Electronic Spectra of Radical Cations and Their Correlation with Photoelectron Spectra

I. Dibenzochrysene and Dibenzanthracenes

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Electronic absorption spectra of the radical cations of 1.2,7.8-dibenzochrysene, 1.2,3.4-dibenzanthracene, 1.2,5.6-dibenzanthracene and 1.2,7.8-dibenzanthracene in boric acid are measured. The transition energies of the cations are calculated using the Longuet-Higgins-Pople and Wasilewski type Open-Shell-SCF-MO methods with limited CI. A comprehensive discussion of the absorption bands is given in the light of the calculations and the photoelectron spectral data for the hydrocarbons. The correspondence between the optical and photoelectron spectra is found to be extremely good with almost negligible matrix shifts, thus highlighting the role of photoelectron spectroscopy in understanding the optical spectra of the radical cations and vice versa. Finally, a correlation diagram for the observed electronic transitions for the radical cations of anthracene and its benzologs is presented from which it is inferred that the optical A-transitions have some sort of correlation with the first IP's of the respective hydrocarbons.

Introduction

In spite of the long history of the optical spectroscopy of radical cations of aromatic hydrocarbons [1–12], it is only after the advent of ultraviolet photoelectron spectroscopy (PES) [13–15] that their importance has been fully realized. This is due to the close relationship that exists between the PE spectra of molecules and the electronic spectra of their radical cations [16–18]. The use of PE spectroscopy as a source of electronic spectral data for radical cations of conjugated systems was first emphasized by Zahradnik and co-workers [19, 20]. A further contribution to the subject came from Shida et al. [21] who studied the correlation between the two types of spectra more explicitly. In spite of these developments, the present state of the literature is far from satisfactory. There are several important aspects of the subject that have either remained in the dark or have not been properly investigated. To mention a few:

(1) The role of the PE spectroscopy in the interpretation of cation spectra, though very well understood, has not been fully exploited. The first and foremost problem is, therefore, a re-examination of the optical spectra for radical cations in the light of the abundance of PES data for aromatics [22–25].

(2) A problem which one often encounters with in PE spectroscopy is the identification of the higher π IP's of polycyclic hydrocarbons which is frustrated due to the overlapping of σ and π bands in that region [26]. It might be interesting to investigate as to what extent the cation spectra, which encompass the entire region from the near ultraviolet to the near infrared, could furnish information about such IP's.

(3) One of the basic differences between the optical and PE spectra is that the former are normally measured in a rigid glass while the latter are measured in the gas phase. The data for matrix shifts might throw some light on structural changes in hydrocarbons, if any, in going from one phase to another [27].

(4) Apart from the known correlations between the optical and PE spectra, it will be interesting to see what further parallelism can be drawn between the electronic transition energies in radical cations and the ionization potentials (IP's) of the corresponding hydrocarbons.

A prerequisite for the study of the above-mentioned problems is the availability of sufficient optical data which are still scarce. To this end we have undertaken a detailed investigation of the electronic spectra of radical cations of a variety of condensed-

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ring systems, viz., benzanthracenes, picenes, polyphenyls, perylenes, coronenes, and pyrenes. This, however, does not include the systems with two, three and four condensed benzene rings whose cation spectra are now well understood. For the sake of convenience, the result for each class of hydrocarbons shall be published separately.

The present paper, which forms the first of the series, deals with the cation spectra of dibenzochrysene and the dibenzanthracenes. Their interpretation is given on the basis of Open-Shell-SCF-MO calculations and PES data. At the end, a correlation diagram for the electronic transitions in the radical cations of anthracene and its benzologs is presented.

Experimental

High-purity boric acid crystals were obtained from E. Merck. The polycyclic aromatic hydrocarbons were provided by Dr. W. Schmidt most of which were from the collection of Professor E. Clar. The details for the preparation of radical cations in boric acid by ultraviolet irradiation and the spectrometers used for absorption measurements are described elsewhere [28].

Computational Details

For the calculation of electronic transition energies and intensities of radical cations, the following Open-Shell-SCF-MO methods are used: (i) The Longuet-Higgins-Pople (LHP) method [29] which is an improved version of the Pariser-Parr-Pople method [30, 31], and (ii) the Wasilewski method [32], which itself is based upon the Open-Shell-SCF method of Roothaan [33]. These methods are based on different approaches and thus their application to a large number of molecular systems offers an opportunity to test their relative merits. In addition, the assignment of the transitions may be made with more confidence. The reason for employing these methods, when more advanced MO theories are available, may be justified for the reason that the latter, in spite of their sophistication, do not offer any significant improvement as regards the calculation of π transition energies [20].

