

THEORETICAL EXAMINATION OF THE DIBENZO-DERIVATIVES OF PERYLENE

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The term systems of condensed aromatic hydrocarbons built up from anthracene and phenanthrene parts were examined using L. C. A. O. treatment and furthermore, calculations were performed regarding the applicability of the perturbation method. The most important properties of the spectra are obtained qualitatively correctly from the results of the calculations, whereas the quantitative agreement is far less good.

1. Introduction

For a few years the perturbation method plays an important role in the theoretical examination of condensed aromatic compounds, especially when L. C. A. O. treatment is used (COULSON [1] and references therein). Its importance consists in its rendering possible the investigation of structural changes in the molecule; e. g. on using it the properties of single aromatic hydrocarbons can be examined as to how they are affected on being condensed into a greater compound. Recently PAUNCZ [2] used this method successfully for the investigation of condensed aromatic compounds built up from identical units.

The aim of this paper is to use the above-mentioned procedure for the investigation of molecules built up from anthracene or phenanthrene parts. The spectra of the following compounds calculated by the L. C. A. O. method will be examined: Of these compounds I and II can be built up from anthracene-, III and IV from phenanthrene- and V and VI from anthracene- and phenanthrene- parts. The members of the single pairs of compounds (I—II, III—IV, V—VI) differ in the relative position of the units.

2. The Method of Calculation

For our treatment the well-known basic assumptions of the HÜCKEL method are used. The calculation of the molecule term system with the L. C. A. O. method consists in the evaluation of the roots of the following secular determinant:

$$|H_{ik} - \varepsilon S_{ik}| = 0, \quad (1)$$

where

$$H_{ik} = \int u_i^* H u_k dx, \quad S_{ik} = \int u_i^* u_k dx, \quad (2)$$

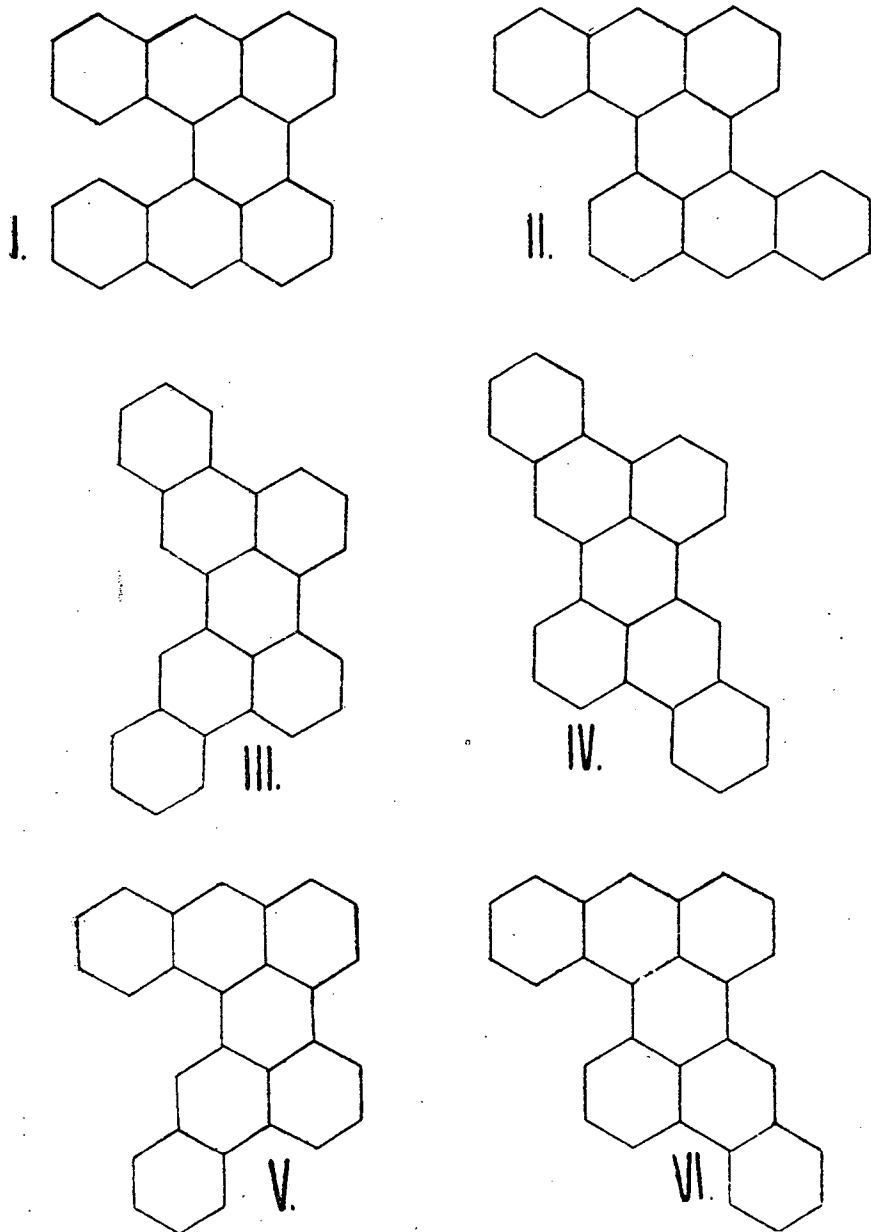


Fig. 1

u_i represents the π electron function belonging to atom i , H the effective Hamilton operator for a single electron, ε the energy value. Relating to the matrixelements (S_{ik} , H_{ik}) the following simplifications are used:

a) $S_{ik} = \delta_{ik}$, b) $H_{ii} = \alpha$, c) H_{ik} only differs from zero when i and k are indices belonging to neighbouring atoms; let us denote this value with β .

The values of β occurring in the anthracene or phenanthrene parts are considered to be equal, while the value of H_{ik} belonging to the bonds connecting the single anthracene or phenanthrene unit is denoted by $\lambda\beta$. Physical and chemical arguments suggest that the value of λ in the molecules investigated is smaller than 1; the lengths of the connecting bonds are greater than those of the other ones occurring in the molecules, i. e. the strengths of the corresponding bonds are smaller than those of the others. For instance, in the case of perylene the dibenzo-derivatives of which are all the six compounds the bond lengths of the bonds connecting the naphthalene parts measured Roentgenographically are 1,50 Å, while the lengths of the remaining bonds are about 1,41 Å (DONALDSON, ROBERTSON and WHITE [3]). On the other hand, the considerable independence of the two parts is shown by the fact that the value of the diamagnetic susceptibility of perylene can be calculated from those of naphthalene and hydrogen without any correction for the central hexagon (SHIBA and HAZATO [4], HAZATO [5]). Let us assume that also for the case when phenanthenes or anthracenes are joined instead of the two naphthalenes, the situation is analogous. Lacking Roentgenographical data we cannot give any definite value for λ for this reason the term system of the molecules will be discussed in the $\lambda = 0$ and $\lambda = 1$ interval. The dependence of the term system on γ will be determined using the following two procedures:

a) Perturbation method

Let us take for the unperturbed problem the case when anthracene and phenanthrene are not joined together and consider the formation of bonds between them as perturbation.

The connecting links should be formed between the atoms $a - a'$ and $b - b'$, resp., where the atoms a and b belong to the first part, a' and b' to the second one. The first order perturbation energy belonging to the i -th level is according to DEWAR [6] and PAUNCZ [2] as follows:

$$\varepsilon_i = \begin{cases} (c_{ai}c_{a'i} + c_{bi}c_{b'i})\lambda\beta, & \text{when the two units are identical} \\ 0 & \text{when they are different,} \end{cases} \quad (3)$$

where c_{ai} and c_{bi} mean the coefficients in the i -th molecular orbital belonging to atom a and b , resp.

