the Configuration Interaction matrix restricted to the $\Phi\begin{pmatrix}\pi^*\\ \pi\end{pmatrix}$ or $\Phi\begin{pmatrix}\pi^*\\ n\end{pmatrix}$ singly excited determinants.

The interaction with other singly, doubly and triply excited determinants is taken into account through a 2^{nd} order perturbation process.

Figure 1b shows the numbering of the double bonds we have chosen in a polyenic aldehyde: The $\pi_{C=O}$ bond is the π_1 bond and all the others double bonds are numbered from the $\pi_{C=O}$ bond; the π_N bond is the terminal $\pi_{C=O}$ bond.

2. $n \rightarrow \pi^*$ Transition Energy

2.1. The Zeroth Order Transition Energy

Table 1 (Column 3) gives the zeroth order $n \rightarrow \pi^*$ transition energies we have calculated from $N = 1$ to $N = 7$.

The values we have obtained are a little higher than those calculated with the delocalized model in the VO approximation in both semi-empirical [19] and *ab initio* methods [35, 36].

Table 1. Calculated $n-\pi^*$ transition energies for $\mathrm{H{-}(CH{=}CH)_{N-1}\overset{H}{C}{=}0}$ polyenic aldehyde for $N=1$ to $N=7$. $E^0_{t,n\pi}$ zeroth oder transition energies. $E^{2,m}_{t,n\pi}$ zeroth order transition energies corrected to the 2nd order by the σ singly excited configurations. $E^2_{t,n\pi}$ 2nd order transition energies. m_σ 2nd correction due to the σ singly excited configurations. $s1$ 2nd order correction due to the $a^+_{q^*} a_p$ delocalization single excitations. $s2$ 2nd order correction due to the $a^*_{p^*} a_p$ polarization single excitations. $d1$ 2nd order correction due to the $a^*_p a_q a^*_{p^*} a_p$ double excitations. $d2$ 2nd order correction due to the $s^*_{p^*} a_p a^*_{p^*} a_p$ double excitations. cm are the cross terms due to the σ singly excited configurations. cs and cd are the cross terms due to the single and double excitations respectively

No.	Experimental transition[a] energies	$E^0_{t,n\pi}$	$E^{2,m}_{t,n\pi}$	$E^2_{t,n\pi}$	m_σ	$s1$	$s2$	$d1$	$d2$	cs	cd	cm
1	4.21[b]	5.79	3.89	3.56	−1.90	+0.59	−2.26	+0.62	+0.71	0.000	0.000	0.000
2	3.71[c]	5.58	3.76	3.29	−1.83	+0.89	−2.52	+0.66	+0.70	− 0.20	0.000	0.000
3		5.57	3.75	3.27	−1.83	+0.91	−2.53	+0.67	+0.70	− 0.23	0.000	0.000
4		5.57	3.75	3.27	−1.83	+0.91	−2.53	+0.67	+0.70	− 0.23	0.000	0.000
5		5.57	3.75	3.27	−1.83	+0.91	−2.53	+0.67	+0.70	− 0.23	0.000	0.000
6		5.57	3.75	3.27	−1.83	+0.91	−2.53	+0.67	+0.70	− 0.23	0.000	0.000
7		5.57	3.75	3.27	−1.83	+0.91	−2.53	+0.67	+0.70	− 0.23	0.00	0.00

[a] This study is restricted to an examination of Frank-London excitation only (the nuclear geometry of each excited state is taken to be the same as the ground state equilibrium geometry. Thus in that case the most appropriate experimental quantities for comparison with calculated transition energy are the energies corresponding to band intensities maxima.

[b] References [1, 4].

[c] References [17].

The $n \rightarrow \pi^*$ is lowered by 0.21 eV from formaldehyde to acrolein.

An analysis of the zeroth order wave function of the $n \rightarrow \pi^*$ state has shown that:

1) The largest weight is obtained for the configuration $\Phi\begin{pmatrix}\pi^*_k\\ n\end{pmatrix}$, this weight decreases a little from $N=1$ to $N=2$ (from 100% to 97.81%), and for $N \geqq 3$ this weight remains nearly constant.

2) The weight of the $\Phi\begin{pmatrix}\pi^*_k\\ n\end{pmatrix}$ configurations (where π_k is a $\pi_{\mathrm{C=C}}$ bond) depends on the proximity of the π_k and the π_1 bonds. The most important weight is obtained when $\pi_k = \pi_2$ i.e. when the $\pi_{\mathrm{C=C}}$ bonds are only separated by a single bond.

