INTERPRETATION OF ELECTRONIC SPECTRA OF LINEAR POLYNUCLEAR *p*-QUINONES BY THE METHOD OF CONFIGURATION ANALYSIS*

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Character of transitions in a series of linear *p*-quinones has been investigated on the basis of configuration analysis. Correlation graphs of the states have been constructed enabling interpretation of the spectra in the terms of local transitions in the fragments and charge-transfer transitions between the fragments. Influence of various types of annelation on the first $\pi\pi^*$ absorption band in the spectra of the mentioned compound class has been investigated qualitatively from the viewpoint of interaction of the frontier MOs of the fragments.

On the basis of experimental and theoretical data about the absorption and luminescence spectra of polynuclear *p*-quinones[1-4] an analysis of electronic transitions was carried out[5] by the method based on comparison of changes of the LCI π-electronic densities at various centres of the given molecule during the transition $S_0 \rightarrow S_n$. The method made it possible to define the donor and the acceptor centres, to separate the molecule into fragments, to determine the character of the transitions (local in the fragments or CT between the fragments), and, therefrom, to construct the correlation graphs of the states. From the results several conclusions could be drawn concerning the influence of the annelation type of the benzene nucleus on character and energy of the first two $\pi\pi^*$ transitions in the investigated *p*-quinones, and it was possible to analyze quantitatively the Hartmann rule[6].

Noteworthy and very useful results in interpretation of electronic spectra of conjugated compounds can be obtained by application of the method of so called configuration analysis which is described elsewhere[7,8]. Using this method we have recently interpreted the electronic spectra of 9,10-anthraquinone and some of its derivatives[9]; the cited communication deals in detail with the advantages and limitations of this method due to the way of fragmentation of the 9,10-anthraquinone molecule.

This paper presents a discussion of electronic spectra of a series of linear *p*-quinones based on results of the configuration analysis. The spectral characteristics were calculated by the method by Pariser, Parr and Pople (PPP) in the approximation of the constant β^c and γ integrals. The parameters used are the same as in our previous papers on quinones[1,2]. Character of the electronic transitions was determined on the basis of configuration analysis.

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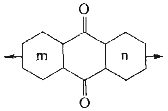
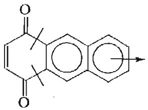
RESULTS AND DISCUSSION

The linear *p*-quinones can be denoted by the symbol $Q[m, n]$ (Scheme 1).



SCHEME 1

The annelation series of linear 1,4-quinones belong to the annelation type $Q[m, n]$, where $m = 0$, $n = 0, 1, 2 \dots$. On the basis of previous results, this type of quinones can be considered as being composed of an enedione and an acene fragment (Model A).



Model A

In terms of the configuration analysis it is then possible to discuss the electronic transitions as local transitions in the endione fragment (so called quinoid transitions), those in acene fragment, and CT transitions between these two fragments. On the basis of the spectral characteristics (PPP) and characters (CA) of transitions it is possible to construct the so called correlation graphs of the transitions $S_0 \rightarrow S_n$. Fig. 1 gives such correlation graph of the transitions $S_0 \rightarrow S_n$ for the annelation series $Q[0, n]$, using the fragmentation according to the Model A. The numbers in the graph give the per cent contribution of the local excited states in the fragments and CT states in the given transition of the corresponding system. Full circle denotes the transitions of very low probability, the symbols $\perp$ and $\|$ denote the direction of polarization of the transition with respect to the long axis of the system. The values in brackets give the r_M factor, which reflects the relevance (in %) of the given fragmentation for the studied system ($r_M \leqq 100\%$) (ref.[9]). The mutually corresponding transitions of different systems are linked with dashed line. From Fig. 1 it can be concluded: it is possible to identify "benzenoid" transitions with the dominant character of L_b or L_a transitions of acenes, "quinoid" transitions with localization in benzoquinone (enedione), and CT transitions connected with a charge transfer from acene to enedione. Whereas the second, intensive transition of 1,4-benzoquinone has a character of local transition in the enedione fragment, retaining this character throughout the annelation series, the first forbidden transition has rather a charge transfer character, especially so with higher members of the annelation series. The both transitions show slight hypsochromic shift with annelation. The benzenoid-type transitions cannot be considered until with 1,4-naphthoquinone. We can see that, due to mixing of the configurations, the acene L_b transition is split into two L_b-type transitions causing thus considerable contribution of the L_b transition to the first transitions of the systems $Q[0, 3]$ and $Q[0, 4]$ (in contrast to the acenes themselves), even though throughout the annelation series the first transition has the predominant character of a transition with charge transfer from the hydrocarbon fragment to the enedione. Energy difference between the both "benzenoid" L_b-type transitions remains practically constant throughout the series. These both L_b "benze-