If the two units to be joined are different, the second order perturbation calculation should be used. In view of the fact, however, that the corresponding levels of anthracene and phenanthrene are close to each other, the second order perturbation calculation does not give any acceptable results.

b) Direct calculation

Both for the examination of the latter case, and the investigation of the reliability of the perturbation treatment, in the former case, it seems useful to determine the dependence of the level on γ by means of a straightforward calculation, too.

For this purpose each line of the secular determinant should be divided by β and the following notation introduced:

$$-x = \frac{\alpha - \varepsilon}{\beta} \quad (4)$$

In the case of the single compounds the polynomial obtained by the reduction of the secular determinant can be transformed into the following form:

$$\text{I. — IV. } \{P_0(x) + \lambda P_1(x) + \lambda^2 P_2(x)\} \{P_0(x) - \lambda P_1(x) + \lambda^2 P_2(x)\} = 0 \quad (5)$$

$$\text{V. — VI. } P_0(x) + \lambda^2 P_2(x) + \lambda^4 P_4(x) = 0.$$

From equation (5) for all x , the λ which makes the secular determinant to zero can be very simply determined. Performing the numerical calculation for all the given x , using a graphical method, it can easily be determined from the obtained results in which way the roots of the secular determinant depend on λ .

In the case of the compounds I. — IV., on the bases of (5), the possibility for the factorisation of the polynomial obtained by the reduction of the secular determinant becomes evident, thus the symmetrical and antisymmetrical levels in respect to reflection or inversion resp. can be treated separately.

The comparison of the results of the direct calculation with those obtained with the perturbation method illustrates up to which value of λ the perturbation calculation gives reliable results.

3. Results of Calculation and Discussion

The results of our calculations show that the term systems of the single pairs of compounds possess a high degree of resemblance, therefore in each case only one of the two term systems of the respective compound is shown in the following three figures. It is sufficient to plot the term systems corresponding to all the positive x , as the level systems of the above mentioned alternant hydrocarbons are symmetrical with respect to the $x=0$ value. The result of the straightforward calculation is shown by a full line, that of the perturbation treatment by a dotted one.

The examination of the figures shows the following.

On comparing the results obtained with the direct method with those received with the perturbation treatment it can be seen that their agreement up to $\lambda = 0,5$ is excellent. For greater values of λ a reliable agreement can be obtained only for the case if the distance of neighbouring levels is not too small, or they do not come too close together with increasing λ . If this occurs the result of the first order perturbation calculation may be incorrect for $\lambda = 1$. For instance, in Fig. 2 the order of the second and third levels changes.

If our results of calculation are compared to the experiment the following can be established.

a) According to the calculation the spectra of the corresponding pair of compounds should exhibit a high degree of resemblance. Experimentally the spectra of only one pair of compounds is known, its examination confirms this conclusion.

