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Commentationes

Interpretation of Pentacyclic Aromatic Hydrocarbon Transitions in Terms of Composite System Approximations

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The observed electronic transitions and transition assignments of three pentacyclic aromatic hydrocarbons, benz(a)naphthacene, dibenz(a,c) anthracene, and 3,4-benzopyrene, are presented. The transitions of the pentacyclic aromatics are correlated with the transitions of tetracyclic aromatic hydrocarbons contained within the structure of the pentacyclic. The results of the experimental correlation are then compared with the results of a theoretical "molecules in molecule" interpretation of the pentacyclic transitions. The results of this comparison indicate that applying a theoretical composite system concept to the interpretation of pentacyclic spectra is justified for the lower energy transitions.

Es wird über die bei den drei pentacyclischen aromatischen Kohlenwasserstoffen: Benz(a)-naphthacen, Dibenz(a,c) anthracen und 3,4-Benzopyren beobachteten Elektronenübergänge und ihre Zuordnung berichtet. Die Übergänge der pentacyclischen aromatischen Kohlenwasserstoffe werden mit Übergängen bei den tetracyclischen aromatischen Kohlenwasserstoffen verglichen, die als Strukturelemente der pentacyclischen auftreten. Danach werden die Ergebnisse der experimentellen Korrelation mit Resultaten der theoretischen „Molekül im Molekül" Interpretation der pentacyclischen Übergänge verglichen.

Dieser Vergleich zeigt, daß bei den Übergängen niedriger Energie die Verwendung des theoretischen Konzepts zusammengesetzter Systeme gerechtfertigt ist.

Introduction

The similarities noted in the ultraviolet and visible absorption spectra of many polycyclic aromatic hydrocarbons have led to a number of studies which have attempted to interpret the electronic transitions of particular molecules in terms of various parts of the molecules. These studies are best exemplified by the "independent systems" or "molecules in molecule" approaches of Simpson [2] and Longuet-Higgins and Murrell [3]. In the "molecules in molecule" (MIM) method, it is assumed that the molecule is a composite system, R-S, and that electronic transitions may be described in terms of local excitations in the two parts, R and S, and electron-transfer transitions arising from excitation of an electron from a molecular orbital in one part to a molecular orbital in another part. Longuet-Higgins and Murrell [3] applied this method to analysis of the spectra of diphenyl, butadiene, and styrene.

Longuet-Higgins and Murrell's [3] theoretical development has served as the basis of a number of later studies. Heilbronner *et al.* [4] applied this composite system approach to acenaphthylene and fluoranthene. These two molecules are characterized as "weakly" non-alternant, which means that they consist of alternant subunits linked by non-essential double bonds in such a way that the subunits retain much of their individuality. A composite systems approach was used by Mori [5] to calculate the electronic transitions of benzyl radical. Experimental work by Johnson and Albrecht [6] indicates that the composite systems approach of Mori [4] predicts the transitions of benzyl radical much better than the conventional molecular orbital treatment. Favini *et al.* [7] have applied the composite systems or MIM theory to the interpretation of the electronic spectra of a large number of aromatic hydrocarbons. This study was unique in that many of the molecules studied normally have significant conjugation between the parts of the composite system model.

The above studies have all been within the framework of the P-P-P semi-empirical theory. Von Niessen [8] has recently proposed a theory of molecules for use in *ab initio* studies within the Hartree-Fock formalism.

The present investigation was prompted by the observation that many electronic transitions of the pentacyclic aromatic hydrocarbons appear, on the basis of extinction coefficient, vibrational structure, and general appearance, to be quite similar to the electronic transitions observed in the tetracyclic aromatic hydrocarbons. In order to try to understand a phenomenon such as this, the obvious approach is by means of the MIM concept in which these molecules are treated as a composite two-part system. Consequently, a composite systems study has been performed on a representative group of three pentacyclic aromatic hydrocarbons: benz(a)naphthacene (BN), dibenz(a,c)-anthracene (DBA), and 3,4-benzopyrene (BP) (see Fig. 1 for structures). Initially, the observed spectra