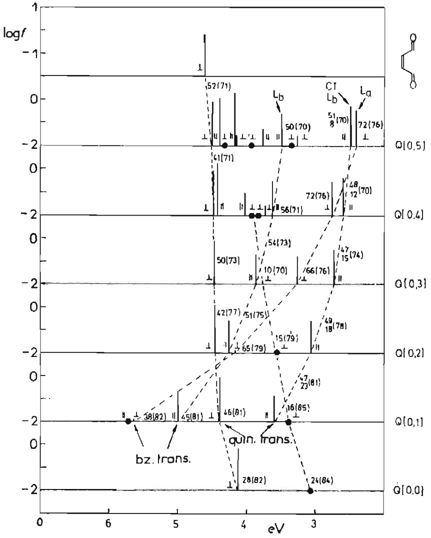


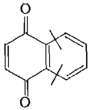
FIG. 1

Correlation Graph of Transitions $S_0 \rightarrow S_n$ for Annelation Series $Q[0, n]$ by Fragmentation according to Model A

bz. trans. "benzeneoid transitions", quin. trans. "quinoid transitions"; full circle denotes the transitions with $\log f < -2$ or the forbidden transitions (D_{2h}).

noid" transitions have a property characteristical for a L_b transition of acenes, *viz* small sensitivity of the excitation energy to the magnitude of the system. The "benzenoid" L_a transition shows a high degree of localization in the acene fragment, its excitation energy being sensitive to the magnitude of the system (it becomes the first transition with the system $Q[0, 5]$), and it is polarized perpendicularly to the long axis of the system (the both latter features are typical of the L_a transition of acenes).

Another way of separation of the quinoid system is the division into quinone and butadiene fragments according to Model B.



Model B

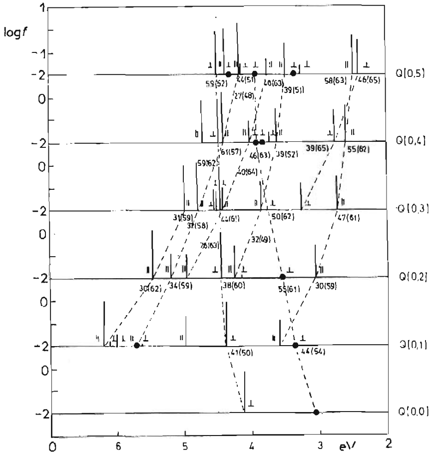


FIG. 2

Correlation Graph of Transitions $S_0 \rightarrow S_n$ for Annelation Series $Q[0, n]$ by Fragmentation according to Model B

Meaning of full circle as in Fig. 1.

This fragmentation was used[5] for analysis of the SCF MOs in the annelation series $Q[0, n]$, the SCF MO with high π-electron localization (high localization number) at the added butadiene being defined as the "new level". Such state was denoted as a "new excited state" in which at least one of the levels between which the electron excitation takes place can be, from our viewpoint, called a "new" level, belonging to a monoexcited configuration with a high weight coefficient (> 50%). Using the concepts of "new level" and "new excited state", we constructed the SCF MO correlation diagram and the correlation graphs of the $S_0 \rightarrow S_n$ transitions, the connection between the MOs or transitions (states) in the given annelation series being carried out on the basis of their symmetry and the noncrossing rule and further according to the correspondence of the states with respect to their characters and weight coefficients of LCI.

