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Influence of σ Systems on the $\pi\pi^*$ Transition Energies: A Simple Application to the Series of Linear Polyenes

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One uses a 2nd order perturbation expression of the transition energies for the series of linear polyenes with π delocalized molecular orbitals and σ fully localized bond molecular orbitals. One only keeps the $\sigma\pi$ coulombic integrals and the local $\sigma\sigma^*$ excitations. Within these assumptions it is possible to demonstrate:

the effect of the monoexcitations on CH and CC bonds mainly depends of the pairing or non pairing character of the considered $\pi\pi^*$ transition. It tends to zero as n^{-1} as the dimension n of the system increases.

the rôle of the $\begin{array}{c|c}\sigma & \sigma^* \\ \pi & \pi^*\end{array}$ excitations increases as n increases and tends towards a limit which depends of the considered $\pi\pi^*$ transition. But the asymptotic final effect of σ system is smaller than for ethylene.

the contribution of the σ system to the actual $\pi\pi^*$ singlet triplet separation decreases towards zero when the dimension of the system increases.

Zur Berechnung der Übergangsenergien einer Reihe linearer Polyene mit delokalisierten π- und lokalisierten σ-Orbitalen wird die Störungstheorie 2. Ordnung herangezogen. Dabei werden nur die $\sigma\pi$-Coulombintegrale und die lokalen $\sigma\sigma^*$-Anregungen berücksichtigt. Dann zeigt sich: 1. Der Einfluß einfacher Anregungen der CH- und CC-Bindungen auf einen $\pi-\pi^*$-Übergang hängt vornehmlich davon ab, ob die π- und π^*-Orbitale gepaart sind. Der Effekt geht wie $1/n$ gegen Null, wenn n die Dimension der Kette ist. 2. Die Rolle der $\begin{array}{c|c}\sigma & \sigma^* \\ \pi & \pi^*\end{array}$-Anregungen steigt mit n gegen einen vom betrachteten $\pi-\pi^*$-Übergang abhängigen Grenzwert. 3. Der Beitrag des σ-Systems zur $\pi-\pi^*$ Singulett-Triplett-Aufspaltung verschwindet für große Systeme.

On utilisé une méthode de perturbation au 2è ordre pour calculer les énergies de transition π-π^* dans la série des polyenes linéaires, en utilisant des orbitales moléculaires π délocalisées et des orbitales moléculaires σ complètement localisées sur les liaisons. On ne conserve que les intégrales coulombiennes σ-π et les excitations σ-σ^* locales. Avec ces hypothèses on peut démontrer que:

– l'effect des monoexcitations sur les liaisons CC et CH est nettement différent pour les transitions entre orbitales appariées et entre orbitales non appariées. Il tend vers zero comme n^{-1} quand le nombre n de carbones augmente;

– le rôle des excitations $\begin{array}{c|c}\sigma & \sigma^* \\ \pi & \pi^*\end{array}$ augmente quand n augmente et tend vers une limite qui dépend peu de la transition considérée. Mais la valeur asymptotique de l'effet final du système σ est nettement plus faible que l'effet du système σ sur l'éthylène;

– la contribution du système σ à la différence d'énergie singulet-triplet tend vers zero quand la dimension du système augmente.

1. Introduction

The σ-π separation hypothesis is understood in very different ways by different authors (for a review of this question see Ref. [1]). The recent progresses of all electrons calculations, both in "*ab initio*" systematics and with more or less parametrized and approximated methods, destroy most of the common ideas about the clear separation and the relative independance of π and σ systems.

As concerns the spectral properties it is known now that the mono-electronic energy levels are completely mixed and that numerous σ-π^* or π-σ^*, even perhaps $\sigma\sigma^*$ transitions, lie in the mean part of the π π^* spectrum. It is also clear from *ab initio* calculations that the π-π^* excited states have important components on σ-σ^* monoexcited configurations: for instance in ethylene a σ-σ^* transition has a coefficient of 0.206 in the first π-π^* singlet state [2], in the formaldehyde molecule a σ-σ^* excited configuration has a 0.408 coefficient in the first order calculated π-π^* wave function [3]. The following questions then become important,

1. is this order of magnitude of σ-π mixing in π-π^* excited states independant of the dimension and specificity of the system?

2. is the influence of the σ system the same on all the π-π^* transitions? Is it a simple translation of the π-π^* spectrum or may it introduce level crossings?

3. for the "corresponding" π-π^* singlet and triplet excited states (when a correspondence is possible) how does the σ system contribute to the singlet-triplet splitting? This contribution appears decisive in small systems [2, 3], but it is not sure that it behaves the same way when the dimension of the π system increases.

These questions are of primordial interest for the theoretical status of the enormous amount of pure π calculations of the π-π^* spectral properties of conjugated molecules. At least one third of the "quantum chemical" calculations of the past ten years were devoted to this question in the Pariser Parr hypothesis [4]. It is important to know the limits of the validity of these works, and to decide wether a π π^* parametrized method is conceivable or not with a reasonable realism.

The present paper tries to bring answer to these questions, simplifying the problem in order to save both the realism of the model and the possibility of an algebraical analysis.

2. Method and Hypothesis

1. We first assume that we have a set of π delocalized molecular orbitals. It is possible to build zeroth-order π-π^* excited states in the virtual orbital approximation, simply by substituting π by π^* Molecular Orbitals in the ground state determinant. We suppose that at least some of these π-π^* excited configurations are not degenerate neither with other π-π^* excited configurations nor with σ-σ^* excited configurations. Let us consider one of such non degenerate excited states, let us call p-q^*, which corresponds to the transition from one occupied molecular orbital p to a virtual orbital q^*. This assumption of non-degeneracy seems reasonable if we consider the lowest π-π^* excited states of molecules with low degree of symmetry. For that reason we cannot treat here the case of cyclic polyenes, which present many degeneracies.