The same set of parameters have been used for both methods and the resonance integrals, β_{pq}, are chosen such that

$$\beta_{pq} = \begin{cases} -2.371, & \text{if the atoms p and q are bonded,} \\ 0, & \text{otherwise.} \end{cases}$$

The values of the ionization potential and electron affinity for carbon atoms in the sp^2 valence state have been taken as: $I^c = 11.22$ and $A^c = 0.69$ eV, respectively. This gives the value of the one-centre Coulomb repulsion integral as:

$$\gamma_{pp}^{cc} = I^c - A^c = 10.53 \text{ eV}.$$

For the evaluation of two-centre integrals, the Mataga-Nishimoto approximation [34] is used which, compared to the Pariser-Parr approximation [30], gives better results for ion radicals [35]. In this approximation,

$$\gamma_{pq}^{cc} = \frac{14.3986}{R_{pq} + (14.3986/\gamma_{pp}^{cc})},$$

where R_{pq} is the distance between the carbon centres p and q. We make yet another approximation that all the systems under investigation are planar and have hexagonal geometries with a constant bondlength of 1.4 Å.

For the construction of the excited state wave functions, only one-electron excitations are considered. The various types of excited state doublet configurations in odd-electron systems may be classified according to the scheme in Fig. 1 [36]:

I: $\quad m - i(1 \leqq i \leqq m - 1) \rightarrow m$,

A: $\quad m \rightarrow m + 1$,

B_1: $\quad m \rightarrow m + i(1 < i \leqq m)$, and

B_2, B_3: $m - i(1 \leqq i \leqq m - 1) \rightarrow m + i(1 \leqq i \leqq m)$,

where $m - i$, m and $m + i$ correspond to the doubly-occupied, singly-occupied and unfilled orbitals, re-

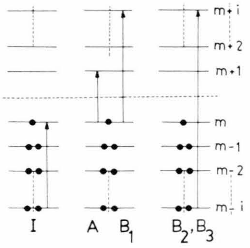

Fig. 1. Classification of one-electron excitations in open-shell systems.

spectively. The classifications B_2 and B_3 in the last type of excitations arise from the two different orientations of the spins α and β, i.e., $1/\sqrt{2}\,(\alpha\beta\alpha-\beta\alpha\alpha)$ and $1/\sqrt{6}\,(2\alpha\alpha\beta-\alpha\beta\alpha-\beta\alpha\alpha)$, in the respective order.

Formulas for evaluating the matrix elements for configuration interaction (CI) calculations in the framework of the LHP method are given by Ishitani and Nagakura [37]. These were used with a minor correction introduced by Zahradnik et al. [38]. For the other method, the corrected version of the formulas given by Wasilewski [39] were employed. Based on these methods a computer program was written. For the CI treatment, the program selected automatically as many lower-energy configurations (with certain energy cut-off) that did not exceed the maximum limit of configurations, taken as 62 in the present case. All the calculations were made on a CDC Cyber 175 Computer at the Leibnitz Computer Centre of the Bavarian Academy of Sciences, Munich.

Results and Discussion

The following figures display the experimental and theoretical results for the electronic transitions in hydrocarbon radical cations. The structures of the hydrocarbons are depicted at the top right of the diagrams. In the absorption spectra, the energies of the prominent peaks are also mentioned. Parts of the spectra with weaker transitions are expanded to several orders of magnitude. The dashed curves correspond to the data taken from other works [9]. The vertical lines on the top show the electronic transition energies for cations derived from photoelectron spectra [25]. This is done on the basis of the fact that the energy difference between the first and $(n+1)$-th peaks in the photoelectron spectra correspond to the transition energy of a radical cation from its ground doublet state to the n-th excited doublet state, i.e.,

$$E_n = \mathrm{IP}_{n+1} - \mathrm{IP}_1, \quad (n \geqq 1),$$

where E_n is the energy for the n-th electronic transition and the IP_i's are the i-th electron energy peaks. As an abbreviation, these vertical lines shall be referred to in the text as "PES diagrams". The results of the calculations employing the LHP and Wasilewski methods are presented as "stick diagrams" where the lengths of the sticks give a measure of the intensities of the transitions in terms of oscillator strength, F. The dotted lines correspond to the forbidden transitions. The calculated polarizations of the allowed transitions are shown as small arrows. At the bottom of the stick diagrams, the designation of each electronic transition is given where only "one-letter" symbols [36] are used to avoid overcrowdedness. For similar reasons, the classification of the weak transitions in the higher-energy region is not given. As is evident from the results of the two calculations, they do not show much variation. For this reason, unless specified, the assignment of the optical bands is based on the LHP method.

A discussion of the electronic spectra of each of the hydrocarbon radical cations is given in the following.