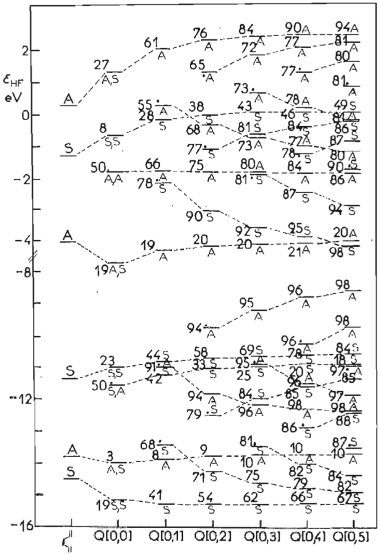


FIG. 3

Correlation Graph of SCF MOs for Annelation Series $Q[0, n]$

Full circles denote the "new" levels formed by addition of *cisoid*-butadiene.

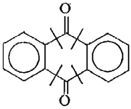
Using the configuration analysis for the fragmentation according to the Model B we obtain the correlation graph of the transitions $S_0 \rightarrow S_n$ (Fig. 2) which is practically identical with that obtained by the analysis of the transitions according to ref.[5]. The linking with the dashed line is carried out, if the given state contains minimum 27% of the reference state. Although the r_M values indicate that the fragmentation according to the Model B is less justified than that according to A, the main conclusions are the same: there exist two series of transitions beginning with $Q[0, 0]$ and corresponding to the "quinoid transitions" in the spectra of higher members of the annelation series $Q[0, n]$; the remaining five transitions start with the system $Q[0, 1]$ and are shifted bathochromically with increasing annelation. Any transition which has no relation to some transition of the lower member of the annelation series can practically be considered "new" (no linkage in the graph).

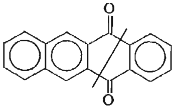
The fragmentation according to the Model B obviously offers no possibility to derive (on the basis of CA) the excited state from such a reference state which would "pass" through the whole annelation series and whose characteristics would be sufficiently known (such as the L_b and L_a excited states of acenes in the case of the Model A); this fact represents a certain drawback of the Model B as compared with A.

If the discussion is restricted to the transitions with high weigth coefficient of one monoexcited configuration, then some useful conclusions about the character of the transitions can already be made on the basis of the correlation graph of the SCF MO levels and localization numbers of these MOs. Figure 3 gives the SCF MO correlation graph for the series $Q[0, n]$, Those orbitals are linked which mutually correspond in their numbers of π-electron localization[5,10] (the "indexes" according to Ohta, Kuroda and Kunii)[10]. The numbers at the individual MOs express the measure of localization (in %) of π-electrons in the hydrocarbon fragment in the given MO (the difference of this number from 100 represents a measured of localization in the enedione fragment); S and A mean symmetrical and antisymmetrical MO, respectively, with respect to the symmetry axis. In spectra of the systems $Q[0, n]$, the first ($n \geqq 2$) and the second ($n \geqq 3$) transitions are very pure 1,1′ and 1,2′ transitions, respectively[5]. Thus from the SCF MO correlation graph an unambiguous conclusion can be drawn in accordance with the results of the configuration analysis: the first transition of the compounds $Q[0, n]$, $n = 2, 3, 4$, is connected with a significant charge transfer from the acene to the enedione fragment, the second transition has a character of local transition in the acene (for $n = 3, 4$); in the system $Q[0, 5]$ the order of the levels 1′ and 2′ is reversed, and the first and the second transitions have the character of local transition in the acene and CT transition from acene to enedione, respectively, which fully agrees with results of the configuration analysis. These results follow from the fact that for $Q[0, n]$, $n = 2, 3, 4$, the characters of the HOMO and the LUMO considerably approach those of the hydrocarbon MO and the acceptor fragment MO, respectively. The correlation graph of the SCF MOs also shows (for $n = 1, 2, 3, 4$) a shift of the LUMO towards higher energies – accordingly, in the given annelation series the electron affinity of the quinones decreases up to $Q[0, 4]$. This characteristical feature of this annelation series disappears starting from the quinone $Q[0, 5]$ in which the LUMO is localized in the hydrocarbon due to crossing of MOs; the LUMO energy decreases in the given series. Thus starting from the member $Q[0, 5]$ further annelation is expected to bring an increase in electron affinity.