2. We assume that we may have a reasonable estimation of the actual pq^* transition energy by making a 2nd order perturbation development of the full configuration interaction matrix on both the ground state and the $p-q^*$ excited state. In such a case the energy corrections are additive, and one may split them in a pure π correction, a $\sigma-\pi$ correction and a pure σ correction. We do not consider

here the π correction, which will be the object of a further paper, and are only interested in the last two ones. It has been demonstrated [5] that important cancellations occur on the final expression of the 2nd order corrected energy, and that for instance the pure σ corrections are the same on the ground state and on the π-π^* excited state and thus may be neglected. We shall only consider the σ-π correction to the π-π^* transition energy.

3. As we only consider non degenerate excited states, we certainly may transform the σ molecular orbitals among themselves, and the σ^* molecular orbitals among themselves. In particular we suppose that we may localize them on the chemical bonds to a large amount. This is confirmed by the analysis of the localizabilities of "*ab initio*" [6] and empirical σ [7] molecular orbitals. We suppose that no important change is introduced by the use of fully localized σ bond orbitals, since they have a very large overlap with the SCF localized MOs. In other words our zeroth order wave function will be analogous to the wave function proposed by McConnell for the study of hyperfine ESR coupling constants on hydrogen atoms [8];

$$\Phi_0 = |\sigma_1\bar{\sigma}_1 \dots \sigma_n\bar{\sigma}_n\pi_1\bar{\pi}_1 \dots \pi_m\bar{\pi}_m|$$

is the zeroth order ground state wave function and the excited state zeroth order wave function is given by

$$\Phi_{p\to q^*} = \frac{1}{\sqrt{2}} |\sigma_1\bar{\sigma}_1 \dots \sigma_n\bar{\sigma}_n\pi_1\bar{\pi}_1 \dots (p\,\bar{q}^* \pm q^*\bar{p}) \dots \pi_m\bar{\pi}_m| \,;$$

in both wave functions the σ orbitals are bond orbitals and the π orbitals are delocalized MOs.

4. In order to simplify our problem we shall use the CNDO approximations for the σ π integrals [9]. We neglect the exchange integrals and the integrals which would involve two different π atomic orbitals. We could introduce for instance the exchange integrals which are responsible of the hyperfine splitting constants on hydrogen atoms and which are introduced in the INDO version of CNDO [10]. This would not change the general behaviour but only introduce some complexities in the calculations (see Appendix A). These types of integrals are responsible of the possible "change" of the number of the π and σ electrons (what Harris calls the "non-conservation" [11]). It will be seen in the discussion of the singlet-triplet splitting that they are not very important.

5. We shall neglect the σ excitations involving two different bonds: for instance one could introduce the σ excitations in which the electron of a CH bond jumps to the antibonding orbital of an adjacent σ C–C bond. These excitations are also neglected in the McConnell successfull treatment. One must recall that the overlap between two bond orbitals, even adjacent, never exceeds 0.2 [7]. The bielectronic $(\sigma\,\pi|\sigma'^*\pi)$ integrals which are involved in our treatment would introduce this overlap factor; as the integrals are used to the square, the influence of these delocalization excitations to our problem should be negligible. Moreover the $(\sigma\,\pi|\sigma'^*\pi)$ integrals are zero in the widely used CNDO hypothesis, when σ and σ' are fully localized bond orbitals; the SCF MOs have a very strong overlap with these fully localized bond orbitals ($\simeq 0.98$).

3. Effect of $\sigma\sigma^*$ Monoexcited States

A. Theoretical Relations

As we suppose the σ orbitals to be very close to the SCF localized MOs, the $\sigma-\sigma^*$ monoexcited states do not interact with the ground state. They interact with the $p-q^*$ excited states by the matrix element

$$2(\sigma\, q^*|\sigma^* p)-(\sigma q^*|p\sigma^*) \quad \text{if they are singlet states},$$

$$(\sigma\, q^*|p\ \sigma^*) \quad \text{if they are triplet states}.$$

$\left(\text{here we use the notation } (ij|kl)=\left\langle i(1)j(2)\left|\frac{1}{r_{12}}\right|k(1)\,l(2)\right\rangle\right)$. The second order correction is

$$[2(\sigma\ q^*|\sigma^*\ p)-(\sigma\ q^*|p\ \sigma^*)]^2/(E_{\sigma\sigma^*}-E_{pq^*})$$

or

$$(\sigma\ q^*|p\ \sigma^*)^2/(E_{\sigma\sigma^*}-E_{pq^*}).$$

With our hypothesis the second integral is zero, since it is a combination of exchange $\sigma\ \pi$ integrals. The triplet is not affected in the CNDO hypothesis by the $\sigma\ \sigma^*$ excited states. "*Ab initio*" calculations confirm that their influence is very small [2, 3]. This explains the difficulties accountered by various authors to find adequate π integrals systematics which would reproduce both the singlet and triplet $\pi\ \pi^*$ spectra.

The singlet is affected by the quantity

$$\Delta E^1=\sum_{\sigma}\sum_{\sigma^*}4(\sigma\ q^*|\sigma^*\ p)^2/(E_{\sigma\sigma^*}-E_{pq^*}). \tag{1}$$

If we only consider the excitations inside the σ bonds and develop p and q^* in the basis of their π atomic orbitals, we get

$$\Delta E^1=\sum_{\sigma}\left[\sum_{k}4(\sigma^*\ k|\sigma\ k)\ (c_{kp}\ c_{pq^*})\right]^2/(E_{\sigma\sigma^*}-E_{pq^*}) \tag{2}$$

The integral $(\sigma^*\ k|\sigma\ k)$ represents the interaction of the dipolar σ-σ^* distribution with the charge in the k^{th} π atomic orbital. This integral decreases as r^{-2} if r is the distance between the σ bond and the π atomic orbital considered. We shall only retain the integrals between the σ bond and the π atomic orbitals of the carbon atoms which are involved in this bond. It would be more reasonable in actual calculations to take into account the interaction at one bond distances. But we are mainly interested here in asymptotic behaviour and it is easy to see that the inclusion of long distance integrals would not affect it: this is mainly due to the fact that in the series of linear polyenes the distance between the first and the r^{th} carbon atoms is proportional to r, and that

$$\sum_{r=1}^{n}\frac{1}{r^2}<\frac{\pi^2}{6}.$$

The inclusion of long distances interactions cannot change the n dependance of the phenomenon except by a constant multiplicative factor (see Appendix B).