(i) 1.2,7.8-Dibenzochrysene Radical Cation

Figure 2 depicts a complete picture of the electronic transitions in the radical cation of 1.2,7.8-dibenzochrysene comprising its absorption spectrum in boric acid, the transition energies inferred from PES, and the calculated spectrum of the cation. The observed spectrum resembles closely with that reported by Shida and Iwata [9] where the cations were produced in sec-butyl chloride by γ-irradiation at 77 °K. In contrast, it shows a marked variation with that of its anion spectrum [9] which reveals its characteristic property. The above workers, however, have not explicitly discussed the assignment of the individual absorption bands. In radical ions, it is usually the lower-energy transitions that are more important as they characterize such species. We, therefore, reproduce in the following the prominent configurations for the first eight doublet excited states along with the oscillator strengths of the electronic transitions. These according to the LHP calculations are:

(1) $I\,[0.984\,(\Phi_{12} \rightarrow \Phi_{13})]$, 0.000;
(2) $I\,[0.974\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.037;
(3) $I\,[0.964\,(\Phi_{10} \rightarrow \Phi_{13})]$, 0.249;
(4) $I\,[0.965\,(\Phi_{9} \rightarrow \Phi_{13})]$, 0.000;
(5) $I\,[0.965\,(\Phi_{8} \rightarrow \Phi_{13})]$, 0.093;
(6) $I\,[0.951\,(\Phi_{7} \rightarrow \Phi_{13})]$, 0.000;
(7) $I\,[0.927\,(\Phi_{6} \rightarrow \Phi_{13})]$, 0.019;
(8) $A\,[0.922\,(\Phi_{13} \rightarrow \Phi_{14})]$, 0.264.

These states may be considered to be "pure" as the mixing with other configurations is negligibly small.

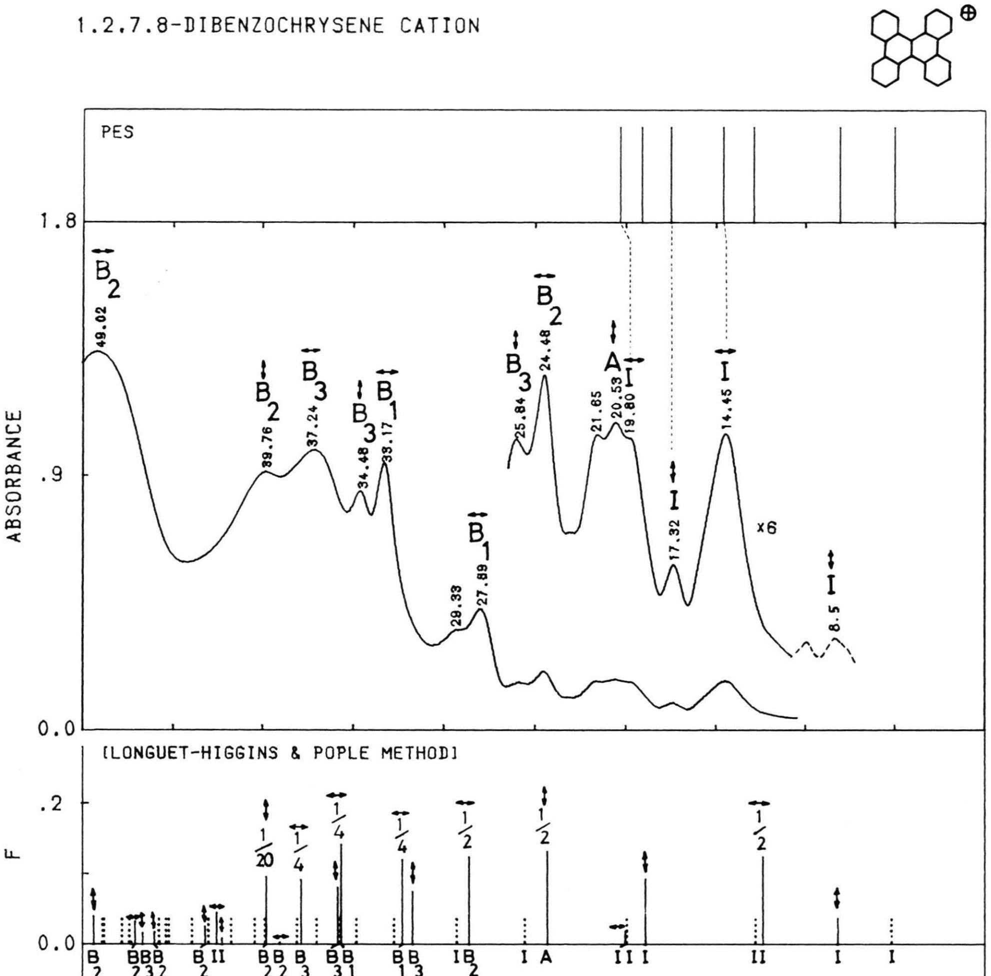

Fig. 2. Electronic absorption spectrum of 1.2,7.8-dibenzochrysene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES). The dashed curve in the absorption spectrum is reproduced from [9].