So, we may conclude from this analysis, that the localized model the $n \rightarrow \pi^*$ excitation remains a localized $n \rightarrow \pi^*_{\mathrm{C=0}}$ excitation, with some very quickly decreasing tails on the others π^* MO's.

We may understand this result from the acrolein molecule (Fig. 1a). In this molecule we can build two localized bonding and (antibonding) MO's: π_1 and π_2 (and π^*_1 and π^*_2) we can consider two excited states the $n \rightarrow \pi^*_1$ and $n \rightarrow \pi^*_2$ states. The energy of these two states is given respectively by Eqs. (1) and (2) if the energy of the ground state is taken as zero

$$E_{n \rightarrow \pi^*_1} = \varepsilon^*_{\pi^*_1} - \varepsilon_n - J_{n\pi^*_1}, \tag{1}$$

$$E_{n \rightarrow \pi^*_2} = \varepsilon^*_{\pi^*_2} - \varepsilon_n - J_{n\pi^*_2}. \tag{2}$$

The antibonding MO's π^*_1 and π^*_2 have nearly the same energy ε (5.21 eV and 4.90 eV respectively).

$J_{n\pi_1^*}$ (and $J_{n\pi_2^*}$) represent respectively the Coulombic repulsion between the charge distribution of the orbitals π_1^* (and π_2^*) and the electrons of the lone pair n. So these two matrix elements have a positive value. Furthermore, the Coulombic repulsion vary in the same way as $1/r$ [r being the distance between the π_1^* (or π_2^*) orbital] and the lone pair n. So $J_{n\pi_1^*}$ has a higher value than $J_{n\pi_2^*}$ and the energy of the state $n \to \pi_1^*$ is lower than the energy of the state $n \to \pi_2^*$.

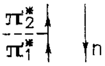
So the lowest $n \to \pi^*$ state is the $n \to \pi_1^*$ state, and the $n \to \pi^*$ excitation is the $n \to \pi_{C=O}$ excitation.

Let us perturb the $n \to \pi_1$ state by the $n \to \pi_2$ state. The coefficient of the $\Phi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix}$ configuration in the first order perturbed wave function is

$$\alpha = \left\langle \Psi^1\begin{pmatrix}\pi_1^*\\ n\end{pmatrix} \middle| \varphi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix}\right\rangle = \frac{\left\langle \varphi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix} \middle| H \middle| \varphi\begin{pmatrix}\pi_1^*\\ n\end{pmatrix}\right\rangle}{E_{n\to\pi_1^*} - E_{n\to\pi_2^*}} \tag{3}$$

with $\left\langle \varphi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix} \middle| H \middle| \varphi\begin{pmatrix}\pi_1^*\\ n\end{pmatrix}\right\rangle = \langle \pi_2^* | F | \pi_1^* \rangle$ where F is the Fock operator.

α is visualized by the Diagramm (d1).



(d1)

representing the π particule delocalization.

The energy difference which appears in the denominator of Eq. (3) is negative since $E_{n\to\pi_1^*} < E_{n\to\pi_2^*}$. The matrix element $\langle \pi_2^* | F | \pi_1^* \rangle$ which appears in the numerator of Eq. (3) is positive if the antibonding π_1^* and π_2^*. Molecular Orbitals have parallel orientation.

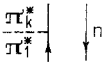
So, the coefficient α is negative, and the wave function describing the $n \to \pi^*$ state will be written at the first order by:

$$\Psi_1 = \Phi\begin{pmatrix}\pi_1^* + \alpha\pi_2^*\\ n\end{pmatrix}.$$

So the excitation remains mostly localized on the $\pi_{C=O}$ bond but we get a negative tail on the $\pi_{C=C}$ bond.

Using again the localized model we may demonstrate that, in a polyene with N double bonds (when the different double bonds are numbered from the $\pi_{C=O}$ bond (π_1) to the N^{th} bond $\pi_{(C=C)_N}$ in the same way as in Fig. 1b), the contribution of an excitation from the lone pair to the k^{th} antibonding orbital $\pi^*_{(C=C)_k}$ depends on the distance between the $\pi_{C=O}$ and the $\pi_{C=C)_k}$ bonds; when $k > 2$ this contribution is nearly negligible.