Then, we must distinguish between the CH bonds, which only imply one C atom, and the CC bonds, which imply two.

B. Effect of the C–H *Bonds*

For the CH bonds the summation is simple:

$$\begin{aligned}\Delta E^1_{\mathrm{CH}} &= 4\sum_{k=1}^{n} (\sigma^*\, k\,|\,\sigma\, k)\,(c_{kp}\, c_{kq^*})^2/(E_{\sigma\sigma^*} - E_{pq^*})\\ &\quad + 8(\sigma^*\, 1\,|\,\sigma\, 1)^2\,(c_{1p}\, c_{1q^*})^2/(E_{\sigma\sigma^*} - E_{pq^*})\,.\end{aligned} \tag{3}$$

We shall suppose that all the $(\sigma^*\, k\,|\,\sigma\, k)$ integrals and $E_{\sigma\sigma^*}$ are equal, and introduce the Hückel values for the π coefficients.

Then

$$\Delta E^1_{\mathrm{CH}} = \frac{16}{(n+1)^2}\,\frac{(\sigma k|\sigma^* k)^2}{E_{\sigma\sigma^*} - E_{pq^*}}\left\{\sum_{k=1}^{n}\sin^2\frac{kp\pi}{n+1}\sin^2\frac{kq^*\pi}{n+1} + 2\sin^2\frac{p\pi}{n+1}\sin^2\frac{q^*\pi}{n+1}\right\}.$$

$$\sin^2\frac{k\pi p}{n+1}\sin^2\frac{k\pi q^*}{n+1}$$

$$= \frac{1}{4}\left[\cos^2\frac{\pi k(p+q^*)}{n+1} + \cos^2\frac{\pi k(p-q^*)}{n+1} - \cos^2\frac{k\pi p}{n+1} - \cos^2\frac{k\pi q^*}{n+1}\right]$$

$$\sum_{k=1}^{n}\cos^2\frac{\pi k(p+q^*)}{n+1} = \sum_{k=1}^{n}\cos^2\frac{\pi k(q^*-p)}{n+1} = \frac{n-1}{2}$$

if $p+q^*$ is different from $n+1$.

$$\sum_{k=1}^{n}\cos^2\frac{k\pi p}{n+1} = \sum_{k=1}^{n}\cos^2\frac{k\pi q^*}{n+1} = -1\,.$$

Thus the effect of CH bonds on non pairing transitions ($q^* \neq n+1-p$) is given by

$$\Delta E^1_{\mathrm{CH}} = \frac{4}{(n+1)^2}\,\frac{(\sigma k|\sigma^* k)^2}{E_{\sigma\sigma^*} - E_{pq^*}}\left[n+1+8\sin^2\frac{p\pi}{n+1}\sin^2\frac{q^*\pi}{n+1}\right]. \tag{4a}$$

For the pairing transitions, the sum becomes

$$\Delta E^1_{\mathrm{CH}} = \frac{4}{(n+1)^2}\,\frac{(\sigma k|\sigma^* k)^2}{E_{\sigma\sigma^*} - E_{pq^*}}\left[\frac{3(n+1)}{2}+8\sin^4\frac{p\pi}{n+1}\right]. \tag{4b}$$

The effect of the CH $(\sigma|\sigma^*)$ monoexcited configurations on the singlet $\pi\,\pi^*$ monoexcited states,

for a given molecule depends of the pairing or non pairing character of the $\pi\,\pi^*$ transition: for large n it is about 3/2 larger for pairing transitions than for non-pairing transitions. In all cases it depends of the considered transition $(p|q^*)$ by the factor $(E_{\sigma|\sigma^*} - E_{p|q^*})^{-1}$

it decreases as n^{-1} as the dimension n of the system increases. (One may neglect the variation of the denominator which tends to a limit for the lowest energy transition.)

C. Effect of the C–C *Bonds*

The C–C bonds involving two carbon atoms the summation becomes

$$\Delta E^1_{\mathrm{CC}} = \frac{16}{(n+1)^2}\,\frac{(\sigma k|\sigma^* k)^2}{E_{\sigma\sigma^*}-E_{pq^*}}\left\{\sum_{k=1}^{n-1}\sin^2\frac{k\pi q^*}{n+1}\sin^2\frac{k\pi q^*}{n+1}\right.$$

$$\left.+\sin^2\frac{(k+1)\pi p}{n+1}\sin^2\frac{(k+1)\pi q^*}{n+1}-2\sin\frac{k\pi p}{n+1}\sin\frac{k\pi q^*}{n+1}\sin\frac{(k+1)\pi p}{n+1}\sin\frac{(k+1)\pi q^*}{n+1}\right\}.$$

The two first terms lead to equal contributions which are immediately deduced from the preceeding result. The last one gives, after development:

$$-\frac{1}{2}(n+1)\cos\frac{p\pi}{n+1}\cos\frac{q^*\pi}{n+1} \qquad \text{for non pairing transitions}$$

and

$$+\frac{n+3}{2}\cos^2\frac{p\pi}{n+1}+\frac{n-1}{4}+\frac{1}{2}\cos\left(\frac{q^*-p}{n+1}\right)\pi \quad \text{for a pairing transition}.$$

This correction is negative, and small for the lowest transition $\left(p=\frac{n}{2},\ q^*=\frac{n+1}{2}\right)$ and large n.

Then the C–C bond excitations lead to

$$\Delta E^1_{\mathrm{CC}}=\frac{(\sigma k|\sigma^* k)^2}{E'_{\sigma\sigma^*}-E_{pq^*}}\,\frac{8}{(n+1)^2}\left[(n+1)\left(1-\cos\frac{p\pi}{n+1}\cos\frac{q^*\pi}{n+1}\right)-4\sin^2\frac{p\pi}{n+1}\sin^2\frac{q^*\pi}{n+1}\right]$$

if the pq^* transition is not a pairing transition.

and to

$$\Delta E^1_{\mathrm{CC}}=\frac{(\sigma k|\sigma^* k)^2}{E'_{\sigma\sigma^*}-E_{pq^*}}\,\frac{8}{(n+1)^2}\left[(2n+1)+(n+3)\cos^2\frac{p\pi}{n+1}+\cos\frac{(q^*-p)\pi}{n+1}-4\sin^4\frac{p\pi}{n+1}\right]$$

if pq^* is a pairing transition.