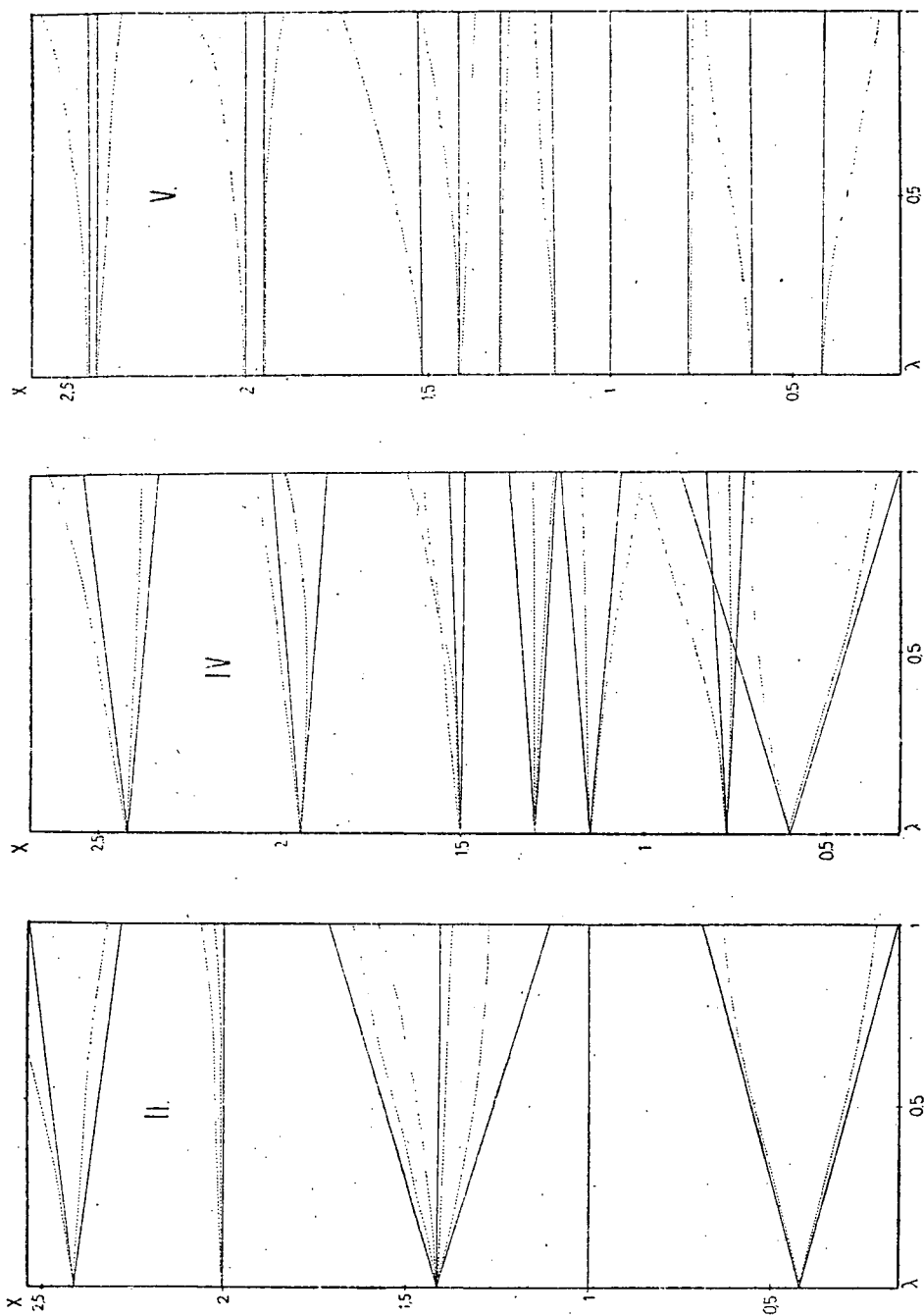


Fig. 2

b) From the calculations for the order of the first transition the following can be obtained: The transition possessing the longest wavelength belongs to compounds built up from anthracene parts, a shorter wavelength corresponds to the compounds built up from anthracene and phenanthrene, and to the third order belongs the pair of compounds consisting of two phenanthrene parts. This conclusion is in agreement with the experimental data as the wavelength of the transition are as follows:

I, 558 m μ II. 546 m μ V. 503 m μ IV. 434 m μ
(CLAR [7], [8]; [9]).

c) While the two former qualitative conclusions have proved to be correct, the quantitative agreement is far less good as a too high value is obtained for the wavelength of the first transition. If the λ value characterizing the strength of the connecting bonds is considered to be 0,5 the calculated value shifts in the right direction diverging, however, still appreciable from the experimental value. This fact shows that beside the above mentioned factor, further refinements of the method must be taken into account. Thus instead of the simplest variant of the L. C. A. O. treatment the S. C. F. method must be used (POPLE [10]) and the interaction of the electrons should be considered. Such calculations are in progress.

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