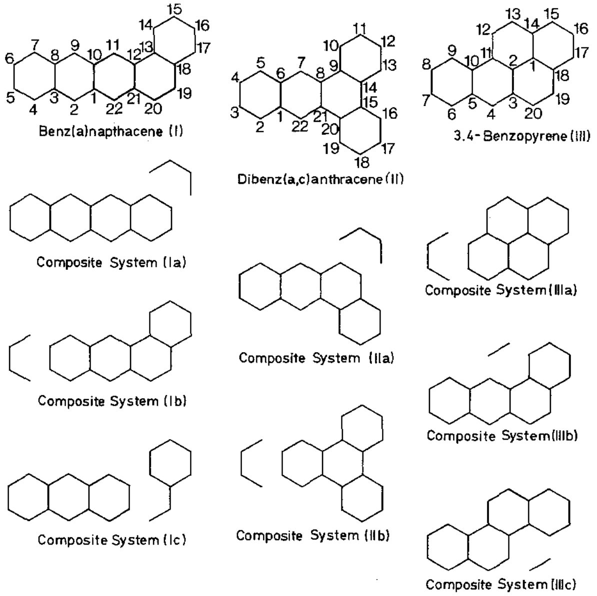

Fig. 1. Structures of compounds and composite system models

of these molecules were systematically examined and, where possible, the transitions correlated to particular tetracyclic aromatic transitions. Following this, the electronic transitions of the pentacyclics were calculated, together with the spectra of various composite system models of each molecule, in order to infer a theoretical composite system basis for the pentacyclic transitions. Finally, the results of the experimental and theoretical MIM interpretations were compared.

Experimental

The experimentally observed transitions of benz(a)naphthacene, dibenz(a,c)anthracene, and 3,4-benzopyrene are given in Tables 1,2 and 3, respectively. The corresponding calculated transitions are also given in these tables.

The observed transitions and extinction coefficients of the pentacyclics were obtained from the room temperature absorption spectra of the hydrocarbons dissolved in *p*-dioxane. Low temperature absorption spectra (77° K) were used as an aid in making transition assignments. The analysis of the experimental tetracyclic aromatic spectra required for the MIM interpretation was done by Becker *et al.* [9].

Table 1. Experimentally observed maximum of transitions of benz(a)naphthacene and corresponding calculated transitions[a]

Transition number	Observed transition energy (eV)	Extinction coefficient of observed transition (1/mole · cm)	Calculated transition energy (eV)	Calculated oscillator strength
I	2.75	36095	2.98	0.371
II	3.92	61657	3.84	0.892
III	4.09	117057	4.21	1.815
IV	4.81	61657	4.98	0.634
V	5.55	36095	5.25	0.327

[a] Considering molecule as single quantum mechanical system.

Table 2. Experimentally observed maximum of transitions of dibenz(a,c)anthracene and corresponding calculated transitions[a]

Transition number	Observed transition energy (eV)	Extinction coefficient of observed transition (1/mole · sec)	Calculated transition energy (eV)	Calculated oscillator strength
I	3.29	697	3.53	0.000
II	3.52	3465	3.74	0.168
III	4.31	146315	4.37	2.285
IV	4.98	52255	4.84	1.263
V	5.68	40264	5.35	0.364
VI	6.00	–	5.92	0.268

[a] See Table 1.

Table 3. Experimentally observed maximum transitions of 3,4-benzopyrene and corresponding calculated transitions[a]

Transition number	Observed transition energy (eV)	Extinction coefficient of observed transition (1/mole · sec)	Calculated transition energy (eV)	Calculated oscillator strength
I	3.07	4029	3.31	0.000
II	3.22	27637	3.12	0.997
III	4.18	57871	4.42	0.871
IV	4.67	43889	4.72	0.662
V	5.47	24352	5.14	1.055
VI	5.93	–	5.78	0.334

[a] See Table 1.

The experimental MIM interpretation of the observed transitions of the pentacyclic aromatic hydrocarbons in terms of observed tetracyclic transitions was based on the correlation of a number of factors. Of primary importance were the relative energies and intensities of the transitions. Other important considerations were the vibrational sequences and general shape of the transitions. Finally the overall aspects of the entire UV spectra of the molecules were considered. The results of this MIM interpretation are summarized in the correlations between columns 4 and 5 of the three correlation diagrams, Figs. 2, 3 and 4.