The effect of the C–C bonds monoexcitations also decreases as n^{-1} when the dimension of the system increases, but one may notice

that it also depends by the numerator expression of the considered π–π^* transition,

that their effect is almost two times larger for large n than the effect of the CH bonds.

The conclusion is that people who make configuration interaction of the monoexcited states will only get a rapid decrease of their lowering in π-π^* transition energies at least as concerns the effect of σ-σ^* transition energies.

4. Role of Higher Excitations

A. Formalism

The general expression of the 2^{nd} order corrected transition energy has been given elsewhere [5]. As concerns the influence of the σ system on a given $\pi-\pi^*$ transition $(p|q^*)$ it may be decomposed as follow.

The effect of almost all the triexcited configurations on the excited state cancels the effect of almost all the diexcited configurations on the ground state. One has only to consider:

1. The effect of the diexcited configurations which have *one* of the (p, q^*) orbitals involved in their excitations; their effect on the ground state must be divided by two. The $\begin{array}{c|c} p & \pi^* \\ \sigma & \sigma^* \end{array}$ configurations give for instance

$$2\sum_{\sigma}\sum_{\sigma^*}\sum_{\pi^*}{}' \, [(\sigma q^*|\sigma^*\pi^*)^2+(\sigma q^*|\pi^*\sigma^*)^2-(\sigma q^*|\sigma^*\pi^*)\,(\sigma q^*|\pi^*\sigma^*)]/(E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle\pi^*\end{array}}-E_{p\,q^*})$$

$$-[(\sigma\, p|\sigma^*\pi^*)^2+(\sigma p|\pi^*\sigma^*)^2-(\sigma p|\sigma^*\pi^*)\,(\sigma p|\pi^*\sigma^*)]/E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle q^*\end{array}}$$

where $\sum'$ excludes $\pi^* = q^*$.

If one only considers the coulomb σ π integrals one gets:

$$A = 2\sum_{\sigma}\sum_{\sigma^*}\sum_{\pi^*}{}' \left[(\sigma q^*|\sigma^*\pi^*)^2/\left(E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle\pi^*\end{array}}-E_{p|q^*}\right)-(\sigma p|\sigma^*\pi^*)^2/E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle\pi^*\end{array}}\right] \tag{5}$$

The symmetrical $\begin{array}{c|c} \pi & q^* \\ \sigma & \sigma^* \end{array}$ configurations give

$$B = 2\sum_{\sigma}\sum_{\sigma^*}\sum_{\pi}{}' \left[(\sigma\pi|\sigma^* p)^2/\left(E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle \pi & \scriptstyle q^*\end{array}}-E_{pq^*}\right)-(\sigma\pi|\sigma^* q^*)^2/E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle \pi & \scriptstyle q^*\end{array}}\right]. \tag{6}$$

One should consider in the same way the role of the $\begin{array}{c|c} \sigma & \pi^* \\ \sigma & q^* \end{array}$ and $\begin{array}{c|c} \pi & \sigma^* \\ p & \sigma^* \end{array}$ configurations. But the matrix elements on both ground and excited states are always σ π exchange integrals. For instance the $\begin{array}{c|c} \sigma & \pi^* \\ \sigma & q^* \end{array}$ configurations would give

$$\begin{aligned} C = 2\sum_{\sigma<\sigma^*}\sum\sum_{\pi^*} \Big[&[(\sigma\sigma'|\pi^* p)^2+(\sigma\sigma'|p\pi^*)^2-(\sigma\sigma'|p\pi^*)\,(\sigma\sigma'|\pi^* p)]/\left(E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\pi^* \\ \scriptstyle \sigma' & \scriptstyle q^*\end{array}}-E_{p|q^*}\right) \\ &-[(\sigma\sigma'|\pi^* q^*)^2+(\sigma\sigma'|\pi^* q^*)^2-(\sigma\sigma'|\pi^* q^*)\,(\sigma\sigma'|q^*\pi^*)]/E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\pi^* \\ \scriptstyle \sigma' & \scriptstyle q^*\end{array}}\Big] \end{aligned} \tag{7}$$

which must be neglected on our hypothesis.

If the two orbitals p and q^* are implied in the diexcitations one must distinguish:

i) the effect of the $\begin{array}{c|c} \sigma & \sigma^* \\ p & q^* \end{array}$ excitations on both the excited and the ground state leads to

$$\sum_{\sigma}\sum_{\sigma^*} 3\,(p\sigma|\sigma^* q^*)^2/E_{\begin{array}{c|c}\scriptstyle\sigma & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle q^*\end{array}}$$

which is neglected.

ii) the effect of the $\begin{array}{c|c} p & \sigma^* \\ p & \sigma^* \end{array}$ excited states leads to

$$\sum_{\sigma^*\leqq\sigma'^*}\sum -2(\sigma^*\sigma'^*|pp)^2/_{\begin{array}{c|c}\scriptstyle p & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle \sigma'^*\end{array}}+(\sigma^*\sigma'^*|pq^*)^2/\left(E_{\begin{array}{c|c}\scriptstyle p & \scriptstyle\sigma^* \\ \scriptstyle p & \scriptstyle \sigma'^*\end{array}}-E_{pq^*}\right).$$

This contribution and the symmetrical one from $\begin{array}{c|c} \sigma & q^* \\ \sigma' & q^* \end{array}$ excited states are both neglected in our hypothesis.

