

TRIPLET-TRIPLET SPECTRA OF ALTERNANT HYDROCARBON MOLECULES

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INTRODUCTION

In the last decade a study has been made of the electronic spectra of various aromatic hydrocarbon positive and negative ions¹⁻⁷. The spectral behaviour of these ions could be explained qualitatively by means of an ASMO treatment similar to that introduced by Pariser and Parr⁸ but with a more restricted configuration interaction.

Very closely related to the spectral behaviour of these ions is that of hydrocarbon molecules in their lowest triplet states. In terms of the MO theory we may say that the lowest triplet of a hydrocarbon molecule is formed by the addition of an electron to the lowest anti-bonding orbital and of a vacancy ("positive hole") to the highest bonding orbital of the ground state molecule. If the hydrocarbon is alternant, the pairing relations^{9,10} between bonding and anti-bonding orbitals tell us that a vacancy in the highest bonding orbital "behaves optically" in the same way as an electron in the lowest anti-bonding orbital. We may therefore expect that the electronic absorption spectra of alternant hydrocarbons in their lowest triplet state look very much like the spectra of the corresponding dinegative (dispositive) ions, at least in the optical region where those excitations appear in which the highest bonding and/or lowest anti-bonding orbitals are involved.

In the present paper this resemblance will be considered in more detail.

GENERAL REMARKS

Let us consider an alternant hydrocarbon with $2n$ tervalent carbon atoms. The π -electrons in this molecule are considered to move in a fixed field of the nuclei and all the residual electrons, so that the total Hamiltonian for the π -electronic system becomes⁸:

$$H = \sum_{\mu} h(\mu) + \sum_{\mu < \nu} e^2/r_{\mu\nu} \quad (1)$$

where $h(\mu)$ is the "core Hamiltonian" and $e^2/r_{\mu\nu}$ is the electron repulsion operator.

As a basis for the configurational description of both the triplet hydrocarbon and the divalent ion the Pople SCF MO's¹⁰ for the closed-shell ground state molecule are chosen:

$$\phi_j = \sum_s c_{sj} \psi_s \quad (2)$$

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which are solutions of the eigenvalue equation:

$$F\phi_j = \mathcal{E}_j\phi_j \tag{3}$$

with

$$\begin{aligned} \mathcal{E}_j &= h_{jj} + \sum_{i=1}^n 2\langle jj|ii\rangle - \langle ji|ji\rangle \\ &= h_{jj} + \Sigma 2J_{ij} - K_{ij} \end{aligned} \tag{4}$$

where

$$h_{jj} = \int \phi_j(\mu)h(\mu)\phi_j(\mu) d\tau_\mu \tag{5}$$

and

$$\langle ji|ji\rangle = \iint \phi_j(\mu)\phi(\mu) \frac{e^2}{r_{\mu\nu}} \phi_j(\nu)\phi_i(\nu)d\tau_\mu d\tau_\nu \tag{6}$$

Since the hydrocarbon is alternant, the coefficients in (2) obey the so-called pairing relations¹⁰:

$$\begin{aligned} c_{sj} &= + c_{sj'} \quad (s = \text{odd}) \\ c_{sj} &= - c_{sj'} \quad (s = \text{even}) \end{aligned} \tag{7}$$

$$j' = 2n + 1 - j$$

where j denotes a bonding MO and j' the "conjugate" anti-bonding MO.