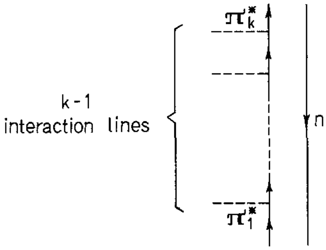
The coefficient of the $\Phi\begin{pmatrix}\pi_k^*\\ n\end{pmatrix}$ configuration in the first order perturbed wave function Ψ_1 vizualized by Diagramm (d2)



(d2)

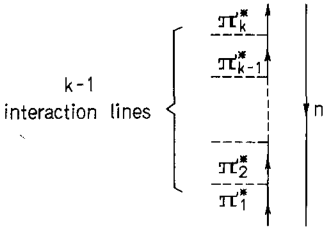
is near zero when the π_1 and the π_k bond are separated by more than one single bond since the matrix element $\langle \pi_1^* | F | \pi_k^* \rangle$ decrease exponentially with the distance between the π_1 and the π_k bonds.

So we have to take into account the coefficient of the $\Phi \begin{pmatrix} \pi_k^* \\ n \end{pmatrix}$ configuration in the $(k-1)^{\text{th}}$ order perturbed wave function. This coefficient is visualized by Diagram (d3) with $(k-1)$ interaction lines.



(d3)

There are $(k-1)!$ diagrams of this type, but the most important one is the Diagram (d4) with all the π bonds ranged in an increasing order from π_1^* to π_k^*.



(d4)

One goes from the diagram giving the coefficient α_{k-1} of the $\Phi \begin{pmatrix} \pi_{k-1}^* \\ n \end{pmatrix}$ configuration in the $(k-2)^{\text{th}}$ perturbated wave function, to the corresponding diagram, giving the coefficient α_k of the $\Phi \begin{pmatrix} \pi_k^* \\ n \end{pmatrix}$ configuration in the $(k-1)^{\text{th}}$ perturbated wave function by adding a supplementary interaction line, so:

$$\alpha_k = \alpha_{k-1} \frac{\langle \pi_k^* | F | \pi_{k-1}^* \rangle}{E_{n \rightarrow \pi_1^*} - E_{n \rightarrow \pi_2^*}}, \tag{5}$$

$$\alpha_k \simeq 0.1\, \alpha_{k-1}\,.$$

If the value of k is sufficiently large the coefficient α_k is negligible.

So considering the $n \rightarrow \pi^*$ transition, the excitation appears to be mostly localized in the $\pi_{\mathrm{C=O}}$ region, and, with regard to the $n \rightarrow \pi^*$ transition energy, a polyenic aldehyde with an infinite number of double bonds N can be considered as an acroleine molecule.

2.2. Comparison between the Localized and the Delocalized Model

In the delocalized model, in the Virtual Orbital (VO) approximation, the $n \rightarrow \pi^*$ excitation is delocalized over all the π system. We may show, that the configuration interaction including the π singly excited configuration tends to relocalize the excitation towards the $\pi_{C=0}$ bond. So after this CI in both, the localized and delocalized models, the $n \rightarrow \pi^*$ excitation appears to be mainly localized in the $\pi_{C=0}$ region.

We take the acrolein molecule as an example (see Fig. 1a). *In the delocalized model*, one may build two excited molecular orbitals φ_1^* and φ_2^* taken as a linear combination of the π_1 and π_2 localized orbitals built on the $\pi_{C=0}$ and the $\pi_{C=C}$ bonds respectively

$$\varphi_1^* = \frac{1}{\sqrt{2}}(\pi_1^* - \pi_2^*), \tag{7}$$

$$\varphi_2^* = \frac{1}{\sqrt{2}}(\pi_1^* + \pi_2^*), \tag{8}$$

As a first approximation, we may use $1/\sqrt{2}$, as coefficient, if we consider that $\langle \pi_1^* | F | \pi_1^* \rangle$ is nearly equal to $\langle \pi_2^* | F | \pi_2^* \rangle$.

The energy of these two MO's will be given by:

$$\langle \varphi_1^* | F | \varphi_1^* \rangle = \tfrac{1}{2}[\langle \pi_1^* | F | \pi_1^* \rangle + \langle \pi_2^* | F | \pi_2^* \rangle] - \langle \pi_1^* | F | \pi_2^* \rangle, \tag{9}$$

$$\langle \varphi_2^* | F | \varphi_2^* \rangle = \tfrac{1}{2}[\langle \pi_1^* | F | \pi_1^* \rangle + \langle \pi_2^* | F | \pi_2^* \rangle] + \langle \pi_1^* | F | \pi_2^* \rangle. \tag{10}$$

$E\varphi_1^*$ [Eq. (9)] and $E\varphi_2^*$ [Eq. (10)] differ by $\langle \pi_1^* | F | \pi_2^* \rangle$ which appears with the minus sign in the expression of $E\varphi_1^*$ and with the plus sign in the expression of $E\varphi_2^*$. Since $\langle \pi_1^* | F | \pi_2^* \rangle$ has a positive value, when the antibonding localized Molecular Orbitals π_1^* and π_2^* have parallel orientations, the energy of the Molecular Orbital φ_1^* is lower than the energy of the Molecular Orbital φ_2^*.