Then there only remains the effect of the $\sigma|\sigma^*$ excitations on the monoexcited state, i.e. the influence of the $\begin{array}{c|c}\sigma & \sigma^* \\ p & q^*\end{array}$ diexcited configurations. They give:

$$D=\sum_{\sigma}\sum_{\sigma^*}\{[(\sigma q^*|\sigma^* q^*)-(\sigma q^*|q^*\sigma^*)-(\sigma p|\sigma^* p)+(\sigma p|p\sigma^*)]^2$$

$$+[(\sigma q^*|\sigma^* q^*)-(\sigma p|\sigma^* p)]^2+[(\sigma q^*|q^*\sigma^*)\pm(\sigma p|p\sigma^*)]^2\}\Big/\left(E_{\substack{\sigma|\sigma^* \\ p|q^*}}-E_{p|q^*}\right)$$

which reduces to

$$D=\sum_{\sigma}\sum_{\sigma^*}2\,[(\sigma q^*|\sigma^* q^*)-(\sigma p|\sigma^* p)]^2\Big/\left(E_{\substack{\sigma|\sigma^* \\ p|q^*}}-E_{pq^*}\right)$$

if one neglects the σ π exchange integrals.

One may treat immediately this last summation. It is clear that for the pairing transitions, where the charge distributions of q^*q^* and $p\,p$ are equivalent, their effect is zero. It would be different from zero for other π π^* excited states, but their contribution of course would vanish as n^{-1}, since the degree of freedom is the same as for the monoexcited states. These configurations are the one involved in an eventual single determinant-variational process on the excited state wave function. It is clear thus that the effect of such a process would not decrease the energy for a pairing transition or would give a lower and lower decrease in energy for an ordinary transition. For instance the effect of the CH $\begin{array}{c|c}p & q^* \\ \sigma & \sigma^*\end{array}$ excitations is given by

$$\Delta E^m_{\mathrm{CH}}=2(\sigma k|\sigma^* k)^2\,\frac{1}{(n+1)^2\,(E_{\sigma\sigma^*})}$$

$$\cdot\left[n+1+2\sin^4\frac{q^*\pi}{n+1}+2\sin^4\frac{p\pi}{n+1}-2\sin^2\frac{q^*\pi}{n+1}\sin^2\frac{p\pi}{n+1}\right]$$

if $p+q^*\neq n+1$.

Then we may focus our attention on the first two contributions A and B. We shall decompose them again into CH and CC excitations.

B. Effect of C–H $\begin{array}{c|c}\pi & \pi^* \\ \sigma & \sigma^*\end{array}$ *Diexcited Configurations*

$$\Delta E^2_{\mathrm{CH}}=2(\sigma k|\sigma^* k)^2\left\{\sum_{\sigma_k}\sum_{v^*}{}'\,\frac{C^2_{kq^*}C^2_{kv^*}}{E(v^*)}-\frac{C^2_{kp}C^2_{kv}}{E'(v^*)}+\sum_{\sigma_k}\sum_{u}{}'\,\frac{C^2_{kp}C^2_{ku}}{E(u)}-\frac{C^2_{kq^*}C^2_{ku}}{E'(u)}\right\}$$

where $\sum_{v^*}'$ is a sum over the virtual π orbitals different from q^* and

$$E(v^*)=E_{\substack{\sigma|\sigma^* \\ p|v^*}}-E_{p|q^*},\qquad E'(v^*)=E_{\substack{\sigma|\sigma^* \\ p|v^*}}.$$

(The corresponding notations over occupied molecular orbitals are evident.)

It is convenient to sum first over k. We are mainly interested now in the asymptotic behaviour. An exact full calculation even in our simplified model would be rather long and tedious. We shall only retain the contributions which give the asymptotic limit i.e. the terms of higher degree in n.

The first summation gives

$$\Delta E^2_{\mathrm{CH}} = 2(\sigma k|\sigma^* k)^2 \left\{ \sum_{v^*}{}' \frac{1}{(n+1)^2} \left[\frac{n+1}{E(v^*)} - \frac{(n+1)}{E'(v^*)} \delta(v^*, p) \right] + \sum_{u}{}' \frac{1}{(n+1)^2} \left[\frac{n+1}{E(u)} - \frac{(n+1)\,\delta(q^*, u)}{E'(u)} \right] \right\}$$

where

$$\delta(v^*, p) = 1 \quad \text{if } p + v^* \neq n+1$$
$$= \tfrac{3}{2} \quad \text{if } p + v^* = n+1$$

(and analogous relations for $\delta(q^*, u)$).

For the investigation of the asymptotic behaviour it is of no account to neglect or include the case $v^* = q^*$ (and $u = p$) and to distinguish the exceptional case where $\delta(v^*, p)$ (and $\delta(q^*, u)$) is equal to 3/2 instead of 1. But the denominators are functions of the index of summation, in a relatively complex way. We shall try two successive analysis, one with a closure approximation about the π-π^* transition energies, and one with a linearisation of the denominator dependence on the indices.

a) *Closure Approximation for the π π^* Transition Energies:* One gets then,

$$\Delta E^2_{\mathrm{CH}} \simeq \frac{(\sigma k|\sigma^* k)^2}{(n+1)} \left[\frac{1}{E(\bar{v}^*)} - \frac{1}{E'(\bar{v}^*)} + \frac{1}{E(\bar{u})} - \frac{1}{E'(\bar{u})} \right].$$

The denominators are mean denominators. One may express them using monoelectronic energies to visualize the dependance of the denominators on the choice of the calculated pq^* transition.

$$E(\bar{v}^*) \simeq E_{\sigma\sigma^*} + \bar{\varepsilon}_{v^*} - \varepsilon_{q^*},$$
$$E'(\bar{v}^*) = E_{\sigma\sigma^*} + E_{pq^*} + \bar{\varepsilon}_{v^*} - \varepsilon_{q^*}$$

(where $\bar{\varepsilon}_{v^*}$ is the mean monoelectric energies of virtual orbitals) and similar relations for the occupied orbitals.