But the calculations reveal that for the higher excited states the mixing does become appreciable. It is obvious from the above that the first, fourth and sixth transitions are forbidden and the same have not been experimentally observed. The assignment of the third and fourth absorption bands needs some elaboration. From intensity considerations, it is absolutely clear that the 14.45 kK absorption should be assigned as $I(\Phi_{10} \rightarrow \Phi_{13})$ which exactly coincides with the fourth line in the PES diagram. Thus the transition $I(\Phi_9 \rightarrow \Phi_{13})$, whose energy has been slightly over-estimated by both the calculations, should lie on the lower-energy side to the former. The reversal in the ordering of these transitions leads to the conclusion that the symmetry assignment of the corresponding close-lying electron peaks (8.80 and 9.01 eV) in the PE spectrum as given by Schmidt [24] should be reversed. This may, in turn, be considered to mean that the Koopmans' molecular orbital picture of the PE spectra is not always valid for overcrowded hydrocarbons such as the present one.

As the hydrocarbon could not be completely converted into the radical cation on irradiation, the spectrum above 30 kK represents a mixture of the hydrocarbon with that of its radical cation. Hence the assignment of the bands in this region is only a tentative one. However, such an assignment may not altogether be erroneous since on theoretical grounds it might be expected that the higher-energy configurations, which are predominantly of type B, may not interact strongly with the lower-energy configurations of types I and A characterizing the cation.

(ii) 1.2,3.4-Dibenzanthracene Radical Cation

The absorption spectrum of 1.2,3.4-dibenzanthracene radical cation is shown in Fig. 3 along with the PES diagram and the results of calculations. The present spectrum is a replica of the cation spectrum in sec-butyl chloride measured by Shida et al., but differs much from that of the anion spectrum [9]. Calculations reveal that the major configurations in the first eight excited states of the cation and the intensities of the corresponding electronic transitions are:

(1) $I\,[0.977\,(\Phi_{10} \rightarrow \Phi_{11})]$, 0.008;
(2) $I\,[0.968\,(\Phi_9 \rightarrow \Phi_{11})]$, 0.151;
(3) $I\,[0.961\,(\Phi_8 \rightarrow \Phi_{11})]$, 0.128;
(4) $I\,[0.918\,(\Phi_7 \rightarrow \Phi_{11})]$, 0.012;
(5) $I\,[0.890\,(\Phi_6 \rightarrow \Phi_{11})]$, 0.031;
(6) $I\,[0.935\,(\Phi_5 \rightarrow \Phi_{11})]$, 0.006;
(7) $AI\,[0.727\,(\Phi_{11} \rightarrow \Phi_{12}) + 0.324\,(\Phi_6 \rightarrow \Phi_{11})]$, 0.124;
(8) $IA\,[0.743\,(\Phi_4 \rightarrow \Phi_{11}) - 0.382\,(\Phi_{11} \rightarrow \Phi_{12})]$, 0.084.

This shows that the configuration mixing becomes significant only after the sixth state. Except for the first transition which surpasses the measurement, all other I-transitions have been observed and show excellent correspondence with the results estimated from the PE spectrum. Like the former, this hydrocarbon also is not fully oxidized and for this reason the assignment of the higher-energy bands may be considered as tentative.

(iii) 1.2,5.6-Dibenzanthracene Radical Cation

1.2,5.6-dibenzanthracene is one of the interesting polycyclic aromatic hydrocarbons because of its carcinogenic property. The absorption spectrum of its radical cation is presented in Fig. 4 and is compared with the calculated spectrum and the PES results. This is an improvement over the cation spectrum reported by Shida and Iwata in sec-butyl chloride [9] as the latter did not cover the region beyond 25 kK. The electronic spectrum of the hydrocarbon radical anion has been measured by the above workers and also by Distler and Hohlneicher [40]. But these are quite different from the cation spectra and particularly the intensities show much variation. To get a better picture of the electronic transitions in the radical cation, we present in the following the main configurations of some of the lower-energy excited states along with the oscillator strengths of the transition energies:

(1) $I\,[0.970\,(\Phi_{10} \rightarrow \Phi_{11})]$, 0.000;
(2) $I\,[0.958\,(\Phi_9 \rightarrow \Phi_{11})]$, 0.200,
(3) $I\,[0.945\,(\Phi_8 \rightarrow \Phi_{11})]$, 0.054;
(4) $I\,[0.946\,(\Phi_7 \rightarrow \Phi_{11})]$, 0.000;
(5) $AI\,[0.697\,(\Phi_{11} \rightarrow \Phi_{12}) + 0.536\,(\Phi_6 \rightarrow \Phi_{11})]$, 0.130;
(6) $I\,[0.908\,(\Phi_5 \rightarrow \Phi_{11})]$, 0.000;
(7) $IA\,[-0.729\,(\Phi_6 \rightarrow \Phi_{11}) + 0.527\,(\Phi_{11} \rightarrow \Phi_{12})]$, 0.284;
(8) $I\,[0.849\,(\Phi_4 \rightarrow \Phi_{11})]$, 0.000;
(9) $B_1B_3[0.713\,(\Phi_{11} \rightarrow \Phi_{14}) - 0.461\,(\Phi_9 \rightarrow \Phi_{12})]$, 0.000;
(10) $B_2B_1\,[0.653\,(\Phi_{10} \rightarrow \Phi_{12}) - 0.580\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.127;
(11) $IB_1\,[-0.480\,(\Phi_3 \rightarrow \Phi_{11}) + 0.457\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.200.

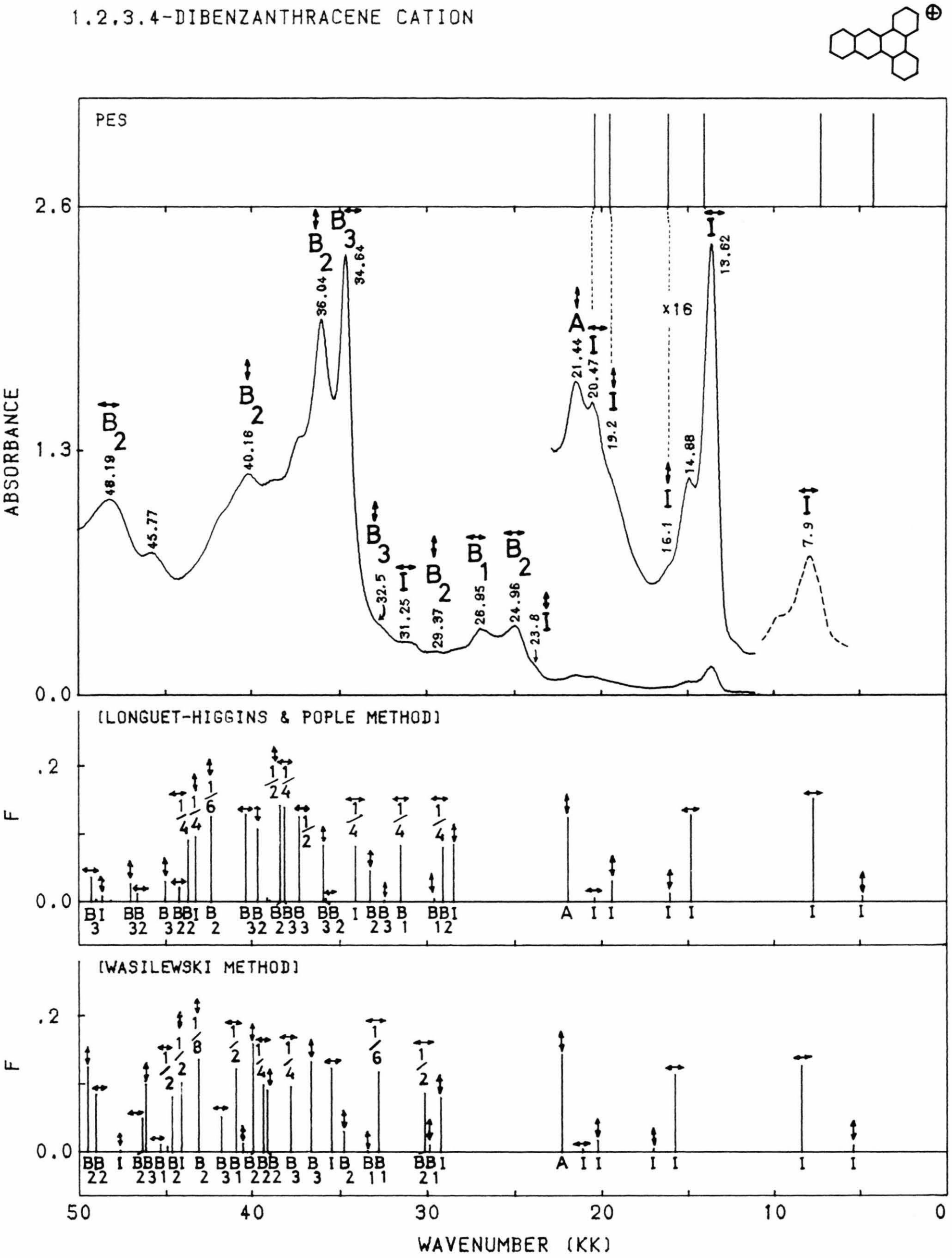

Fig. 3. Electronic absorption spectrum of 1.2,3.4-dibenzanthracene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES). The dashed curve in the absorption spectrum is reproduced from [9].

