

ABSORPTION SPECTRA OF SOME AROMATIC COMPOUNDS CALCULATED BY MEANS OF THE ELECTRON GAS METHOD

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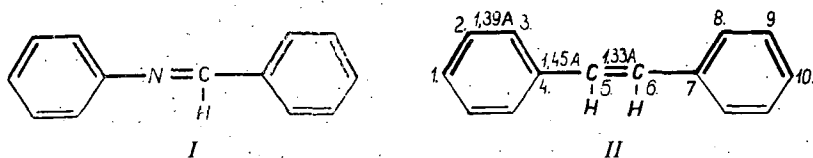
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In this paper the light absorption of benzaniline is interpreted by a simplified perturbation method. Furthermore, the electronic states of azobenzene are calculated like in a previous paper [1] by means of the electron gas method in one-dimensional square well potential with finite potential steps. Finally the consequences due to the transformation of stilbene, benzaniline and azobenzene to condensed aromatic systems are discussed. Calculated wavelengths of the bands are given and comparisons with the experimental values made.

1. The calculation of the absorption maxima of benzaniline by a simplified perturbation method

Benzaniline (I) may be theoretically deduced from stilbene (II) substituting the $-\text{CH}=\text{C}-$ group by a nitrogen atom. This way of placing benzaniline between stilbene and azobenzene is in accordance with the experimental fact that the absorption maxima of stilbene, benzaniline and azobenzene shift in the order of the enumeration towards the longer wavelengths. For the calculation of the absorption spectrum of benzaniline we start from the corresponding energy states of stilbene. Let us take the change of the energy arising at the substitution of a $-\text{CH}=\text{C}-$ group by $-\text{N}=\text{C}-$ in the stilbene molecule into account. The present calculation is based on the results con-



cerning stilbene. In case of stilbene, as customary at the utilization of the electron gas model, the π -electron system is placed in a linear box the size of which is determined by the dimensions of the molecule. The length of the linear box is $L = 12,57 \text{ \AA}$. The two π -electrons of the isolated double-bond of stilbene stay on a lower potential. For the half-width of this "potential-step" $a = 0,665 \text{ \AA}$ has been chosen. This is equal to the atomradius of one of the C atoms of the ethylene bond.



In the case of benzaniline as well as in that of stilbene at the formation of the electron gas ten π -electrons are taken into consideration. A certain electronic state of benzaniline can be obtained if we add the perturbation energy — appearing at the place of the N atom $\left(\frac{L}{2} - a = b\right)$ — to the corresponding energy values of stilbene:

$$E_{\text{Benz.}} = E_{\text{Stilb.}} + \varepsilon \quad (1)$$

where ε is the perturbation energy. In our case in order to obtain the energy states of benzaniline the ε perturbation of the energy states of stilbene must be determined. To calculate these perturbation energies the following relation (see Appendix) is employed:

$$\varepsilon \approx -2(\Delta U \cdot a) \cdot \psi_{\text{Stilb.}}^2(b) \quad (2)$$

where $\Delta U = 4,2293 \cdot 10^{-12}$ erg is the difference between the ionisation potentials of nitrogen and carbon and

$$\psi(b) = \sqrt{\frac{2}{L}} \sin \frac{n\pi b}{L} \quad (3)$$

in which $n = 1, 2, 3, \dots$ is a quantum number. The highest level occupied in the normal state of stilbene molecule is E_3^A . This energy state is also regarded as the highest filled up level of benzaniline. The value of the wave function at the place b belonging to the state E_3^A is

$$\psi_3^A(b) = 0,2689 \cdot 10^4 \text{ cm}^{-\frac{1}{2}} \quad (4)$$

For the following level (E_3^B) — unfilled in the normal state — the value of the wave function is