So the lowest delocalized $n \rightarrow \pi^*$ state will be the $n \rightarrow \varphi_1^*$ state and the $n \rightarrow \pi^*$ transition will be delocalized over the two π_1 and π_2 bonds.

Let us perturb the $n \rightarrow \varphi_1^*$ state by the $n \rightarrow \varphi_2^*$ state. The energy difference between the two states $n \rightarrow \varphi_1^*$ and $n \rightarrow \varphi_2^*$ will be given by: $\Delta E = E_{n \rightarrow \varphi_1^*} - E_{n \rightarrow \varphi_2^*}$.

$$\Delta E = \left\langle \begin{pmatrix} \varphi_1^* \\ n \end{pmatrix} \middle| F - J_n \middle| \begin{pmatrix} \varphi_1^* \\ n \end{pmatrix} \right\rangle - \left\langle \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix} \middle| F - J_n \middle| \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix} \right\rangle. \tag{11}$$

If $J_{n\varphi_1^*} = J_{n\varphi_2^*}$ in the same way as in CNDO/2 parametrization, we get

$$\Delta E = -2\langle \pi_1^* | F | \pi_2^* \rangle \tag{12}$$

so ΔE is negative.

The coefficient of the $\Phi \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix}$ configuration in the first order perturbated wave function is given by:

$$\alpha = \left\langle \Psi \begin{pmatrix} \varphi_1^* \\ n \end{pmatrix} \middle| \varphi \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix} \right\rangle = \frac{\left\langle \varphi \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix} \middle| H \middle| \varphi \begin{pmatrix} \varphi_1^* \\ n \end{pmatrix} \right\rangle}{\Delta E} \tag{13}$$

with

$$\begin{aligned} \left\langle \varphi \begin{pmatrix} \varphi_2^* \\ n \end{pmatrix} \middle| H \middle| \varphi \begin{pmatrix} \varphi_1^* \\ n \end{pmatrix} \right\rangle &= \langle \varphi_2^* | F - J_n | \varphi_1^* \rangle \\ &= -\tfrac{1}{2}(\langle \pi_1^* | J_n | \pi_1^* \rangle) - (\langle \pi_2^* | J_n | \pi_2^* \rangle). \end{aligned} \tag{14}$$

Since the Coulombic repulsion $\langle \pi_1^* | J_n | \pi_1^* \rangle$ has a larger positive value than the Coulomb repulsion $\langle \pi_2^* | J_n | \pi_2^* \rangle$ (for the reasons already mentioned) the difference $\langle \pi_1^* | J_n | \pi_1^* \rangle - \langle \pi_2^* | J_n | \pi_2^* \rangle$ is positive and the numerator is negative because of the minus sign which appears in this expression [Eq. (14)]; so the coefficient α is a positive number.

When the interaction between the $\Phi\begin{pmatrix}\varphi_1^* \\ n\end{pmatrix}$ and $\Phi\begin{pmatrix}\varphi_2^* \\ n\end{pmatrix}$ states is taken into account by a first order perturbation theory, the wave function Ψ_1 describing the $n \to \pi^*$ state may be written at the first order by

$$\Psi_1 = \Phi\begin{pmatrix}\varphi_1^* + \alpha\varphi_2^* \\ n\end{pmatrix}, \tag{15}$$

$$\Psi_1 = \Phi\begin{bmatrix}1/\sqrt{2}[\pi_1^*(1+\alpha) + \pi_2^*(\alpha - 1)] \\ n\end{bmatrix}. \tag{16}$$

For the representation of the $n \to \pi^*$ state, the best Molecular Orbital is more important on the π_1^* virtual orbital than on the π_2^* one's.

Since α is a positive number smaller than 1, the Molecular Orbital π has a negative tail on the π_2 bond, in the same way as, in the localized model.

When considering the $\pi \to \pi^*$ transition of polyenic systems, in the delocalized model, the Configuration Interaction relocalizes the excitation with respect to the VO approximation, reducing the long range charge transfer excitations. In the $n \to \pi^*$ transition, the relocalization due to the Configuration Interaction is still more pronounced, the excitation being brought to the C=O region.