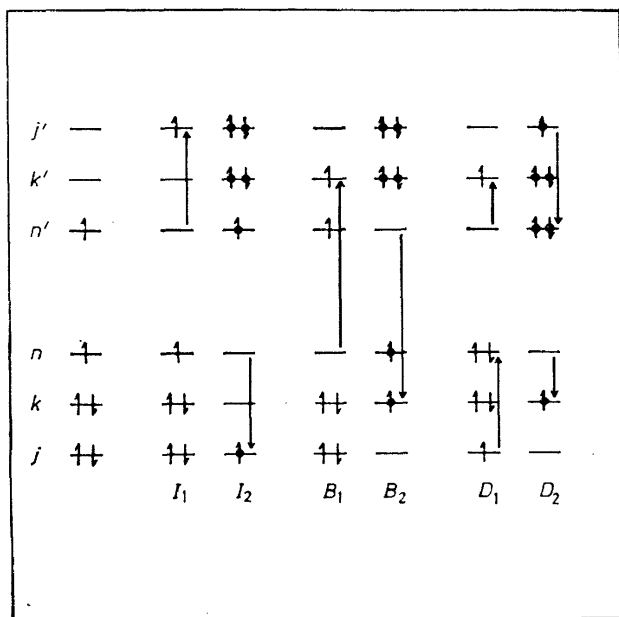


Figure 1. Schematic representation of lower π-electron excitations in alternant triplet hydrocarbons. The circles denote vacancies

From these relations the following equalities can be derived:

$$J_{jk} = J_{jk'} = J_{j'k} = J_{j'k'} \quad (8)$$

$$K_{jk} = K_{j'k'}; K_{jk'} = K_{kj'} \quad (9)$$

$$M_{jk'} = e \int \phi_j(\mu) r_{\mu} \phi_{k'}(\mu) d\tau_{\mu} = M_{kj'} \text{ (transition dipole moment)} \quad (10)$$

$$\mathcal{E}_k + \mathcal{E}_{k'} = \mathcal{E}_j + \mathcal{E}_{j'} \text{ or } \mathcal{E}_{j'} - \mathcal{E}_k = \mathcal{E}_{k'} - \mathcal{E}_j \quad (11)$$

From (11) it is seen that in the SCF MO level diagram the bonding and conjugate anti-bonding levels will be located symmetrically with respect to a certain energy as is illustrated schematically in *Figure 1*.

THE TRIPLET HYDROCARBON

Figure 1 illustrates two kinds of description, *viz.*, the electron and vacancy description. The promotion of an electron from $j \rightarrow k'$ can also be considered as the promotion of a vacancy from $k' \rightarrow j$. For an identical description a vacancy should have opposite charge and energy but the same spin as the electron¹¹. In *Figure 1* half of the promotions in the triplet hydrocarbon are illustrated by electrons and half of them by vacancies. It is seen from the figures that there exists a perfect symmetry between the vacancy and electron excitations. This suggests that the two configurations I_1 and I_2 (as well as the other pairs) have the same energies. This can be proved very easily with the aid of matrix algebra. The proof, however, is so similar to the one given by MacLachlan¹¹ for similar cases that it will not be given here.

Restricting ourselves to electron excitations in which the highest bonding and/or anti-bonding orbitals are involved, the following wave-functions for the "ground" and lower excited triplet configurations are reached.

$${}^3\Psi_0 = j^2k^2nn' \quad (12)$$

$$\left. \begin{array}{l} n' \rightarrow j' \\ j \rightarrow n \end{array} \right\} {}^3\Psi_I = \frac{1}{\sqrt{2}} [j^2k^2nj' \pm k^2n^2jn'] \quad (13)$$

$$\left. \begin{array}{l} n \rightarrow k' \\ k \rightarrow n' \end{array} \right\} {}^3\Psi_B = \frac{1}{\sqrt{2}} [j^2k^2n'k' \pm j^2n'^2kn] \quad (14)$$

j and k are chosen arbitrarily and different from each other in order to make the further considerations more general.

Contrary to the closed-shell ground state molecule in the triplet hydrocarbon low-lying double-excited configurations occur, *e.g.*:

$$\left. \begin{array}{l} n' \rightarrow j' \\ k \rightarrow n \\ n' \rightarrow k' \\ j \rightarrow n \end{array} \right\} {}^3\Psi_D = \frac{1}{\sqrt{2}} [j^2kj'n^2 \pm jk'k^2n^2] \quad (15)$$