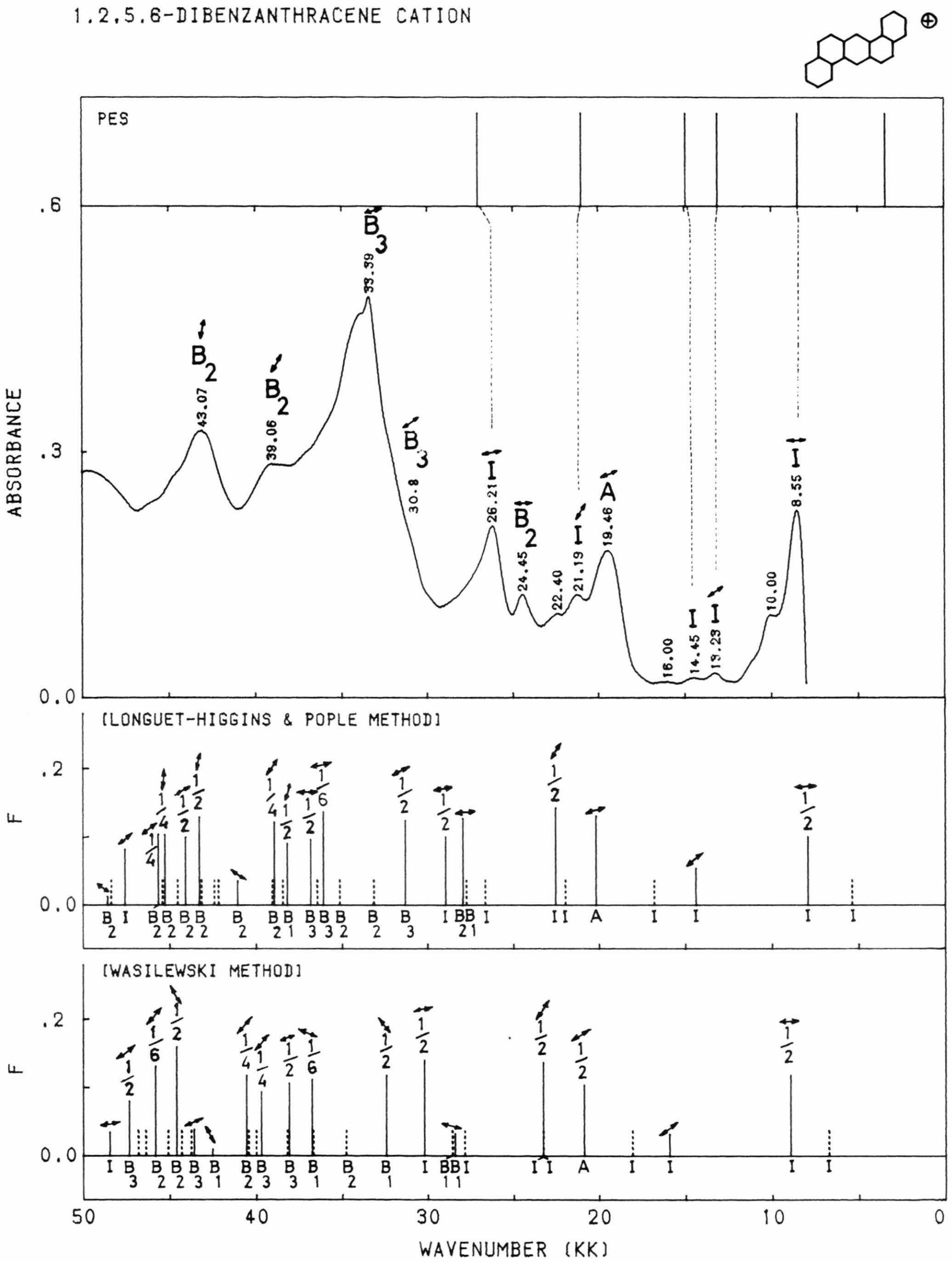

Fig. 4. Electronic absorption spectrum of 1.2,5.6-dibenzanthracene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