2.3. Second Order Energy Correction

The second order energy correction involves the corrections due 1) to the $\Phi\begin{pmatrix}\pi^* \\ \sigma\end{pmatrix}$ configurations, 2) to the doubly and triply excited configurations.

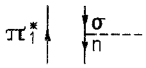
Table 1 (Columns 4 and 5) gives respectively the $n \to \pi^*$ transition energies after the correction due to the $\Phi\begin{pmatrix}\pi^* \\ \sigma\end{pmatrix}$ configurations ($E^{2m}_{t,n\pi^*}$) and after the full second order correction ($E^{2}_{t,n\pi^*}$). We have noticed that:

1) In the same way as E_t^0, $E^{2,m}_{t,n\pi^*}$ and $E^{2}_{t,n\pi^*}$ decrease from $N = 1$ to $N = 3$, then these quantities remain constant. This result is not surprising since all the second order corrections vary from $N = 1$ to $N = 3$, then they remain constant (see Table 1).

Experimentally we do not know the $n \to \pi^*$ singlet transition of a polyenic aldehyde with $N > 2$, but we know that the $n \to \pi^*$ transition energy of a polyenic aldehyde do not decrease so quickly as the $\pi \to \pi^*$ transition energy [3]. The semi-empirical calculations (with NNDO method) of Baird *et al.* [45] show that the $n \to \pi^*$ triplet transition energies of the polyenic aldehydes (from $N = 1$ to $N = 6$) has a constant value for $N \geqq 3$.

2) The $\Phi\begin{pmatrix}\pi^* \\ \sigma\end{pmatrix}$ singly excited configurations have a very important lowering effect on the $n \to \pi^*$ transition energies (-1.90 eV when $N = 1$, and -1.83 eV $N = 2$). These corrections represent the delocalization of the hole n towards the σ bonds.

In our calculation, we just consider the contribution of the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma\end{pmatrix}$ configurations to the first order perturbated wave function, vizualized by a diagram very similar to the Diagram (d1)



In formaldehyde the lowering effect is due to the two $\Phi\begin{pmatrix}\pi^*\\ \sigma\ \mathrm{CH}\end{pmatrix}$ configurations. In acrolein, the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{C-C}}\end{pmatrix}$ configurations (with σ_{CH} and $\sigma_{\mathrm{C-C}}$ adjacent to the $\sigma_{\mathrm{C=0}}$ bonds) are the most important $\Phi\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ configurations. The lowering effect of the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{CH}}\end{pmatrix}$ configurations is more important than the lowering effect of the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma_{\mathrm{C=0}}\end{pmatrix}$ configurations. We can easily understand why the hole delocalization does not extend very far [since the interaction matrix element between the $\Phi\begin{pmatrix}\pi_1^*\\ \sigma\end{pmatrix}$ and $\Phi\begin{pmatrix}\pi_1^*\\ n\end{pmatrix}$ configurations decrease exponentially with the distance between the σ bond and the lone pair n].

Even if we had considered higher orders of perturbation corrections, our results would not be significantly changed, since the contribution of any σ_k bond in the k^{th} order perturbed wave function would be visualized by a diagram with the σ_k ranged in an increasing order similar to the Diagram (d4).

So, in the same way as the step by step delocalization of the particle, the step by step delocalization of the hole decreases exponentially with the distance from the C=0 bond.

As this level of calculation, we can compare the results we have obtained in formaldehyde in the localized model, when including the $\Phi\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ configurations by a Rayleigh Schrödinger perturbation series, with the calculations mode in formaldehyde with the delocalized model when including the singly excited configuration by a Configuration Interaction method (CIS approximation) by both semi-empirical (CNDO/2) [19] and *ab initio* methods [35, 36]. The lowering effect due to the $\Phi\begin{pmatrix}\pi^*\\ \sigma\end{pmatrix}$ configurations upon the $n \rightarrow \pi^*$ transition energy is more important with the localized model than with the delocalized model. With the semi-empirical CNDO/2 method in the CIS approximation [19] a 0.41 eV lowering effect has been obtained, and with *ab initio* calculations the lowering effect due to the σ monoexcited configurations are: 0.43 eV [36], 0.32 eV (with a minimal STO-4G basis) [35] and 0.17 eV (with an extended 4-31G basis) [35]. This fact is quite easy to understand since when using LCAO-MO-SCF wavefunctions [43, 44], the lone pair orbital n has a significant amplitude on the hydrogens and the carbons adjacent to the C=0 bond, while in the localized model the lone pair orbital n is taken as a $2py$ lone-pair orbital on oxygen. So in the localized model the hole n is localized on oxygen at the zeroth order approximation and the configuration interaction with the $\Phi\begin{pmatrix}\pi^* \\ \sigma_{\mathrm{CH}}\end{pmatrix}$ tends to delocalize the hole n towards the σ_{CN} bonds (or the $\sigma_{\mathrm{C-C}}$ bond) adjacent to the $\pi_{\mathrm{C=0}}$ bond.