$$\psi_3^B(b) = 0,3350 \cdot 10^4 \text{ cm}^{-\frac{1}{2}} \quad (5)$$

Setting (4) and (5) into (2), we obtain

$$\varepsilon_3^A = -0,4067 \cdot 10^{-12} \text{ erg} \quad (6)$$

and

$$\varepsilon_3^B = -0,6311 \cdot 10^{-12} \text{ erg} \quad (7)$$

So the first excitation energy of benzaniline differs by the value

$$\Delta\varepsilon_1 = \varepsilon_3^B - \varepsilon_3^A = -0,2244 \cdot 10^{-12} \text{ erg} \quad (8)$$

from that of stilbene. In our previous calculations [1] the energy values of stilbene are given. So we have for the first transition of stilbene

$$\Delta E_{1, \text{Stilb.}} = E_3^A - E_3^B = 6,6452 \cdot 10^{-12} \text{ erg} \quad (9)$$

Thus for benzaniline the energy needed for the first excitation is

$$\Delta E_{1, \text{Benz.}} = \Delta E_{1, \text{Stilb.}} + \Delta\varepsilon_1 = 6,4208 \cdot 10^{-12} \text{ erg} \quad (10)$$

According to the formula

$$\lambda = \frac{h \cdot c}{\Delta E} \quad (11)$$

this energy difference corresponds to the band appearing at 3093 Å. On comparing this result with the experimental value (about 3120 Å [2]) it can be seen that both the direction and the degree of the shift are in good agreement. Similarly, the other bands of benzalaniline can be computed on taking the transitions $E_2^B \rightarrow E_3^B$, $E_3^A \rightarrow E_4^A$ and $E_2^B \rightarrow E_4^A$ into account. Table I shows a comparison of the results and the observed values.

Table I:

Wavelengths (in m μ)	
Observed	Calculated
312	309
262	271
200	211
	192

2. The electronic states of azobenzene calculated by means of the electron gas method with finite potential steps

In a previous paper [1] the application of the electron gas method in one-dimensional square well potential with finite potential steps for the calculation of electronic states of stilbene was presented. It was assumed that the π -electrons of the molecule form nonbranched electron gas. Owing to the isolation of the ethylene bond parts of various potentials could be distinguished in the molecule. Within the molecule the parts of various potentials were considered to be constant by sections. In the case of azobenzene the procedure is similar. Presumably nonbranched electron gas expands along the bonds traced thickly in Fig. 1. Further a potential step is supposed at the place of the $-\text{N}=\text{N}-$ bond. The following considerations are used to estimate the dimensions of this "potential step". Owing to the more expressive isolation of the $-\text{N}=\text{N}-$ bond the height of the "potential step" may be assumed to be greater for azobenzene than for stilbene. This is well illustrated by the bond distances

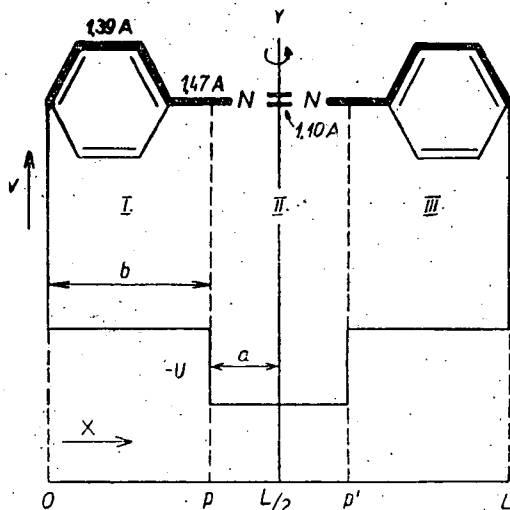


Fig. 1

(Fig. 1). To estimate the height of the "potential step", however, the ionisation potentials of the benzene and the $\text{HN}=\text{NH}$ molecule should be used. When a picked out electron leaves the π -electron system of benzene to enter into the electron system of the $-\text{N}=\text{N}-$ bond it must do a work. This work may be replaced by the difference between the ionisation potentials of benzene and diimide molecules. The ionisation potential of benzene is 9,19 eV [3], but that of $\text{HN}=\text{NH}$ molecule is unknown. Therefore, the energy invested in the process $\text{N}(s^2p^3, V_3) \rightarrow \text{N}^+(s^2p^2, V_2) + e^-$ (13,81 eV [4]), must be considered. Consequently we obtain