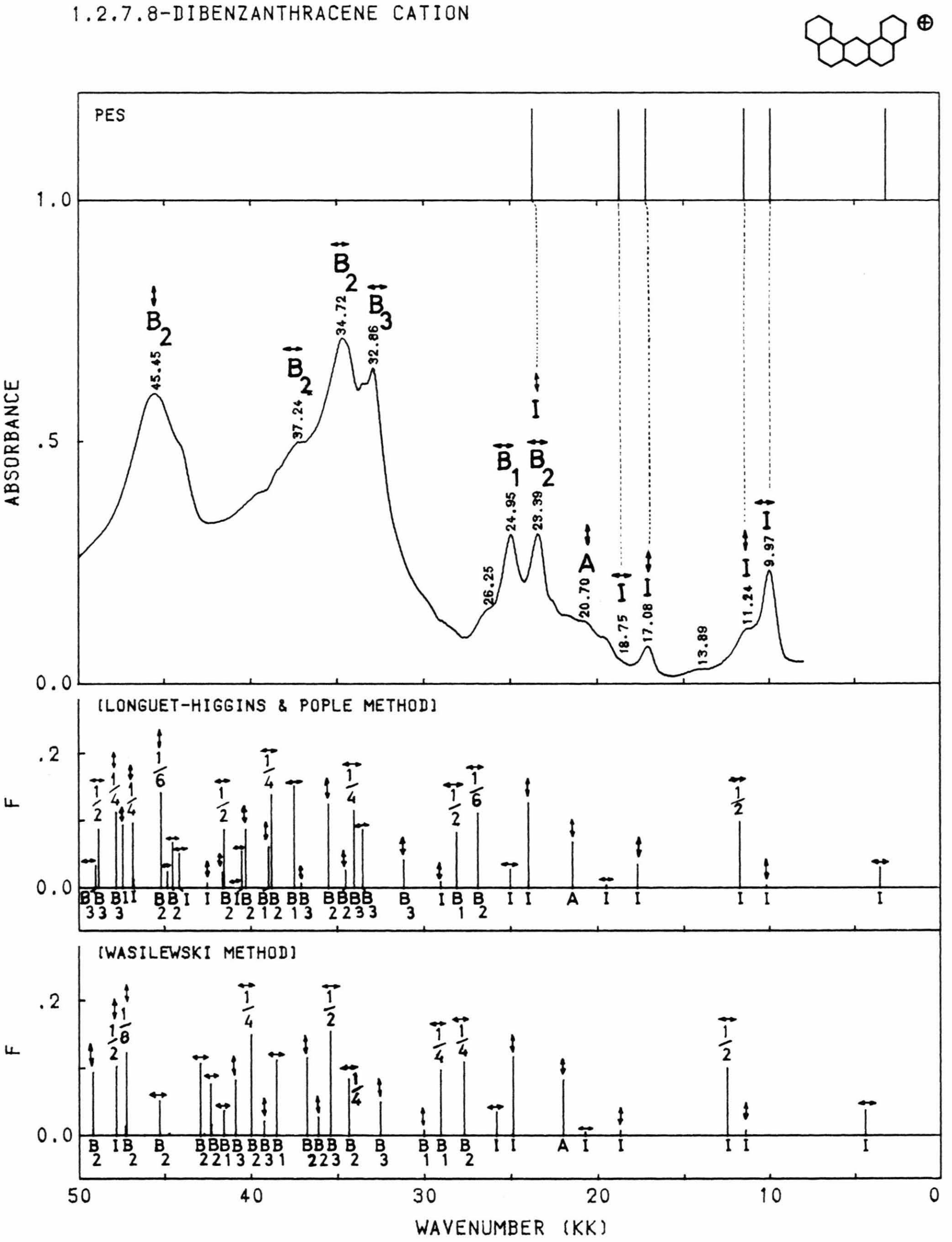

Fig. 5. Electronic absorption spectrum of 1.2,7.8-dibenzanthracene radical cation and its comparison with the calculated spectrum and the transition energies estimated from the photoelectron spectrum (PES).

The first five *I*-type of states may be considered as "pure" as the mixing with other configurations is insignificantly small. All the major absorption bands in the cation spectrum have been identified and the *I*-transitions are in excellent accord with the results estimated from the PE spectrum. The calculations reveal that there are some *I*-transitions (e.g., the sixth and eighth in the above) that do not appear in the PES diagrams. These presumably correspond to non-Koopmans states. This is, however, not possible to ascertain from the experiment as the above-mentioned transitions are electronically forbidden.

(iv) 1.2,7.8-Dibenzanthracene Radical Cation

Like its predecessor, 1.2,7.8-dibenzanthracene also belongs to the family of carcinogenic hydrocarbons. The spectrum of its radical cation, which has not been reported earlier, is shown in Fig. 5 together with the results of MO calculations and the PES diagram. In the literature, the spectrum of the hydrocarbon anion radical also has not appeared. The major configurations for the first eight excited doublet states and the intensities of the corresponding electronic transitions are as follows:

(1) $I\,[0.971\,(\Phi_{10} \rightarrow \Phi_{11})]$, 0.030;
(2) $I\,[0.949\,(\Phi_9 \rightarrow \Phi_{11})]$, 0.003;
(3) $I\,[0.960\,(\Phi_8 \rightarrow \Phi_{11})]$, 0.196;
(4) $IA\,(0.835\,(\Phi_7 \rightarrow \Phi_{11}) - 0.432\,(\Phi_{11} \rightarrow \Phi_{12})]$, 0.035;
(5) $I\,[0.935\,(\Phi_6 \rightarrow \Phi_{11})]$, 0.004;
(6) $AI\,[0.646\,(\Phi_{11} \rightarrow \Phi_{12}) + 0.463\,(\Phi_5 \rightarrow \Phi_{11})]$, 0.068;
(7) $IA\,[-0.797\,(\Phi_5 \rightarrow \Phi_{11}) + 0.331\,(\Phi_{11} \rightarrow \Phi_{12})]$, 0.126;
(8) $IB_1\,[0.762\,(\Phi_4 \rightarrow \Phi_{11}) + 0.318\,(\Phi_{11} \rightarrow \Phi_{13})]$, 0.027.