3) $E^2_{t,n\pi^*}$ has a lower value than $E^{2,m}_{t,n\pi^*}$. Table 1 shows that the single excitations $a^+_{q^*}a_p|{}^{\pi^*}_{n}\rangle$ and the double excitations $a^+_{q^*}a_q a^+_{p^*}a_p|{}^{\pi^*}_{n}\rangle$ (or $a^+_{p^*}a_p a^+_{p^*}a_p|{}^{\pi^*}_{n}\rangle$) have an increasing effect upon the $n \to \pi^*$ transition energies. But the single excitations $a^+_{p^*}a_p|{}^{\pi^*}_{n}\rangle$ have a decreasing effect upon the $n \to \pi^*$ transition energy which is more important than the preceding increasing effect.

The $a^+_{p^*}a_p|{}^{\pi^*}_{n}\rangle$ single excitations (polarization excitations) give a stronger interaction with an excited determinant $\Phi\begin{pmatrix}l^* \\ k\end{pmatrix}$ than with the ground state, so they represent the repolarization of an excited state with regards to the ground state.

Our calculations have shown that during the $n \to \pi^*$ excitation the energy gain obtained by the repolarization of the π bonds is more important than the energy gain obtained by the repolarization of the σ bonds (-1.46 eV versus -0.81 eV in formaldehyde and -1.58 eV versus -0.94 eV in the others aldehydes).

The coefficient of the $\Phi\begin{pmatrix}j^* & p^* \\ i & p\end{pmatrix}$ doubly excited determinant, in the first order perturbed wave function is given by:

$$C = \left\langle \Psi^1 \middle| \Phi\begin{pmatrix}j^* & p^* \\ i & p\end{pmatrix} \right\rangle = \frac{\left\langle \Phi\begin{pmatrix}j^* & p^* \\ i & p\end{pmatrix} \middle| H \middle| \Phi\begin{pmatrix}j^* \\ i\end{pmatrix} \right\rangle}{E^* - E_{\substack{i \to j^* \\ p^* \to p^*}}}. \tag{17}$$

The interaction matrix element R between the $\Phi\begin{pmatrix}j^* \\ i\end{pmatrix}$ and $\Phi\begin{pmatrix}j^* & p^* \\ i & p\end{pmatrix}$ configurations is given by Eq. (18)

$$R = F_{pp^*} + a_{pj^*} - a_{pi}. \tag{18}$$

The Fock matrix element F_{pp^*} is zero since in ground state polarities have been made optimized.

The matrix elements a_{pj^*} and a_{pi}, given by Eqs. (19) and (20), represent charge-dipole interactions

$$a_{pj^*} = (pp^*, j^*j^*), \tag{19}$$

$$a_{pi} = (pp^*, ii). \tag{20}$$

So the difference $a_{pj^*} - a_{pi}$ represent the dipole-dipole interaction $(pp^*, j^*j^* - ii)$.

In formaldehyde, the coefficient of the $\Phi\begin{pmatrix}\pi_1^* & \pi_1^* \\ n & \pi_1\end{pmatrix}$ determinant upon the $n \to \pi^*$ state in the first order perturbed wave function is very important 0.18. The interaction matrix element has a very large value (4.09 eV); the interaction of the dipole $\pi_1\pi_1^*$ with the charge of the particle $\pi_1^*\pi_1^*$ is more important than the interaction of the dipole $\pi_1\pi_1^*$ with the charge of the hole (-5.62 eV versus -1.53 eV).

In formaldehyde the only σ bond which becomes significantly repolarized during the $n\to\pi^*$ transition is the $\sigma_{C=O}$ bond. The values of $a_{\sigma\pi_1^*}$ and $a_{\sigma n}$ we have obtained are nearly the same than the values of $a_{\pi_1\pi_1^*}$ and $a_{\pi_1 n}$, but the contribution of $\Phi\begin{pmatrix}\sigma^*\pi_1^*\\ \sigma\ \ n\end{pmatrix}$ is weak because the energy difference ΔE which appears in denominator of Eq. (17) is very large (-40.04 eV).