$$U = 7,3966 \cdot 10^{-12} \text{ erg} \quad (12)$$

for the height of the "potential step". Owing to the incomplete data concerning the ionisation potentials only the treatment with "one potential step" can be carried out. The starting points of the "potential step" are assumed to be at the half-width of the bond distances lying between the benzene and the diimide group, so we have $a = 1,285 \text{ \AA}$. The length of the linear box mentioned above is $L = 12,38 \text{ \AA}$. This was obtained by adding the bond distances from the first to the tenth C atom. Each carbon atom uses three of its valency electrons and three of its sp_x, p_y hybrid orbitals and each nitrogen atom uses two of its valency electrons and the p_x, p_y orbitals to form σ -bonds among the neighbouring atoms. The isolated pairs of electrons of the N atoms stay in the most stable s orbital neither taking part in the binding nor in the formation of the electron gas. The fourth valency electron and the p_z orbital of each carbon atom, as well as the remaining electron and the least stable p_z orbital of both N atoms form electron gas. Hence the atoms considered in our calculations contribute with altogether ten π -electrons to the formation of the electron gas.

In consequence of the symmetry of the molecule (C_2) we have two eigenfunction systems independent from each other, *i. e.*, a symmetrical and an antisymmetrical one. The symmetrical wave functions are

$$\psi_1^A = A \sin [\alpha x] \quad (13a)$$

$$\psi_{II}^A = B \cos \left[\beta \left(x - \frac{L}{2} \right) \right] \quad (13b)$$

$$\psi_{III}^A = A \sin [\alpha(L-x)] \quad (13c)$$

and the antisymmetrical ones

$$\psi_1^B = A \sin [\alpha x] \quad (14a)$$

$$\psi_{II}^B = B \sin \left[\beta \left(x - \frac{L}{2} \right) \right] \quad (14b)$$

$$\psi_{III}^B = -A \sin [\alpha(L-x)] \quad (14c)$$

where

$$\alpha = \frac{\sqrt{2mE}}{\hbar}, \quad \beta = \frac{\sqrt{2m(E+U)}}{\hbar}$$

By the use of the conditions

$$\begin{aligned} \psi_1(P) &= \psi_{II}(P), & \psi'_1(P) &= \psi'_{II}(P) \\ \psi_{II}(P') &= \psi_{III}(P'), & \psi'_{II}(P') &= \psi'_{III}(P') \end{aligned} \quad (15)$$

and

$$\psi_1(x=0) = \psi_{III}(x=L) = 0 \quad (16)$$

we obtain the relations:
for the symmetrical case

$$\frac{\alpha}{\operatorname{tg}[\alpha b]} = \beta \cdot \operatorname{tg}[\beta a] \quad (17)$$

and for the antisymmetrical case

$$\frac{\alpha}{\operatorname{tg}[\alpha b]} = -\frac{\beta}{\operatorname{tg}[\beta a]} \quad (18)$$

where $b = \frac{L}{2} - a$.

By means of these relations, using the values of the quantities L , U and a , the eigenvalues can be calculated in a graphic-numerical way. On the levels defined by the energy values obtained as the result of the computation, according to the PAULI exclusion principle, not more than two of the electrons can coexist in the same quantum state. Thus the five lowest levels will be filled up by the ten π -electrons considered in the normal state. The wavelengths of the absorption maxima belonging to the transitions between certain levels can be computed by the expression (11). The disagreement between the calculated and observed [5] values is significant, this may be due to the unfortunate choice of the used parameters — though this seemed to be rather plausible — and besides to the approximate nature of our calculation. Better agreement can be obtained by varying the empiric parameters U and a . The results are listed in Table II.

Table II.