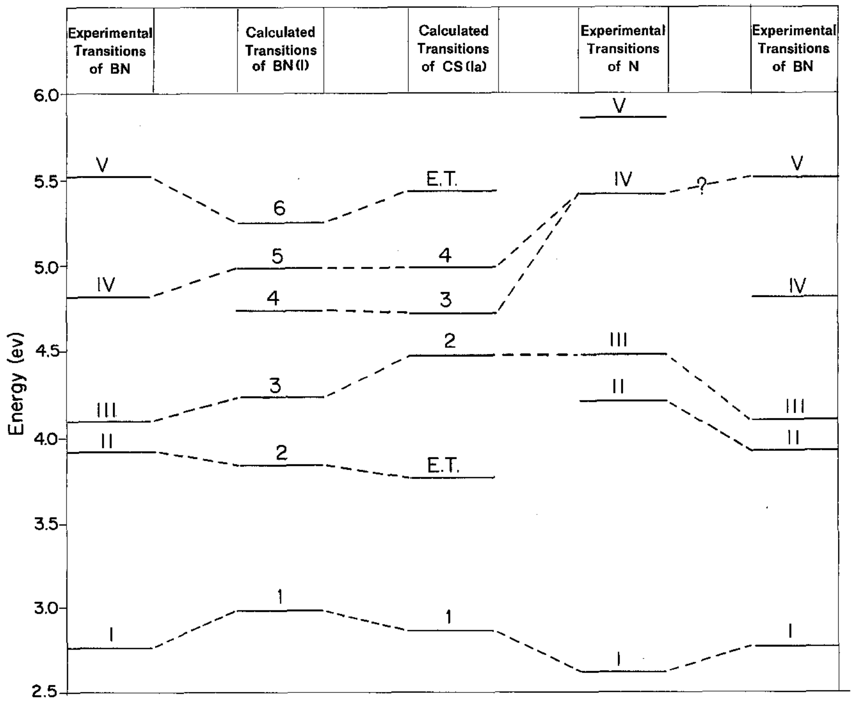

Fig. 2. Summary of theoretical and experimental transitions of Benz(a)naphthacene (BN) and its appropriate composite system (CS) model, together with correlations resulting from "molecules in molecule" interpretations. Experimental transitions of Naphthacene (N) from Ref. [9]. E.T. denotes degenerate pair of formally forbidden electron-transfer transitions

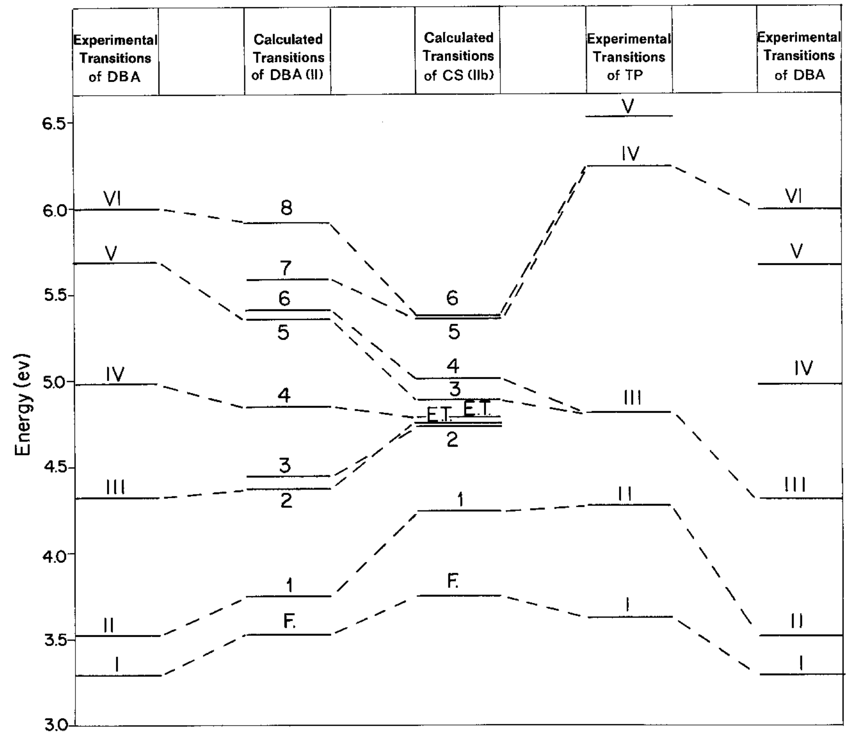

Fig. 3. Summary of theoretical and experimental transitions of Dibenz(a,c)anthracene (DBA) and its appropriate composite system (CS) model, together with correlations resulting from "molecules in molecule" interpretations. Experimental transitions of Triphenylene (TP) from Ref. [9]. E.T. denotes degenerate pair of electron-transfer transitions and F. denotes a formally forbidden transition