If q^* and p are in the mean parts of the monoelectronic energies π spectrum, then $\bar{\varepsilon}_{v^*} - \varepsilon_{q^*}$ and $\bar{\varepsilon}_u - \varepsilon_p$ are negligible and the effect of the CH bonds becomes

$$\Delta E^2_{\mathrm{CH}} \simeq 2(\sigma k|\sigma^* k)^2 \left[\frac{1}{E_{\sigma\sigma^*}} - \frac{1}{E_{\sigma\sigma^*} + E_{\pi\pi^*}} \right].$$

b) *Linearisation of Denominator Variations:* Using the preceeding expressions of $E(v^*)$ and $E'(v^*)$, one may write

$$\Delta E^2_{\mathrm{CH}} - \frac{2(\sigma k|\sigma^* k)^2}{n+1} \left\{ \sum_{v^*} \frac{1}{E_{\sigma\sigma^*}} \left(1 - \frac{\varepsilon_{v^*} - \varepsilon_{q^*}}{E_{\sigma\sigma^*}} \right) - \frac{1}{E_{\sigma\sigma^*} + E_{pq^*}} \left(1 - \frac{\varepsilon_{v^*} - \varepsilon_{q^*}}{E_{\sigma\sigma^*} + E_{pq^*}} \right) + \sum_{u} \frac{1}{E_{\sigma\sigma^*}} \left(1 - \frac{\varepsilon_p - \varepsilon_u}{E_{\sigma\sigma^*}} \right) - \frac{1}{E_{\sigma\sigma^*} + E_{pq^*}} \left(1 - \frac{\varepsilon_p - \varepsilon_u}{E_{\sigma\sigma^*} + E_{pq^*}} \right) \right\}$$

by developing $(1 + X)^{-1}$ to the first order. Then one gets first the result one had for the closure approximation plus a correction. For the calculation of this correction one needs an evaluation of the dispersion of the monoelectronic energies. We made use of the expressions of the Hückel monoelectronic energies: one knows that the lowest Hückel transition energy is bad since it tends to zero in the series of linear polyenes, while it should tend to a non zero limit, but one may assume however that it gives a reasonable evaluation of the difference between occupied (or virtual) molecular orbitals. It introduces a parameter β, which is negative:

$$\varepsilon_p = 2\beta \cos\frac{p\pi}{n+1}\,.$$

One then gets

$$\begin{aligned}\Delta E^2_{\mathrm{CH}} = (\sigma k|\sigma^* k)^2 \Bigg\{ & 2\left(\frac{1}{E_{\sigma\sigma^*}} - \frac{1}{E_{\sigma\sigma^*}+E_{pq^*}}\right)\\ & + (\varepsilon_{q^*}-\varepsilon_p)\left(\frac{1}{E^2_{\sigma\sigma^*}} - \frac{1}{(E_{\sigma\sigma^*}+E_{pq^*})^2}\right)\\ & + 4\beta\,\frac{1}{E^2_{\sigma\sigma^*}} - \frac{1}{(E_{\sigma\sigma^*}+E_{pq^*})^2}\left[\sum_{v^*}\cos\frac{v^*\pi}{n+1} - \sum_{u}\cos\frac{u\pi}{n+1}\right]\Bigg\},\end{aligned}$$

$$\sum_{v^*=\frac{n}{2}+1}^{n} \cos\frac{v^*\pi}{n+1} = -\sum_{u=1}^{n/2}{}' \cos\frac{u\pi}{n+1} = \frac{1}{2}\left(1 - \frac{1}{\sin\dfrac{\pi}{2(n+1)}}\right).$$

By developing the last sinus, one gets as final result

$$\begin{aligned}\Delta E^2_{\mathrm{CH}} = (\sigma k|\sigma^* k)^2 \Bigg\{ & 2\left(\frac{1}{E_{\sigma\sigma^*}} - \frac{1}{E_{\sigma\sigma^*}+E_{pq^*}}\right)\\ & + \left(\frac{1}{E^2_{\sigma\sigma^*}} - \frac{1}{(E_{\sigma\sigma^*}+E_{pq^*})^2}\right)\left(\varepsilon_{q^*}-\varepsilon_p+\frac{8\beta}{\pi}\right)\Bigg\}.\end{aligned}$$

The last term is related with the difference between the pq^* transition energy and a mean $\pi\ \pi^*$ transition energy and should be relatively small.

C. Effect of the C–C $\begin{array}{c|c}\pi & \pi^*\\ \sigma & \sigma^*\end{array}$ *Diexcited Configurations*

Analogous developments lead to the following result.

a) *Closure Approximation:*

$$\begin{aligned}\Delta E^2_{\mathrm{C-C}} = 2(\sigma k|\sigma^* k)^2 \Bigg[& 2\left(\frac{1}{E_{\sigma\sigma^*}} - \frac{1}{E_{\sigma\sigma^*}+E_{\pi\pi^*}}\right)\\ & + \left(\frac{2}{\pi}\ \cos\frac{q^*\pi}{n+1} - \cos\frac{p\pi}{n+1}\right)\left(\frac{1}{E_{\sigma\sigma^*}} + \frac{1}{E_{\sigma\sigma^*}+E_{pq^*}}\right)\Bigg].\end{aligned}$$

This second term may be large, but for the lowest transition energy and large n the cosinus are both small and this term is small. The result is then very close to the effect of the analogous CH diexcited configurations, multiplied by a factor 2.

b) *Linearization of Denominator Variations:* One gets in the same way

$$\begin{aligned}\Delta E^2_{\mathrm{C-C}} = 2(\sigma k|\sigma^* k)^2 \Bigg[& 2\left(\frac{1}{E_{\sigma\sigma^*}} - \frac{1}{E_{\sigma\sigma^*}+E_{pq^*}}\right) + \frac{1}{\beta\pi}(\varepsilon_{q^*}-\varepsilon_p)\left(\frac{1}{E_{\sigma\sigma^*}} + \frac{1}{E_{\sigma\sigma^*}+E_{pq^*}}\right)\\ & + \left(\frac{1}{E^2_{\sigma\sigma^*}} - \frac{1}{(E_{\sigma\sigma^*}+E_{pq^*})^2}\right)\left(\frac{3}{2}(\varepsilon_{q^*}-\varepsilon_p) + \frac{8\beta}{\pi}\right)\\ & + \frac{1}{E^2_{\sigma\sigma^*}}\,\frac{\varepsilon^2_{q^*}-\varepsilon^2_p}{\beta\pi} - \frac{1}{(E_{\sigma\sigma^*}+E_{pq^*})^2}\,\frac{2\varepsilon_{q^*}\varepsilon_p}{\beta\pi}\Bigg].\end{aligned}$$

5. Discussion

The peculiar significance of the corrections introduced by the linearisation of the denominator variations are questionable, since they rest on the use of the Hückel repartition of monoelectronic energies. We have introduced this correction to demonstrate that it does not affect the general trend obtained with the closure approximation. Actual calculations should avoid some of the approximations that we used in order to make the derivation algebraically feasible to the end. Applications will be given in a later paper.

