

# ELECTRONIC SPECTRA AND SEMIEMPIRICAL CALCULATIONS ON DINEGATIVE IONS OF ACENAPHTHYLENE, FLUORANTHENE AND ACEHEPTYLENE

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Electronic spectra of the dinegative ions of acenaphthylene, fluoranthene and 2,4-dimethylaceheptylene prepared in dimethoxyethane by alkali metal reduction have been measured. The observed transition energies are not well interpreted by standard PPP calculations. A better agreement was achieved with a modified version of the PPP method, where the non-diagonal core matrix elements even for non-neighbouring carbon atoms were retained.

In the paper<sup>1</sup> we reported the electronic spectra of radical anions of acenaphthylene, fluoranthene and 2,4-dimethylaceheptylene. As the open-shell approach to a standard PPP method appeared to afford reasonable interpretation of these spectra, it was of interest to us whether the closed shell PPP calculations give reasonable results for acenaphthylene, fluoranthene and aceheptylene dinegative ions, too. Thus this paper represents a contribution to our attempt to develop a general computational method of the PPP-type, which would estimate various physico-chemical properties adopting a single set of semiempirical parameters regardless of the electronic state, oxidation level and spin multiplicity of the system studied. Concerning the preparation and spectral measurements of the dinegative ions the details have been given previously<sup>1</sup>.

## CALCULATIONS

We employed a standard PPP method in a form described previously<sup>2</sup> and its modified version. The latter differs from the former by assuming non-zero resonance integrals ( $\beta_{\mu\nu}$ ) even between atoms which are not joined by a chemical bond. These integrals were estimated by means of the following expression

$$\beta_{\mu\nu} = 0.5246 \frac{2\alpha_{\mu}\alpha_{\nu}}{\alpha_{\mu} + \alpha_{\nu}} S_{\mu\nu}(2 - |S_{\mu\nu}|), \quad (1)$$

combining formulae of Cusachs<sup>3</sup> and Yeranov<sup>4</sup>. Here  $\alpha_{\mu}$  and  $\alpha_{\nu}$  are the one-centre core integrals, the  $S_{\mu\nu}$  elements were evaluated as analytical integrals for Slater's  $2p_z$  atomic orbitals. Bond

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lengths,  $r_{\mu\nu}$ , between the neighbouring atoms were re-evaluated after each iteration by means of the Julg's formula<sup>5</sup>

$$r_{\mu\nu} = \sqrt{\frac{3.25}{\vartheta_{\mu} + \vartheta_{\nu}}} (1.523 - 0.19p_{\mu\nu}), \quad (2)$$

where  $p_{\mu\nu}$  is a bond order,  $\vartheta_{\mu}$  and  $\vartheta_{\nu}$  are exponents for Slater  $2p_z$  atomic orbitals. The adopted numerical values for one-centre core matrix elements were based on the data of Hinze and Jaffé<sup>6</sup>. In a configuration interaction treatment we assumed all singly excited states arising from electron promotions between the five highest occupied and the five lowest unoccupied molecular orbitals.

In the 2,4-dimethylacephylene dianion the methyl groups were ignored, therefore, the results of the actual calculations refer to the unsubstituted dianion. Here, however, the methyl substitution is believed not to cause any considerable change in the nature of the absorption curve.

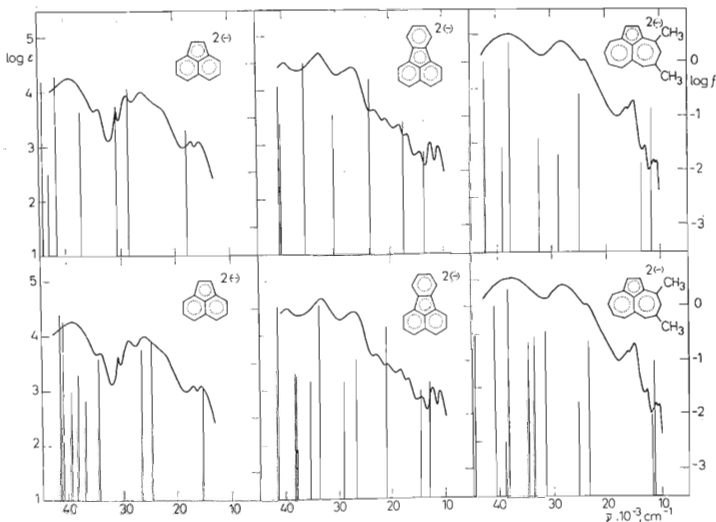


FIG. 1

Electronic Spectra of Acenaphthylene, Fluoranthene and 2,4-Dimethylacephylene Dinegative Ions and Results of Semiempirical Calculations

Vertical lines calculated electronic transitions. At the top we have results of standard PPP-calculations; at the bottom results obtained by a modified version of the PPP-method assuming all core matrix elements. The left side scales concern experimental intensities; the right side scales the calculated ones ( $f$  the theoretical oscillator strengths).