The σ_{CH} bonds are not significantly repolarized during the $n\to\pi^*$ excitation since the interaction of the dipole $\pi_1\pi_1^*$ with the charge $\sigma_{CH}^*\sigma_{CH}^*$ has the same sign and nearly the same values, than the interaction of the dipole $\pi_1\pi_1^*$ with the charge nn: so the dipole-dipole interaction $(\sigma_{CH}\sigma_{CH}^*, \pi_1^*\pi_1 - nn)$ is nearly zero. When passing from formaldehyde to acrolein, we have to take into account:

α) the repolarization of the $\pi_{C=0}$ bond induced by the excitation $n\to\pi_{C=0}^*$ which is nearly the same as in formaldehyde.

β) the repolarization of the $\pi_{C=0}$ bond induced by the $n\to\pi_2^*$ excitation, but this effect is negligible in spite of a strong matrix element between the $\Phi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix}$ and the $\Phi\begin{pmatrix}\pi_2^*\pi_1^*\\ n\ \ \pi_1\end{pmatrix}$ (-6.88 eV); but the contribution of the $\Phi\begin{pmatrix}\pi_2^*\\ n\end{pmatrix}$ configuration upon the wave function of the $n\to\pi^*$ state is very weak.

γ) the repolarization of the π_2 bond induced by the $n\to\pi_1^*$ excitation, but this effect is very weak, since the dipolar term $a_{\pi_2\pi_1^*} - a_{\pi_2 n}$ is nearly zero.

In the polyenic aldehydes the repolarization of some bonds during the $n\to\pi^*$ excitation is a very localized phenomenon. The C=0 region is the only one to be repolarized. The $\pi_{C=0}$ and the $\sigma_{C=0}$ bonds are repolarized mostly by the $\pi\to$C=0 excitation since the weight of the others excitations $n\to\pi_{(C=C)_k}$ decreases exponentially; the other π or σ bonds are not significantly repolarized by the $n\to\pi_{C=0}^*$ excitation since the dipole-dipole $(\pi_k\pi_k^*, \pi_1^*\pi_1^* - nn)$ or $(\sigma_k\sigma_k^* - \pi_1^*\pi_1^* — nn)$ interaction decreases as $1/R^3$.

The lowering effect of the doubly excited determinants upon the $n\to\pi^*$ state has been also obtained on both semi-empirical [20, 21] and *ab initio* calculations [31, 33].

3. Conclusion

This work shows that in the $n\to\pi^*$ excitation, the delocalization of the hole and of the particle does not extend very far. So the $n\to\pi^*$ excitation appears to be localized in the $\pi_{C=0}$ region: This fact explains very well why the $n\to\pi^*$ transition energy of a polyenic aldehyde reaches a constant value for a very small value of the number n of double bonds.

After Configuration Interaction, both the delocalized and localized models appear to be equivalent. In the same way as in the $\pi\to\pi^*$ excitation, the CI used in delocalized model tends to relocalize the excitation, but in the case of the $n\to\pi^*$ excitation, the relocalization of the excitation does not come from a reducing of the long range delocalization effects: the CI simply relocalizes the excitation towards the C=0 regions.

We have also shown that in the same way as in all excited states, the $n \rightarrow \pi^*$ state presents a charge migration i.e. a charge reorganisation with regards to the ground state, so some bonds are repolarized during the $n \rightarrow \pi^*$ excitation. This phenomenon is also localized in the $\pi_{C=0}$ region.

So all polyenic aldehydes with an infinite number of double bonds N, are similar to acrolein with regards to the $n \rightarrow \pi^*$ excitation.

We thank Dr. J. P. Malrieu for many fruitful discussions and for his interest and very helpful critiscisms.