The main general results of this analysis may be summarized in the following points:

The effect of the CH $\sigma\sigma^*$ monoexcited states on the singlet $\pi\ \pi^*$ excited states decreases as n^{-1}.

The effect of the CC $\sigma\sigma^*$ monoexcited states on the singlet $\pi\ \pi^*$ excited states decreases as n^{-1} for large values of n. Their effect is about two times larger than the effect of the CH $\sigma\sigma^*$ monoexcited states. Both effects depend on the pairing or non pairing character of the $\pi\ \pi^*$ transition.

It results from the preceeding remarks that the effect of the σ system on the $\pi\ \pi^*$ transition energies vanishes for large n systems if calculated by monoexcited configuration interaction only.

The effect of configurations $\begin{array}{c|c}\sigma & \sigma^* \\ \pi & \pi^*\end{array}$ which are taken into account in the variational procedure on the $\pi\ \pi^*$ excited state, which is zero on ethylene and all pairing transitions, first increases and then decreases as n^{-1} when the dimension of the system increases. The most common procedures for the calculation of transition energies completely fail to reproduce the effect of the σ system for conjugated systems large enough, they lack some specific effects on pairing transitions which might change the order of the bands.

The effect of the $\begin{array}{c|c}\sigma & \sigma^* \\ \pi & \pi^*\end{array}$ di-excitations on both ground and excited states, diminishes the transition energy, by an increasing quantity. Their effect is zero on ethylene, but becomes rapidly more important than the previous one and tends towards a non zero asymptotic value. The C–C bonds appear again to be more important than the CH bonds for large n, at least for the lowest $\pi\ \pi^*$ transition energy.

We have tried to plot in Fig. 1 the evolution of the different contributions in some simple cases, taking $E_{\sigma\sigma^*} = E_{pq^*}$ and the closure approximation formulae for the effect of the diexcited configurations. It seems that the effect of the σ system is much smaller any way in very large polyenes than in ethylene. *Ab initio* calculations give about 3–4 eV for the effect of the $\sigma\ \sigma^*$ monoexcited states on the $\pi\ \pi^*$ transition energy of ethylene: the limit may be about 0.5 eV for large polyenes. This quantity is not negligible and it is certainly worthwile to take it into account in the calculations.

Moreover as the effect of the σ system depends

on the considered π-π^* transition energy in a given molecule,

on the dimension of the conjugated system, from one molecule to another, it seems dubious that one may rationalize the use of universal π parameters which would implicitly take into account the effect of the σ system on π π^* transition energies in a proper way.

This appears peculiarly as concerns the singlet-triplet splitting: the σ system diminishes that splitting by about 2 eV in ethylene in the CNDO approximations and 3–4 eV in *ab initio* calculations [2, 3]. The effect of the diexcited configurations, which is the leading part of the σ system effect for large conjugated molecules, is the same on the singlet and triplet excited states. Then the contribution of the σ system to the singlet-triplet splitting should tend to zero when the dimension of the system increases.

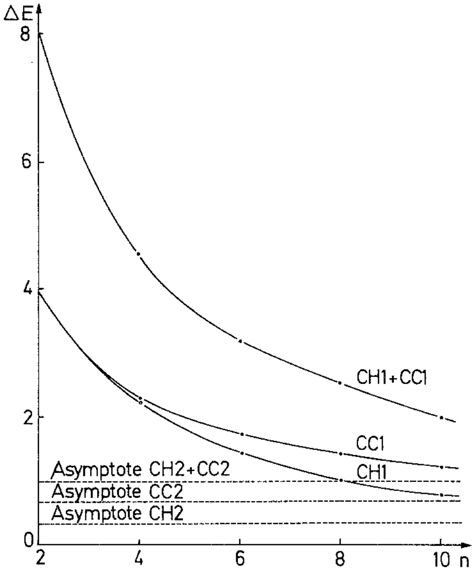

Fig. 1. Variation of various contributions, CC1 = effect of CC $\sigma|\sigma^*$ monoexcited states, CH1 = effect of CH $\sigma|\sigma^*$ monoexcited states, CC2 = effect of CC $\begin{pmatrix}\sigma|\sigma^* \\ \pi|\pi^*\end{pmatrix}$ diexcited states, CH2 = effect of CH $\begin{pmatrix}\sigma|\sigma^* \\ \pi|\pi^*\end{pmatrix}$ diexcited states

Another conclusion of this work is that people who refine the various π models to reproduce the evolution of the π-π^* transition energies in the test series of linear polyenes neglect a factor which is of the same order of magnitude than the improvement they introduce [12].

Appendix A

Effect of the INDO *Hypothesis*

In the INDO approximation one introduces the σ-π exchange integrals on the same carbon atom. Then the integrals of the types $(\sigma\,\pi|\pi\,\sigma^*)$ are no longer zero. Concerning σ-σ^* monoexcited states, one would get

$$\Delta E_S^1 = \sum_{\sigma} \sum_{\sigma^*} [2(\sigma\, q^* | \sigma^*\, p) - (\sigma\, q^* | p\, \sigma^*)]^2 / (E_{\sigma\sigma^*} - E_{pq^*})$$

instead of Eq. (1) for the singlet state and

$$\Delta E_{\mathrm{T}}^{1} = \sum_{\sigma} \sum_{\sigma^*} (\sigma\, q^* \,|\, p\, \sigma^*)^2 / (E_{\sigma\sigma^*} - E_{pq^*})$$

instead of zero for the triplet state.