## RESULTS AND DISCUSSION

Electronic spectra of the three dianions under study are presented in Fig. 1. For their interpretation we first employed a standard computational treatment of the PPP-type. The results are seen in Fig. 1 to give a correct picture of the complexity of the electronic spectra, however, the quantitative agreement is not as good as that usually found for parent hydrocarbons or their mononegative ions<sup>7,8</sup>. Therefore, we attempted to interpret these spectra by means of a modified computational scheme assuming all core matrix elements. This procedure which was tested on a representative set of 80 conjugated compounds of various structural types appears to be suitable for applications to various properties of conjugated molecules in ground and excited states<sup>9</sup>. The adoption of this approach is seen (Fig. 1) to lead to a somewhat better agreement between the experimental and the theoretical spectra. Similarly as with aceheptylene anion radical<sup>1</sup>, the order of the two first electronic transitions predicted by the theory appears to be reversed. The electronic spectra of the dianions studied are very similar to the spectra of the corresponding radical anions<sup>1</sup> (Fig. 2). Some similarity in the electronic spectra of mono- and dinegative ions was also found for benzenoid hydrocarbons<sup>10</sup>,  $\alpha,\omega$ -diphenylpolyenes<sup>11</sup>, and dibenzocyclobutadiene<sup>12</sup>. This finding is as expected on grounds of the HMO theory, which predicts for mononegative and dinegative ions the same electronic transitions from the highest singly and doubly occupied molecular orbital, respectively. We attempted to obtain a deeper insight into similarities and differences in the electronic spectra of parent hydrocarbons, their radical anions, and dinegative ions on grounds of the SCF theory. The SCF transition energy for the closed shell systems (*i.e.* for the parent

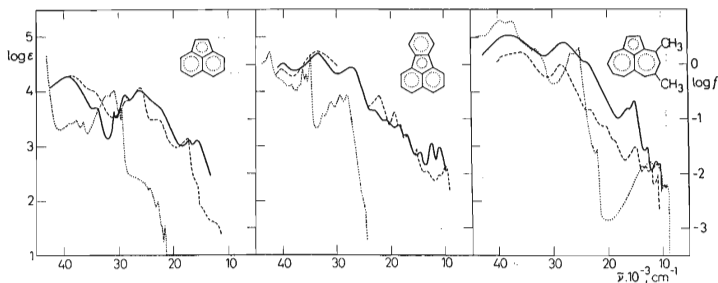


FIG. 2

Absorption Curves of Acenaphthylene<sup>14</sup> in Hexane, Fluoranthene<sup>14</sup> in Methanol, 2,4-Dimethylaceheptylene<sup>15</sup> in Hexane (·····) and Their Mono (----) and Dinegative (—) Ions in Dimethoxyethane

hydrocarbons and their dinegative ions) can be expressed as

$$\Delta^1 E_{i \rightarrow j} = \varepsilon_j^{\text{SCF}} - \varepsilon_i^{\text{SCF}} - J_{ij} + 2K_{ij}, \quad (3)$$

while for the open shell systems (*i.e.* for radical anions) the following expressions hold<sup>13</sup>

$$\Delta^2 E_{i \rightarrow m} = \varepsilon_m^{\text{SCF}} - \varepsilon_i^{\text{SCF}} + \frac{1}{2}(J_{mm} + K_{im} - 2J_{im}), \quad (4)$$

$$\Delta^2 E_{m \rightarrow j} = \varepsilon_j^{\text{SCF}} - \varepsilon_m^{\text{SCF}} + \frac{1}{2}(J_{mm} + K_{mj} - 2J_{mj}), \quad (5)$$

where  $i, m, j$  are indices for doubly occupied, singly occupied and unoccupied molecular orbitals in the ground state configuration. The electronic promotions from doubly occupied MO's into empty MO's need not be considered here because the configurations formed in this way have unimportant weights in the low-lying excited doublet states of the radicals under study. As an example we present the results of calculations for acenaphthylene (Fig. 3). As can be noticed, some electronic transitions are specific for the parent hydrocarbon, its radical anion or dianion, while some others are formally analogous in a couple parent hydrocarbon-dinegative ion or radical anion-dinegative ion. Of course, a meaningful comparison can be made only for upper states which mix with other configurations very little.

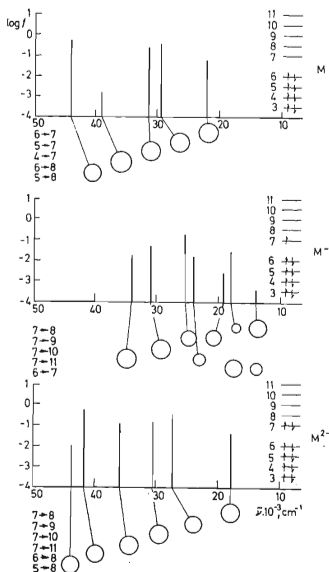


FIG. 3

Results of LCI SCF Calculations for Acenaphthylene (M) and Its Mono ( $M^-$ ) and Dinegative Ion ( $M^{2-}$ )

Vertical lines: calculated transition energies and oscillator strengths ( $f$ ),  $\circ$  the weights of main configurations in excited state wave functions. The open shell calculation<sup>1</sup> for  $M^-$  is based on MO's of Longuet-Higgins and Pople.

After analyzing the "common" transitions in parent hydrocarbons and their dinegative ions by means of Eq. (3), we found the respective differences in the contributions coming from orbital energies ( $\epsilon_j - \epsilon_i$ ) and electronic repulsion ( $2K_{ij} - J_{ij}$ ) to be small and amount to about 0.2 eV and 0.3 eV, respectively. No such a similarity can be found from Eqs (3)–(5) for a couple parent hydrocarbon–radical anion or radical anion–dinegative ion. Here electronic repulsion contributions differ considerably (because of being composed of different Coulomb and exchange integrals), however, differences of the same magnitude are found even for contributions coming from orbital energies.

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