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With the aid of (1), (2), (3) and the pairing properties (7) the following transition energies and transition dipole moments are obtained:

$$E_{\text{I}}^{\pm} = \mathcal{E}_n - \mathcal{E}_j + J_{nn} - J_{nj} \mp K_{nj} \quad M_{0,\text{I}}^{-} = m_{jn} \cdot \sqrt{2}; \quad M_{0,\text{I}}^{+} = 0 \quad (16)$$

$$E_{\text{B}}^{\pm} = \mathcal{E}_{n'} - \mathcal{E}_k - J_{nk} + K_{nk'} - K_{nk} + K_{nn'} \mp K_{nk'} \\ M_{0,\text{B}}^{-} = m_{nk'} \sqrt{2}; \quad M_{0,\text{B}}^{+} = 0 \quad (17)$$

$$E_{\text{D}}^{\pm} = 2\mathcal{E}_n - \mathcal{E}_j - \mathcal{E}_k + J_{nn} - J_{jk} \mp K_{jk} \quad M_{0,\text{D}}^{-} = 0 \quad (18)$$

For a further configuration interaction the following matrix elements are needed:

$$\langle I^{\pm} | H | B^{\pm} \rangle = \langle nk' | nj \rangle - \langle jk | nn' \rangle \mp \langle nk' | nj \rangle \quad (19)$$

$$\langle I^{\pm} | H | D^{\pm} \rangle = \langle jj | nk \rangle \mp \langle jn | jk \rangle \quad (20)$$

$$\langle B^{\pm} | H | D^{\pm} \rangle = \langle jn | nm \rangle \quad (21)$$

THE DINEGATIVE ION

In *Figure 2* the lower excitations in the hydrocarbon dinegative ion have been illustrated schematically. Instead of the dinegative ion we could also have chosen the dipositive ion since for alternant hydrocarbons the pairing properties lead to the same spectral behaviour for both^{11,12}.

In order to obtain the most clear parallel between the triplet hydrocarbon and the ion *Figure 2* distinguishes between promotion of electrons with spin

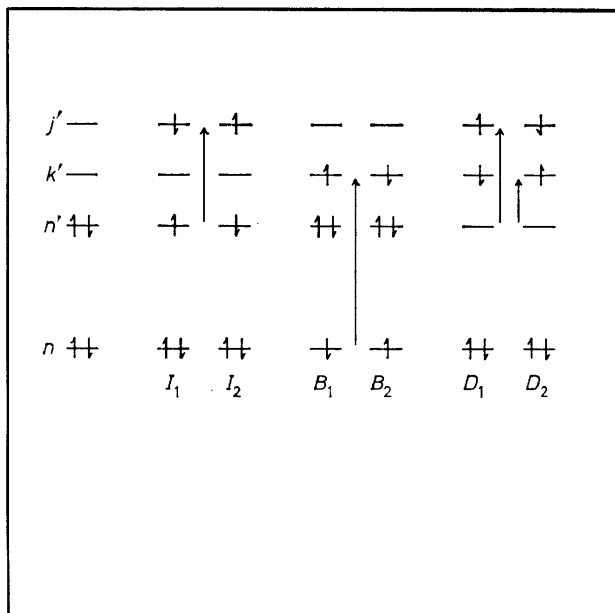


Figure 2. Schematic representation of lower π -electron excitations in alternant hydrocarbon dinegative ions

up or down. This implies that the configuration I_1 and I_2 (as well as the others) are no eigenfunctions of the spin operator S^2 . It is clear that the energies of I_1 and I_2 (as well as for the other pairs) will be the same. They are therefore combined again in + and - combinations. In this way the following configurational functions ($S_z = 0$) are obtained:

$${}^1\Psi_0 = n^2 n'^2 \quad (22)$$

$$\Psi_{\text{I}}^{\pm} = n^2 n' j' \frac{1}{\sqrt{2}} [\alpha\beta \pm \beta\alpha] \quad (23)$$

$$\Psi_{\text{B}}^{\pm} = n'^2 n k' \frac{1}{\sqrt{2}} [\alpha\beta \pm \beta\alpha] \quad (24)$$

$$\Psi_{\text{D}}^{\pm} = j' k' \frac{1}{\sqrt{2}} [\alpha\beta \pm \beta\alpha] \quad (25)$$

These linear combinations are eigenfunctions of S^2 but with different eigenvalues, *i.e.*, singlet and triplet functions. For the sake of comparison the functions are indicated by + and - where + corresponds to the triplet and - to the singlet configurations.