Let us now consider the annelation series type $Q[2, n]$ where $n = 0, 1, 2$. From topological viewpoint this means gradual additions of the *cisoid*-butadiene fragments at the side containing a smaller hydrocarbon fragment. Figure 4 gives the correlation graph of the transitions $S_0 \rightarrow S_n$ for this series obtained on the basis of the configuration analysis according to the Model B (the reference system is $Q[2, 0]$); it is seen that this type of annelation results in shifting the transitions with both $\parallel$ and $\perp$ polarizations towards higher energies. The behaviour of the $\parallel$ polarized transitions is quite opposite in this annelation type than in the series $Q[0, n]$, which has the concrete consequence that extension of the system in this series results in a hypsochromic shift of the first absorption band in the spectrum. This finding agrees with the Hartmann rule[6] discussed in detail on the basis of the annelation graphs in ref.[5]

The series $Q[m, m]$ makes no annelation series in the sense used by us, because each system $Q[m, m]$ represents in fact the first member of the annelation series $Q[m, n]$ for $n \geqq m$. Making a higher system from a lower one thus represents simultaneous addition of two *cisoid*-butadienes, one to each side of the lower system. Hence it is obvious that neither the fragmentation A nor B afford a reference system. However, it is possible to carry out the fragmentation according to the Model C and, on the basis of the configuration analysis, to characterize the electronic transitions as the acene ones and charge-transfer acene → carbonyl. The resulting graph is given in Fig. 5. The conclusions obtained from this graph concerning the behaviour of the "benzenoid" transitions during extension of the system are analogous with those obtained from the discussion of Fig. 1, and the both agree with the analysis of the Hartmann rule in our previous paper[5].


Model C


Model D

The Models C and D were used for configuration analysis in the annelation series $Q[2, n]$, $n = 0, 1, 2$. The results are given in Fig. 6. Discussing the transitions in the terms of naphthalene fragments, the first band in the spectra of $Q[2, 0]$ and $Q[2, 1]$ can be described as a transition type L_b. However, the first transition in $Q[2, 2]$

contains two components which are the excitonic combination of the L_b transitions of two naphthalene fragments. The substantially higher intensity of the first band in the spectrum of $Q[2, 2]$ as compared with that of $Q[2, 0]$ can be explained by high transition probability of the excitation to the "in-phase" combination. Similar results are obtained by fragmentation according to the Model D, the difference being, however, in that the transitions of the quinones are derived from those of the naphthoyl

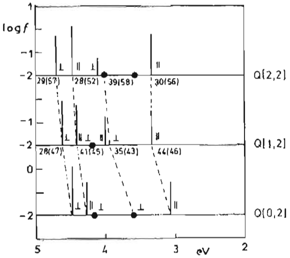


FIG. 4

Correlation Graph of Transitions $S_0 \rightarrow S_n$ for Annelation Series $Q[2, n]$ ($n = 0, 1, 2$) by Fragmentation according to Model B

Meaning of full circle as in Fig. 1.

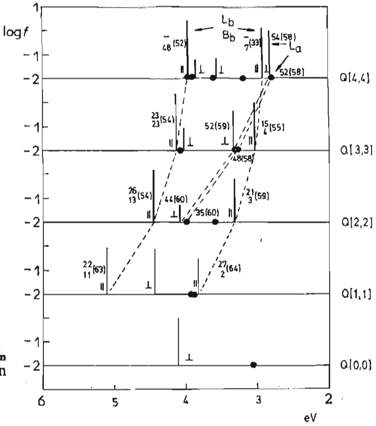


FIG. 5

Correlation Graph of Transitions $S_0 \rightarrow S_n$ for Quinones Type $Q[m, n]$ by Fragmentation according to Model C

Meaning of full circle as in Fig. 1.

fragments. Different linking between the systems $Q[0, 2]$ and $Q[1, 2]$ in Figs 4 and 6 is due to the different fragmentations used for construction of the two graphs.