In the case of BN, transitions I, II, and III are clearly naphthacene-like, implying a composite system model containing naphthacene and cis-butadiene. Transition IV does not resemble any naphthacene transition; however, transition V may slightly resemble the fourth transition of naphthacene.

On the whole, the transitions of DBA most clearly approximate the observed spectra of triphenylene, implying a composite system model composed of triphenylene and cis-butadiene. Transitions IV and V of DBA cannot be related to any observed triphenylene transitions. In the absorption spectra of triphenylene (see Ref. [9]), a large energy gap exists between the third and fourth observed transitions. It is in this region that transition IV and V of DBA appear. A possible explanation of this phenomenon is that the triphenylene transitions in this region are forbidden due to the high symmetry of triphenylene, but become allowed in the less symmetrical DBA molecule. Transition VI is correlated to the fourth triphenylene transition.

The observed transitions of BP can be clearly correlated with the observed transitions of pyrene. This, of course, implies a composite system model consisting of pyrene and cis-butadiene.

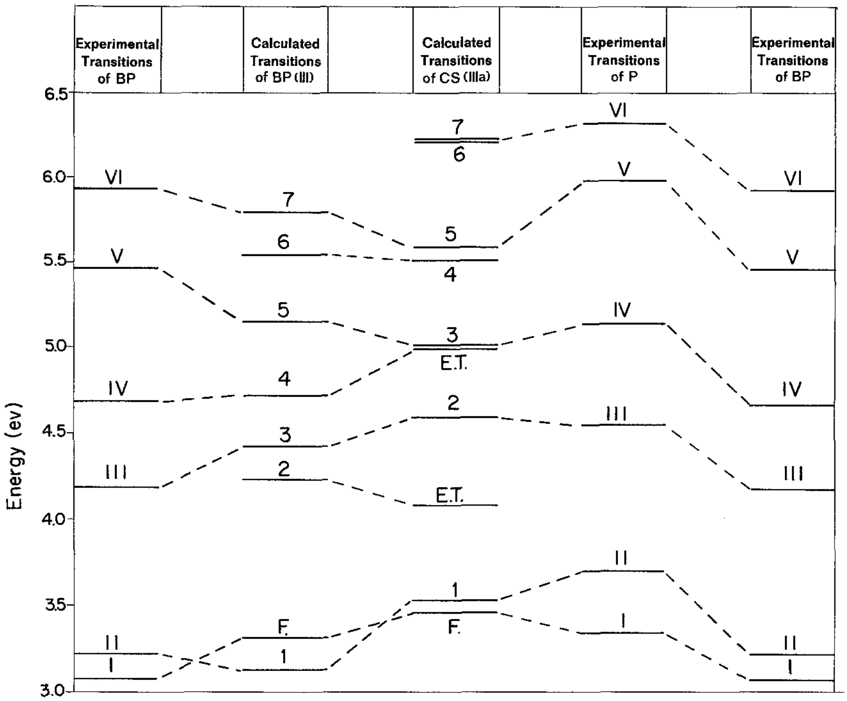

Fig. 4. Summary of theoretical and experimental transitions of 3,4-Benzopyrene (BP) and its appropriate composite system (CS) model, together with correlations resulting from "molecules in molecule" interpretations. Experimental transitions of Pyrene (P) from Ref. [9]. E.T. denotes degenerate pair of formally forbidden electron-transfer transitions and F. denotes a formally forbidden transition

Theoretical

The theoretical spectra were determined by standard Pariser-Pople-Parr (P-P-P) semi-empirical SCF-MO calculations with configuration interaction. Only π electrons were considered. The Pariser [10] approximation was used for the one-center repulsion integrals, γ_{ii}, while the Mataga [11] approximation was used for two-center repulsion integrals, γ_{ij}. The valence state ionization potential and electron affinity of a $2p\pi$ carbon atom were taken as 11.42 eV and 0.58 eV, respectively. Standard aromatic type geometry was assumed for all calculations with bond lengths equal to 1.40 Å. In the CI calculations, a maximum of 50 of the lowest energy singly excited configurations having an energy within 8.0 eV of the ground state were used to determine the excited state wave functions.