For the transition energies and transition dipole moments it is found:

$$\begin{aligned} E_{\text{I}}^{\pm} &= \mathcal{E}_n - \mathcal{E}_j + J_{j,n} - J_{nn} \mp K_{j,n} \quad {}^3M_{0,\text{I}} = 0 \\ {}^1M_{0,\text{I}} &= M_{jn} \sqrt{2} \end{aligned} \quad (26)$$

$$\begin{aligned} E_{\text{B}}^{\pm} &= \mathcal{E}_{n'} - \mathcal{E}_k + J_{nk} - 2J_{nn} + K_{nk'} - K_{nk} + K_{nn'} \mp K_{nk'} \\ {}^3M_{0,\text{B}}^+ &= 0; \quad {}^1M_{0,\text{B}}^- = M_{nk'} \sqrt{2} \end{aligned} \quad (27)$$

$$E_{\text{D}}^{\pm} = 2\mathcal{E}_n - \mathcal{E}_j - \mathcal{E}_k - J_{nn} + J_{jk} \mp K_{jk} \quad M_{0,\text{D}}^{\pm} = 0 \quad (28)$$

The matrix elements for the mixing between (22), (24) and (25) are exactly the same as (19), (20) and (21).

COMPARISON BETWEEN THE TRIPLET HYDROCARBON AND THE DIVALENT ION

If the secular determinant for configuration interaction is now made up, a very interesting result is found. All the off-diagonal matrix elements are the same for the triplet hydrocarbon and the dinegative ion. The same is true for the transition dipole moments. The only difference between the two determinants is a shift in the diagonal terms. This shift, however, is not a constant but varies from configuration to configuration. The first order energies of the triplet-triplet transitions relative to the transitions in the dinegative ion become:

$$\begin{aligned} \delta_{\text{I}} &= 2J_{nn} - 2J_{jn} \\ \delta_{\text{B}} &= 2J_{nn} - 2J_{nk} \\ \delta_{\text{D}} &= 2J_{nn} - 2J_{jk} \end{aligned}$$

As far as data are available it is seen that J_{nn} is always larger than the

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other coulomb integrals. Hence we may expect a blue shift on going from the dinegative ion to the triplet.

For molecules with a certain symmetry, *e.g.*, D_{2h} , the number of allowed excitations and consequently the number of excited configurations that becomes relevant, is fairly small and the energy differences between configurations of the same symmetry representation relatively large. In such a case the differences between the various δ 's will have little influence on the configuration interaction so that apart from a frequency shift we may expect the spectra of the triplet hydrocarbon and the dinegative ion to be very much alike.