References

1. McMurry, H. L., Mulliken, R. S.: Proc. Natl. Acad. Sci. **26**, 312 (1940); McMurry, H. L.: J. Chem. Phys. **9**, 231 (1941); Mulliken, R. S.: J. Chem. Phys. **3**, 564 (1935)
2. Kasha, M.: Discuss. Faraday Soc. **9**, 14 (1950)
3. Jaffé, H. H., Orchin, M., in: *Theory and applications of ultraviolet spectroscopy*. New York: Wiley 1964
4. Price, W. C.: J. Chem. Phys. **3**, 256 (1935)
5. Walsh, A. D.: Proc. Roy. Soc. (London) A **185**, 176 (1946)
6. Cohen, A. D., Reid, C.: J. Chem. Phys. **24**, 85 (1956)
7. Robinson, G. W., DiGiorgio, V. E.: Can. J. Chem. **36**, 31 (1958)
8. DiGiorgio, V. E., Robinson, G. W.: J. Chem. Phys. **31**, 1678 (1959)
9. Fleming, G., Anderson, M. M., Harrison, A. J., Pickett, L. W.: J. Chem. Phys. **30**, 351 (1959)
10. Henderson, J. R., Muramoto, M.: J. Chem. Phys. **43**, 1215 (1965)
11. Barnes, E. E., Simpson, W. T.: J. Chem. Phys. **39**, 670 (1963)
12. Udvarhazi, A., El Sayed, M. A.: J. Chem. Phys. **42**, 3335 (1965)
13. Johnson, W. C., Simpson, W. T.: J. Chem. Phys. **48**, 2168 (1968)
14. Walsh, A. D.: Trans. Faraday Soc. **41**, 498 (1945)
15. Eberhart, W. H., Renner, H.: J. Mol. Spectry. **6**, 483 (1961)
16. Hollas, J. M.: Spectrochim. Acta **19**, 1425 (1965)
17. Becker, R. S., Inuzuka, K., King, J.: J. Chem. Phys. **52**, 5164 (1970)
18. Blout, E. R., Fieds, M. J.: J. Am. Chem. Soc. **70**, 189 (1948)
19. Giessner–Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **13**, 265 (1965)
20. Giessner–Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **17**, 120 (1970)
21. Giessner–Prettre, C., Pullman, A.: Theoret. Chim. Acta (Berl.) **18**, 14 (1970)
22. Anno, T., Sado, A.: J. Chem. Phys. **26**, 1759 (1957)
23. Sidman, J. W.: J. Chem. Phys. **27**, 429 (1957)
24. Parks, J. M., Parr, R. G.: J. Chem. Phys. **32**, 1657 (1960)
25. Pilar, F. L.: J. Chem. Phys. **47**, 884 (1967)
26. Plotnikov, U. G.: Opt. Spektrosk. **20**, 217 (1966)
27. Inuzuka, K., Becker, R. S.: Bull. Chem. Soc. Japan **45**, 1557 (1972)
28. Edwards, T. G., Grinter, R.: Theoret. Chim. Acta (Berl.) **12**, 387 (1968)
19. Devaquet, J.: Am. Chem. Soc. **94**, 5160 (1972)
30. Ho, J. C., Segal, G. A., Taylor, H. S.: J. Chem. Phys. **56**, 1520 (1972)
31. Jungen, M., Labhart, H.: Theoret. Chim. Acta (Berl.) **9**, 345 (1968)
32. Ditchfield, R., Del Bene, J. E., Pople, J. A.: J. Am. Chem. Soc. **94**, 703 (1972)
33. Whitten, J. L., Hackmeyer, M.: J. Chem. Phys. **51**, 5584 (1969)
34. Buenker, R. J., Peyerimhoff, S.: J. Chem. Phys. **53**, 1368 (1970)
35. Del bene, J. F., Ditchfield, R., Pople, J. A.: J. Chem. Phys. **55**, 2236 (1971)
36. Dunning, T. H., McKoy, V.: J. Chem. Phys. **48**, 5263 (1968)
37. Simpson, W. T.: J. Am. Chem. Soc. **73**, 5363 (1951); **77**, 6164 (1955)
38. Pople, J. A., Walmsley, S. M.: Trans. Faraday Soc. **58**, 441 (1962)
39. Murrell, J. B.: J. Chem. Phys. **37**, 1162 (1962)
40. Langlet, J.: Theoret. Chim. Acta (Berl.) **27**, 441 (1962)
41. Labglet, J., Malrieu, J. P.: Theoret. Chim. Acta (Berl.) **30**, 59 (1973)

42. Denis, A., Langlet, J., Malrieu, J. P.: Theoret. Chim. Acta (Berl.) **29**, 117 (1973)
43. Flygare, W. H., Pochan, J. M., Kerley, G. I., Caves, T., Karplus, M., Aung, S., Pitzer, R. M., Chan, S. I.: Chem. Phys. **45**, 2793 (1966)
44. Aung, S., Pitzer, R. M., Chan, S. I.: J. Chem. Phys. **45**, 3457 (1966)
45. Baird, N. C.: Mol. Photochem. **5** (2), 203 (1973)

Dr. J. Langlet
Institut de Biologie Physico-Chimique
Laboratoire de Biochimie Théorique
associé au C.N.R.S.
13, Rue P. et M. Curie
F-75005 Paris V, France