If we only keep the atomic $(\sigma\, k \,|\, \sigma^* k)$ integral with the $2p_z$ orbitals of carbon atoms involved in the σ bond, it is easy to see that one gets

$$\Delta E_{\mathrm{CH}}^{1} \simeq 4 \sum_{k=1}^{n} [2(\sigma^* k | \sigma\, k) - (\sigma\, k | k\, \sigma^*)]^2\, c_{kp}^2 c_{kq^*}^2 / (E_{\sigma\sigma^*} - E_{pq^*})$$

instead of Eq. (3) for the singlet state and

$$\Delta E_{\mathrm{CH}}^{1} = \sum_{k=1}^{n} (\sigma\, k | k\, \sigma^*)^2\, c_{kp}^2\, c_{kq^*}^2 / (E_{\sigma\sigma^*} - E_{pq^*})$$

instead of zero for the triplet state.

Then everything goes the same way except that we have $(2(\sigma\, k | \sigma^* k) - (\sigma\, k | k\, \sigma^*))^2$ instead of $2(\sigma\, k \,|\, \sigma^* k)^2$ for the singlet: the effect of the monoexcited σ-σ^* states on the singlet state is slightly diminished (since $(\sigma\, k | \sigma^* k) \gg (\sigma\, k | k\, \sigma^*)$) and the effect on the triplet is small instead of zero. But the general tendencies remain the same: the effect of the monoexcited states decreases as n^{-1} when n increases (for both singlet and triplet states now).

As concerns the higher excited states, the effect is somewhat more complex. The terms already calculated, A and B, are decreased by an analogous phenomenon: one has $(\sigma\, k | \sigma^* k)^2 + (\sigma\, k | k\, \sigma^*)^2 - (\sigma\, k | \sigma^* k)(\sigma\, k | k\, \sigma^*)$ instead of $(\sigma\, k | \sigma^* k)$. But other terms are introduced which are zero in the CNDO hypothesis, for instance C. It is easy to see from Eq. (7) that they would lead to a smaller effect than A and B, and tend to a non zero asymptote. The limit of the effect of higher excitations would be slightly increased.

Appendix B

Long Distances $(\sigma\, k \,|\, \sigma^* k)$ Integrals

We have only used the integrals between the dipolar distribution σ-σ^* and the charges kk of the $2p_z$ orbitals of the carbon atoms involved in the considered σ bond. The $(\sigma\, k \,|\, \sigma^* k)$ integrals decrease as r^{-2} at long distances but one may wonder if $(\sigma_{\mathrm{AB}}\, k_{\mathrm{c}} \,|\, \sigma_{\mathrm{AB}}^* k_{\mathrm{c}})$ is always small compared with $(\sigma_{\mathrm{AB}} k_{\mathrm{B}} \,|\, \sigma_{\mathrm{AB}}^* k_{\mathrm{B}})$. If we use the CNDO hypothesis we get for the butadiene molecule

$(\sigma_{\mathrm{AB}}\, k_{\mathrm{B}} \,|\, \sigma_{\mathrm{AB}}^*\, k_{\mathrm{B}}) = 2.1$ eV for a CH bond, 3.0 eV for the CC bond,
$(\sigma_{\mathrm{AB}}\, k_{\mathrm{C}} \,|\, \sigma_{\mathrm{AB}}^*\, k_{\mathrm{C}}) = 1.5$ eV for a CH bond, 2.0 eV for the CC bond,

when k_c is the nearest neighbour of A or B. At two bonds distances the integrals begin to be negligible ($\simeq 0.3$ eV).

The neglect of all $(\sigma_{\mathrm{AB}}\, k_{\mathrm{C}} \,|\, \sigma_{\mathrm{AB}}^*\, k_{\mathrm{c}})$ is a rather poor hypothesis, but it is easy to see again that the inclusion of one bond distance $(\sigma_{\mathrm{AB}}\, k_{\mathrm{c}} \,|\, \sigma_{\mathrm{AB}}^*\, k_{\mathrm{c}})$ would not introduce qualitative changes in the general tendencies. Let us consider for instance the effect of the σ-σ^* monoexcited states. Eq. (1) would lead to

$$\begin{aligned}\Delta E^1 = 4 \sum_{\sigma_k} [&(\sigma\, k \,|\, \sigma\, k) . C_{kp} C_{kq^*} + (\sigma^* (k+1) \,|\, \sigma (k+1))\, C_{k+1p} C_{k+1q^*} \\ &+ (\sigma^* (k-1) \,|\, \sigma (k-1))\, C_{k-1p} C_{k-1q^*}]^2 / (E_{\sigma\sigma^*} - E_{pq^*})\end{aligned}$$

instead of

$$\Delta E^1 = 4 \sum_k (\sigma^* k | \sigma k)^2 \, C^2_{kp} C^2_{kq^*} / (E_{\sigma\sigma^*} - E_{pq^*}) \, .$$

Then neglecting end effects

$$\begin{aligned}\Delta E^1_{\mathrm{CH}} \simeq {} & (4(\sigma^* k | \sigma k)^2 + 2(\sigma^*(k+1) | \sigma(k+1))^2 \sum_k C^2_{kp} C^2_{kq^*} \\ & + 16 (\sigma^* k | \sigma k) (\sigma^*(k+1) | \sigma(k+1)) \sum_k C_{kp} C_{kq^*} C_{k+1\,p} C_{k+1\,q^*} \\ & + \; 8 (\sigma^*(k+1) | \sigma^*(k+1))^2 \sum_k C_{k-1\,p} C_{k-1\,q^*} C_{k+1\,p} C_{k+1\,q^*}) / (E_{\sigma\sigma^*} - E_{pq^*})\end{aligned}$$

The first term of this expression gives the same result then in our previous approximation except that $(\sigma^* k | \sigma k)^2$ is replaced by $(\sigma^* k | \sigma k)^2 + 2(\sigma^*(k+1) | \sigma(k+1))^2$ the second and third summations give some negative contributions, both varying as $1/n$ when n increases, and depending of p and q^* as $\cos \frac{p\pi}{n+1} \cos \frac{q^* \pi}{n+1}$. They become smaller and smaller when the dimension increase: if p and q^* remain the highest occupied and the lowest empty levels. (Cf. the discussion of the effect of CC bonds.) The inclusion of the one bond distance integrals enlarges significantly the amount of the effect but does not modify the asymptotic behaviour. The same conclusion holds for the higher excitations.

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