Calculations were performed on all composite system models shown in Fig. 1. Essentially three calculations were made for each composite system model. The spectra were first calculated with the resonance integrals, β_{ij}, between all bonded centers set to -2.318 eV with the exception of the bonds connecting the component parts of the composite system for which β_{ij} was set to 0.0 eV. In the second calculation, the β_{ij} for the bonds connecting the two moieties of the composite system were changed to -1.00 eV. And third, the spectra were calculated with β_{ij} equal to -2.318 eV for all bonded centers including the bonds between the composite system parts.

The theoretical development presented by Longuet-Higgins and Murrell [3] is applicable to the present calculations with the zero resonance integrals between the two parts of the composite system. However, the manner in which the effects of finite resonance integrals between the parts is treated is somewhat different in this present study. In the presence of finite resonance integrals between the component parts, the self-consistent MO's will no longer simply be the orbitals of the two subsystems R and S which would be found if both were treated as separate quantum mechanical systems; instead, they are a set of MO's spanning the entire composite system. Longuet-Higgins and Murrell assumed in their treatment of a molecule as a component system that the MO's of the composite system did not change upon introducing finite resonance integrals between the subsystems. In their concept of a composite system, the increased interaction of the component parts results only in changed configuration interaction and not in alteration of the MO's. In other words, the limit of a strongly interacting composite system is not the subject molecule treated conventionally as a single quantum mechanical system. In the present study, the passing from a weakly interacting composite system to a completely interacting system is accomplished by allowing the resonance integrals to increase in magnitude, starting at zero,

Table 4. Comparison of excitation energies of 3,4-benzopyrene (III) and composite system models (IIIa), (IIIb) and (IIIc) with $\beta_{RS} = -1.0$ eV

3,4-Benzopyrene (III)		Composite system (IIIa)		Composite system (IIIb)		Composite system (IIIc)	
Excitation energy (eV)	f	Excitation energy (eV)	f	Excitation energy (eV)	f	Excitation energy (eV)	f
3.120	0.997	3.357	0.966	3.421	0.000	3.536	0.000
3.312	0.000	3.419	0.000	3.449	0.543	3.615	0.690
4.199	0.000	4.125	0.000	4.276	1.072	4.438	0.000
4.225	0.048	4.237	0.057	4.366	0.000	4.689	0.000
4.419	0.871	4.376	0.003	4.651	0.000	4.712	0.104
4.424	0.000	4.387	0.000	4.759	0.972	4.727	1.583
4.671	0.000	4.678	0.595	4.783	0.000	4.899	0.330
4.719	0.662	4.809	0.710	4.842	0.098	4.955	0.000
5.141	1.055	4.835	0.000	4.934	0.302	5.115	0.828
5.263	0.000	5.081	0.000	5.276	0.000	5.447	0.000
5.432	0.000	5.260	0.000	5.347	0.000	5.576	0.000
5.542	0.046	5.442	0.000	5.457	0.038	5.563	0.000
5.638	0.000	5.447	0.704	5.616	0.000	5.696	0.121
5.782	0.334	5.542	0.236	5.688	0.504	5.793	0.000
5.973	0.000	5.760	0.571	5.817	0.000	5.818	0.148
6.031	0.044	6.059	0.000	5.827	0.633	5.878	0.121
6.146	0.000	6.061	0.004	6.081	0.000	5.967	0.014
6.244	0.324	6.133	0.122	6.123	0.339	6.141	0.000
6.401	0.450	6.234	0.000	6.239	0.365	6.342	0.245
6.448	0.000	6.417	0.173	6.272	0.000	6.360	0.000
		6.445	0.000	6.488	0.000	6.402	0.277
		6.478	0.998			6.483	0.040