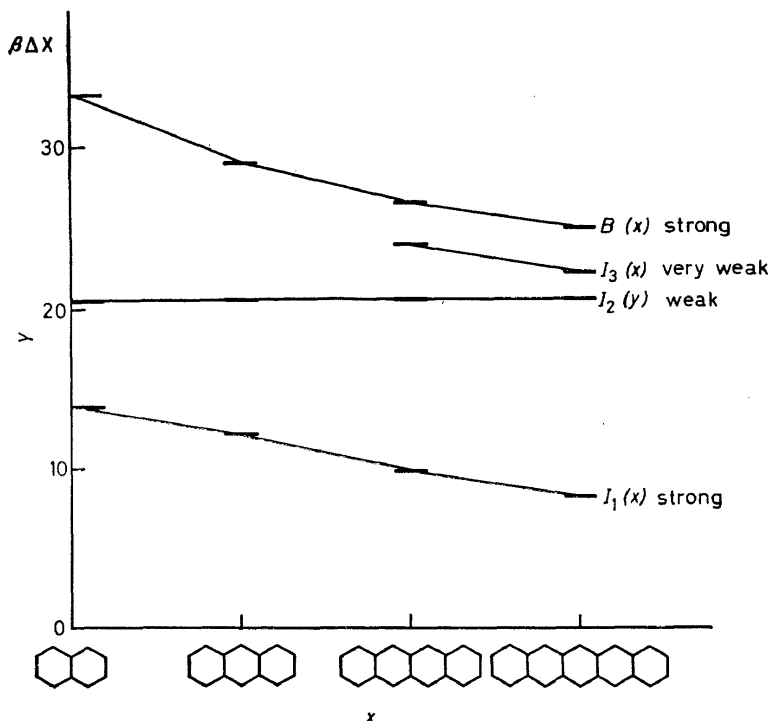


Figure 3. Lower π -electron excitations in polyacenes according to Hückel calculations ($\beta = -2.5$ eV)

Let us now turn to some examples. Porter and Windsor¹³ have measured triplet-triplet spectra of a fairly large number of aromatic hydrocarbons. Among these spectra those of the triplet tetracene and pentacene are most suitable for a comparison since they show a few characteristic absorption bands.

In Figure 3 are shown the lower allowed electron excitations for a number of polyacenes. For the energy scale the corresponding Hückel energies were used. It should be noted that these Hückel energies are not comparable with the SCF MO energies defined in (4). For a direct qualitative insight the Hückel energies are much more appropriate since the others as a consequence of the SCF formulation may deviate considerably from the configuration energies.

It is seen from *Figure 3* that in the near ultraviolet one excitation of type B (x -polarized) occurs, giving rise to two excited configurations B^\pm . There is also only one short axis⁴ polarized I type transition and one double excitation, also short axis polarized. For naphthalene and anthracene there is only one long axis polarized $I(x)$ type excitation, but for tetracene and pentacene a new $I(x)$ appears. The transition probability for the latter is very small, however, since it is located fairly close to the $B(x)$, it may steal intensity by mixing with the latter.

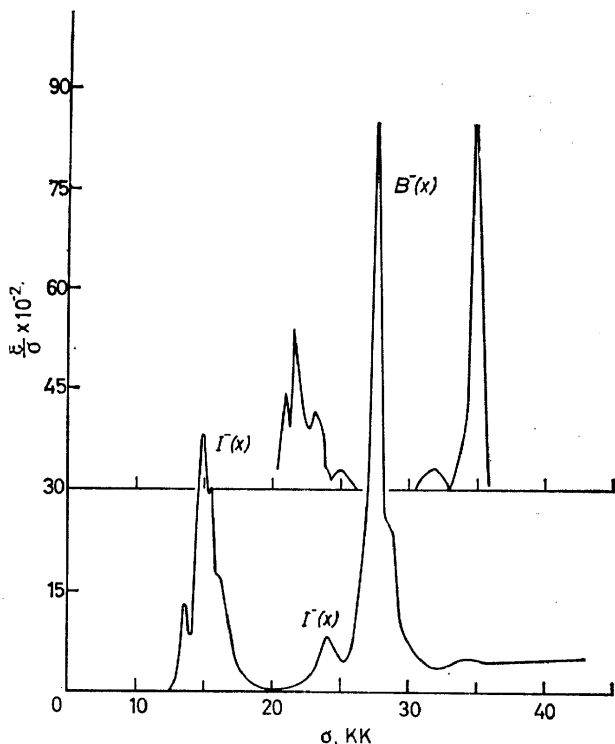


Figure 4. Electronic absorption spectra of triplet tetracene¹³ (top) and the tetracene dinegative ion⁷ (bottom). The polarizations x have been measured experimentally

In accordance with this prediction we have recently found three x -polarized transitions in the spectra of the tetracene and pentacene dinegative ions. The assignments are given in *Figures 4* and *5*. We have found no evidence for the much weaker y -polarized transitions. The three bands observed all correspond to the spin-allowed singlet-singlet transitions in the dinegative ions.

Comparing the spectra of the dinegative ions with the corresponding triplet-triplet spectra of the hydrocarbon molecule there is indeed a very close correspondence. The triplet-triplet spectrum of pentacene shows some irregularities probably due to some impurity. The three (or two) observed bands are without doubt long axis polarized and correspond to transition to ${}^3I_1^-$, ${}^3I_2^-$ and ${}^3B^-$.