The first electronic transition which is estimated at ~ 3 kK, has evaded the detection. But all the prominent absorption bands in the cation spectrum have been identified. The cation spectrum has two strong bands at 23.39 and 34.72 kK. The Wasilewski method gives a better estimate of their intensities which leads to the assignment of the above bands as B_2 and B_1, respectively. The calculations predict yet another I-transition with an appreciable intensity which in the first instance seems difficult to locate in the observed spectrum. But its position may be estimated from the sixth line in the PES diagram which almost coincides with the 23.39 kK optical band. Thus we assume that the B_2 and I transitions are superimposed. Both the theories predict a large number of electronic transitions in the region above 30 kK, but the absorption spectrum displays relatively few bands. In such a case, the interpretation is attempted on the basis of the calculated intensities for the transitions.

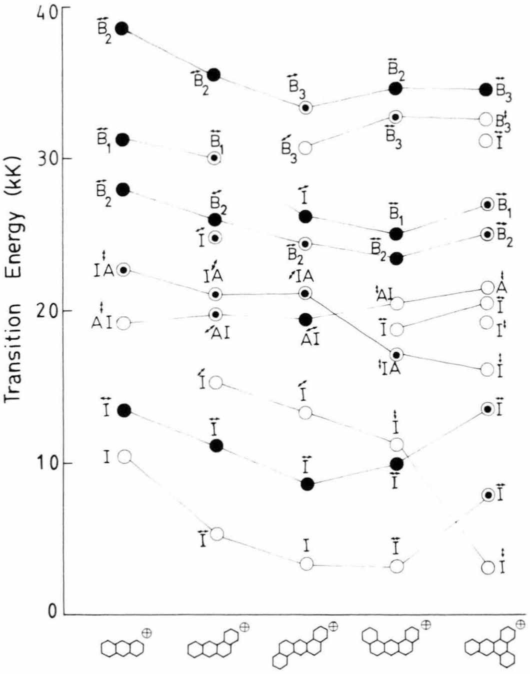

Fig. 6. Correlation diagram for the electronic transitions in the radical cations of anthracene and its benzologs. The circles show the relative intensities of the transitions: (●) strong, (⊙) medium, (○) weak or forbidden.

Correlation Diagram

Figure 6 demonstrates the correlation between the observed electronic transitions in the radical cations of anthracene, 1.2-benzanthracene, and dibenzanthracenes. This is to investigate the behaviour of the different transitions in moving from one system to another in a methodical manner. The position of the first optical transition in the dibenzanthracenes, which could not be experimentally determined, is estimated from the PES data. In spite of the different symmetries of the hydrocarbons, the transitions do show some definite trends. While the first two I-transitions show a decreasing tendency initially and then move upwards, the third and fourth I-transitions* are on the decrease throughout. The movement of the B-transitions is generally similar to the first two I-transitions. On the other hand, the A-transition shows a very slight upward movement which, for practical purposes, may be considered as inappreciable. The near-constancy of the energies of this last type of the transition suggests that they have some sort of relationship with the first IP's of

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* Wherever feasible, the fourth I-transition and the A-transition are designated by "two-letter symbols".

the hydrocarbons whose experimental values are: 7.41, 7.41, 7.38, 7.40 and 7.39 eV, respectively. The slight departure in the energies of the *A*-transitions from a constant value might be due to the structures of the hydrocarbons. A similar correlation has also been noticed in peri-condensed systems where the *A*-type of absorption bands are well-pronounced [41].

Conclusions

The paper establishes that the correspondence between the optical and photoelectron spectra is extremely good for all the systems considered. The absence of any appreciable matrix-shift indicates that the structures of the hydrocarbons do not show any change upon ionization. At places the complementary aspects of the two types of spectra have also come into the picture. But it could not be possible to identify the higher π IP's of the hydrocarbons as the corresponding *I*-transitions in radical cations are too weak to be observed. From the correlation diagram it appears that the optical *A*-transitions in radical cations may be correlated with the first IP's of the hydrocarbons, but a definite conclusion in this respect can not be drawn unless sufficient optical data are available. A study of other hydrocarbon radical cations is in progress.

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