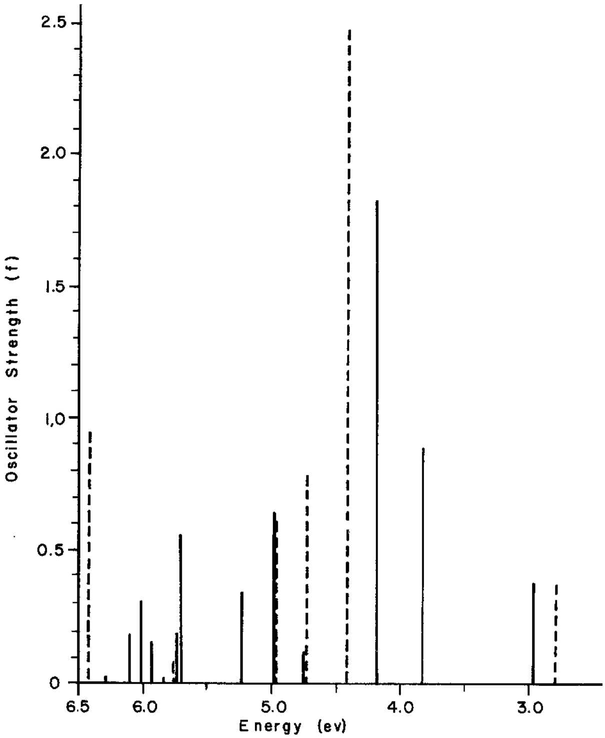

Fig. 5. Calculated absorption spectra of benz(a)naphthacene (I), shown as solid lines, and composite system (Ia), shown as dashed lines

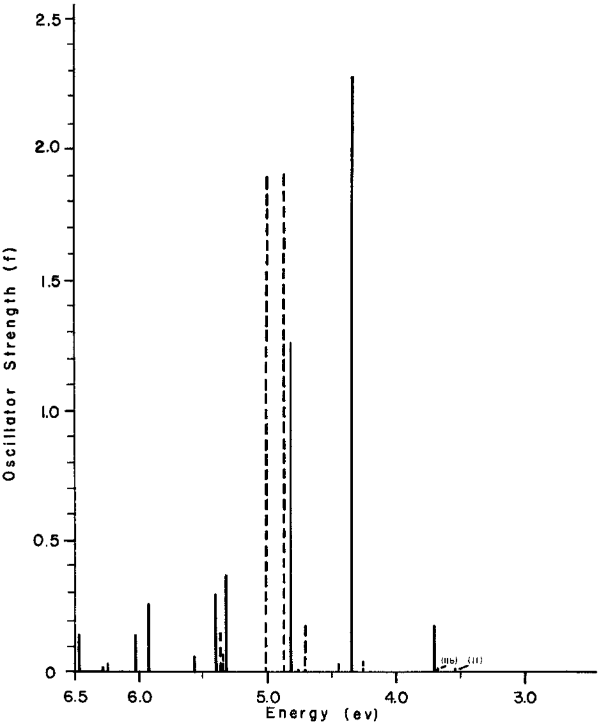

Fig. 6. Calculated absorption spectra of dibenz(a,c)anthracene (II), shown as solid lines, and composite system (IIb), shown as dashed lines