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The theory predicts zero probabilities for the transitions to the corresponding ${}^3I_1^+$, ${}^3I_2^-$ and ${}^3B^+$. This is however not such a strict forbiddness as for the singlet-triplet transitions in the dinegative ions. In the latter case the transitions are spin-forbidden, whereas for the triplet hydrocarbon the theoretical intensities are zero because of the neglect of differential overlap

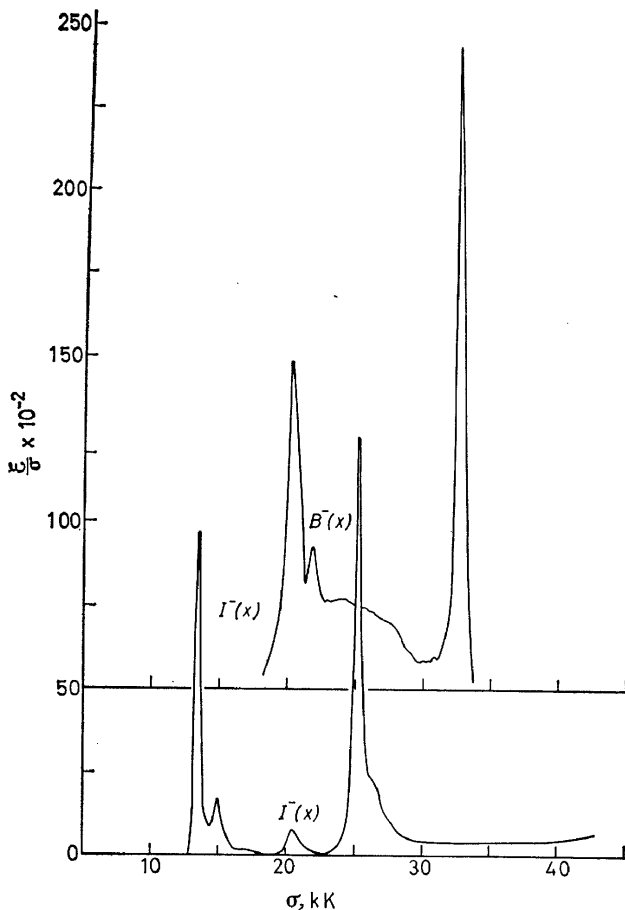


Figure 5. Electronic absorption spectra of triplet pentacene¹³ (top) and the pentacene dinegative ion⁷ (bottom)

in the ASMO treatment of Pariser and Parr⁸. In reality these transitions may become finite though very weak. A case like this is comparable with that of the 1L_b transitions of the ground state hydrocarbon molecules. Within the scope of the same theory these transitions are also forbidden, but in some cases where they appear as the first absorption band, they can be observed as very weak transitions (*e.g.*, naphthalene and pyrene¹⁴).

This possibility that at least the lowest triplet-triplet transitions to ${}^3I_1^+$ might be observable leads to some interesting perspective. If with the aid of flash techniques with higher intensities it were possible to observe this weak transition, a fairly reliable estimate could be made about the location

of the lowest excited triplet state in the dinegative ion making use of the resemblance of the two spectra. We have tried to observe this excited triplet of the dinegative ion by means of e.s.r. techniques by measuring a glassy solution of the disodium salts under intensive illumination. These experiments remained negative, very likely because of the fact that the low-lying triplet states are so close to the ground state that intersystem crossing shortens the lifetime of the triplet considerably.

Porter and Windsor have also tried to explain their triplet-triplet spectra of the polyacenes using for that purpose the energies and intensities calculated by Pariser^{8b}. Since, however, Pariser restricted himself to those configurations which are singly excited with respect to the closed-shell ground state, he missed some excited configurations which are doubly excited with respect to the ground state but singly excited with respect to the lowest triplet. Among them are the configurations B^\pm of which the B^- contributes to a very strong absorption in the triplet-triplet spectrum.

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