The electronic transitions of the systems discussed can be investigated very effectively from the synthetical viewpoint in the terms of the molecular building units on the basis of interactions between their frontier MOs. It is well known that stabilization of the ground state (which results in a hypsochromic effect) depends on the extent of the HOMO–LUMO interaction of the molecular fragments, whereas stabilization of the excited state (which results in a bathochromic effect) depends on the extent of the HOMO–HOMO and the LUMO–LUMO interactions. The interaction between the frontier MOs of the fragments is controlled by their shape (symmetry) and by the magnitude of the expansion coefficients at the centres of the interaction sites. Let us investigate from this viewpoint the interaction between the frontier MOs of enedione and naphthalene considering two transition types: local

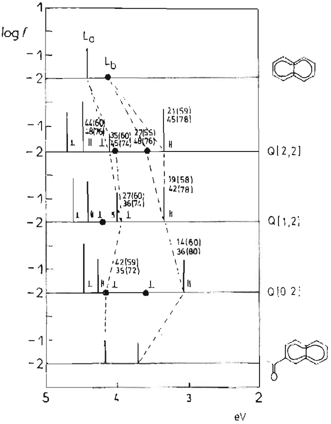


FIG. 6

Correlation Graph of Transitions $S_0 \rightarrow S_n$ for Annelation Series $Q[2, n]$ Related to Local Transitions in Naphthalene (Model C, upper numbers) and to Local Transitions in Naphthoyl Fragment (Model D., lower numbers)

Meaning of full circle as in Fig. 1.

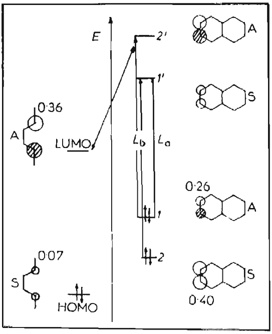


FIG. 7

Schematic Representation of Interactions between Frontier MOs of Enedione and Naphthalene

Double-headed arrow denotes the interaction between the MOs.

transitions in naphthalene (L_a and L_b) and the CT ones between the occupied MOs of naphthalene and the LUMO of enedione. The scheme in Fig. 7 shows several important facts. The L_a transition corresponds to a very pure 1,1′ transition in naphthalene. As the LUMO–LUMO and the HOMO–HOMO interactions of the fragments cannot be anticipated for symmetry reasons, the L_a transition is not affected by interaction with enedione (Fig. 6). The L_b excited state of naphthalene arises from the first order configurational interaction of the 2,1′ and the 1,2′ transitions. Both the symmetry aspect and magnitude of the expansion coefficients will favour strong interactions between the 2′ naphthalene level and the LUMO of the enedione. All this leads to a CT (L_b) state with a marked shift to lower energies (even with the system $Q[0, 4]$ the transition to this state is at lower energies than the L_a transition localized in the acene fragment).

The aspect of interaction between the frontier MOs of the fragments can also explain qualitatively different effect of such annelation when addition of *cisoid*-butadiene can form systems belonging to various annelation series: *e.g.* $Q[0, 2] \rightarrow$ $\rightarrow Q[0, 3]$ (the annelation series $Q[0, n]$) and $Q[2, 0] \rightarrow Q[2, 1]$ (transition to the annelation series $Q[2, n]$). Let us consider now the frontier orbitals of *cisoid*-butadiene and 1,4-anthraquinone (Fig. 8). The *cisoid*-butadiene and quinone have the characters of donor and acceptor fragments, respectively. From Fig. 8 it follows that a strong HOMO–HOMO interaction can be expected, if *cisoid*-butadiene is added to the quinone at the side of the naphthalene ring; this interaction results in destabilization of the ground state and in a bathochromic shift of the first absorption band in the spectrum. If the *cisoid*-butadiene is added at the quinone-ring side, the HOMO–HOMO interaction will be very weak due to small values of the expansion coefficients at 2,3-positions of the quinone. However, due to symmetry and magnitude of coefficients, the HOMO–LUMO interaction can be expected leading to hypsochromic shift of the first absorption band. Thus the annelations $Q[0, 2] \rightarrow Q[0, 3]$ and $Q[0, 2] \rightarrow Q[1, 2]$ can result in marked bathochromic

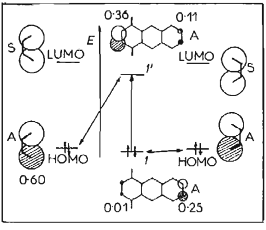


FIG. 8

Schematic Representation of Interaction between Frontier MOs of *cisoid*-Butadiene and 1,4-Anthraquinone

Double-headed arrow denotes the interaction between the MOs.

and hypsochromic shifts of the first absorption band, respectively. The above discussion shows that the synthetical MO model leads to conclusions which fully agree with those of CA and with experimental positions of the absorption bands and theoretical spectra[5] (PPP).

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