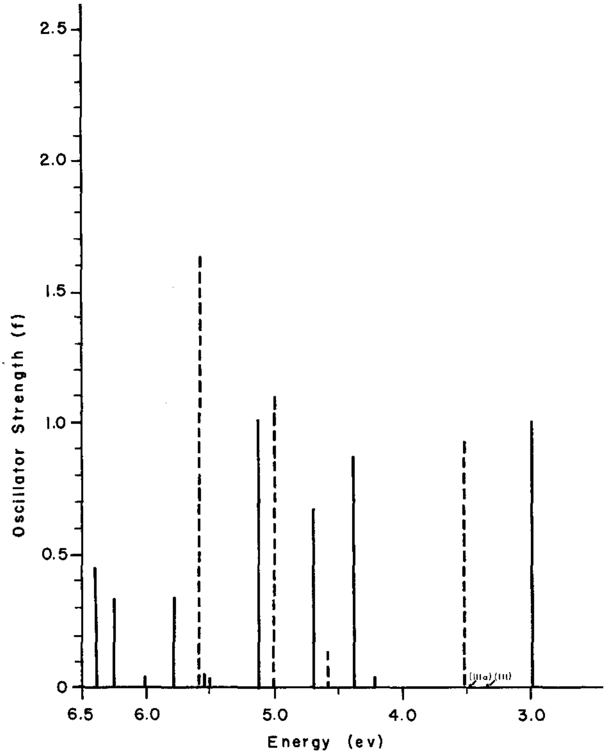

Fig. 7. Calculated absorption spectra of 3,4-benzopyrene (III), shown as solid lines, and composite system (IIIa), shown as dashed lines

in both the solution for the self-consistent MO's and in the determination of the excited state wave functions by configuration interaction. This implies that the molecule treated as a single system gives the best results but that there exists a composite system which is a close approximation to the subject molecule. This is apparently the same viewpoint as that taken by Heilbronner *et al.* [4] in their work.

The purpose of the calculations for the "weakly" interacting composite system, that is, β_{ij} equal to -1.00 eV between the component parts, was twofold. First, the most appropriate composite system model for a given molecule was chosen primarily on the basis of how closely the spectra of the composite system with intermediate interaction approximated the spectra of the molecule treated as a single system. For an example, Table 4 compares the transitions of the three composite system models of BP, β_{ij} equal to -1.00 eV between the two parts, with the transitions of BP calculated with β_{ij} equal to -2.318 eV between all bonded centers. Second, these intermediate interaction calculations aided in the correlation of composite system transitions with those of the subject molecule.

The calculated spectra of BN, DBA, and BP, together with the superimposed spectra of the most appropriate composite system model ($\beta_{ij} = 0.0$ eV), are given in Figs. 5, 6, and 7. The results of the correlation of the calculated transitions of a composite system model with the calculated transitions of the modeled pentacyclic aromatic are summarized in the correlations between columns 2 and 3 of Figs. 2, 3 and 4.

Discussion

The correlation diagrams shown in Figs. 2, 3 and 4, summarize the results of the study. The diagrams give both the experimental and theoretical MIM correlations discussed above. The correlations of the calculated and observed pentacyclic transitions given in Tables 1, 2 and 3, and the correlations of the calculated and observed tetracyclic transitions, taken from Becker *et al.* [9], complete the diagrams. The agreement between experimental and theoretical spectra was good, considering that no particular effort was made to achieve a precise fit in this study.

Since the correlations presented begin and end with the observed pentacyclic transitions, columns 1 and 5, one may follow the correlation lines from an observed transition in column 1 to the same transition in column 5 if the experimental and theoretical MIM interpretations lead to the same conclusion regarding the transition "origin". This is not possible when the experimental and theoretical MIM interpretations are not in agreement.

No attempt was made to correlate a pentacyclic transition with one of a smaller molecule when it appeared that the pentacyclic transition originated from one of a degenerate pair of forbidden electron-transfer transitions in the non-bonded composite system model. Consequently, no correlation lines appear in these cases.

Conclusion

The comparison of the theoretical and experimental composite system interpretations of the electronic transitions of BN, DBA, and BP reveals generally good agreement. In all cases, there was agreement between the theoretical and experimental results regarding which particular composite system models were the best approximations to the subject molecules. This agreement indicates that the application of the MIM concept in interpreting at least the first three transitions of these pentacyclics seems justified. However, interpretations of the individual transitions disagreed in some instances, particularly in the case of higher energy transitions. Furthermore, the experimental and to some extent the theoretical composite system interpretation of the higher transitions were much less clear. Although the treatment of molecules by means of the MIM method would benefit greatly by a more rigorous theoretical justification, the results of the investigation indicate the soundness of the basic concept.

It must be noted that there possibly are other schemes by which the theoretical interpretation of the transitions could be made to agree more closely with the experimental interpretation for some individual transitions. However, the objective of this work was to verify if the MIM concept was a valid approach for analyzing the complete spectra of the pentacyclic aromatic hydrocarbons. Consequently, all the theoretical interpretations were based on the foregoing premise and agreement or disagreement between the theoretical and experimental interpretations was taken as evidence for or against this objective.

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