Wavelengths (in m μ)				
Observed	Calculated			
	$U = 7,3966 \cdot 10^{-12}$ erg			$U = 15,0 \cdot 10^{-12}$ erg
	$a = 1,285$ A	$a = 0,69$ A	$a = 2,02$ A	$a = 0,63$ A
450	530	420	465	415
330	260	265	245	265
~200	210	215	230	210

Similarly the absorption maxima of the derivatives of azobenzene may be computed where the effect of the groups in ortho-, meta-, para-positions could be considered as a factor, either lengthening or shortening the length of the linear box. On the other hand, e.g., the benzalazine's spectrum could be calculated by the electron gas method with "two potential steps".

3. The light absorption of phenanthrene

As a third example let us consider the case of phenanthrene derived from stilbene by setting up a connection between the third and the eighth C atoms (branching points) of the stilbene (Fig. 2). Presumably the homogeneous π -electron system will develop simultaneously with the formation of the aromatic system. The bond distances in the molecule will be nearly identical on every side and the isolation observed in the case of stilbene will cease to exist. In this case zero potential is assumed to be everywhere within the molecule, thus the absorption maxima of phenanthrene can be calculated, by the simple branched electron gas model [6]. In accordance with the above — for the sake of simplicity — let us only take the part of the molecule resembling stilbene into consideration (traced thickly in Fig. 2).

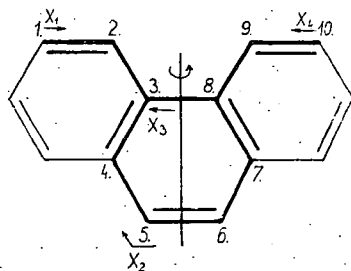


Fig. 2

in which $\alpha = \sqrt{zE}$.

In consequence of the symmetry of the molecule (C_2) the solutions may be symmetrical and antisymmetrical. Thus the energy values are computable by the following relations [6]:

$$\text{ctg} \left[\alpha \cdot \frac{4l}{2} \right] - \text{tg} \left[\alpha \cdot \frac{5l}{2} \right] - \text{tg} \left[\alpha \cdot \frac{l}{2} \right] = 0 \quad (19)$$

and

$$\text{ctg} \left[\alpha \cdot \frac{4l}{2} \right] + \text{ctg} \left[\alpha \cdot \frac{5l}{2} \right] + \text{ctg} \left[\alpha \cdot \frac{l}{2} \right] = 0 \quad (20)$$

Table III.

Wavelengths (in m μ)			
Observed			Calculated
Phenanthrene	Phenanthridine	Diphenazon	
330	340	370	375
293	328	350	325
280	300	310	—
275	270	—	—
252	250	250	250
220	~ 200	~ 200	220

The wavelengths of the allowed transitions are listed in Table III. They are compared with the experimental values [7]. Satisfactory agreement can be seen.

Similarly as in the case of phenanthrene the phenanthridine may be derived from the benzaniline and the diphenazon from the azobenzene. The

correctness of our conception concerning the aromatic systems, viz., that owing to the absence of the isolation potential steps should not be assumed, is verified by the fact that the positions of the bands (apart from the vibrational structure) of phenanthrene, phenanthridine [8] and diphenazon [9] are not far from one another. The insignificant shift (towards the longer wavelengths) of the bands of phenanthridine and diphenazon — as compared to that of phenanthrene — might be calculated with a simplified perturbation calculation as shown in the case of benzalaniline.

Appendix

According to (1) $E_{\text{Benz.}} = E_{\text{Stilb.}} + \varepsilon$ where the perturbation energy ε is given by the integral

$$\varepsilon = -\Delta U \int \psi^2 dx.$$

If $a < \frac{2L}{n}$ and $\psi_{\text{Stilb.}}^2(x) = f(x)$ then the above integral — apart from the factor $-\Delta U$ — has the form

$$\int_{\alpha}^{\beta} f(x) dx.$$

In our case the assumption $a < \frac{2L}{n}$ is realized for $0,665 < \frac{2 \cdot 12,57}{5}$ and $0,665 < \frac{2 \cdot 12,57}{6}$, respectively. Further considering the form of $\psi^2(x)$ which occurs in (3), we obtain that $f(x)$ changes slowly in the range (α, β) . Accordingly the First Mean Value Theorem can be applied in the form

$$\int_{\alpha}^{\beta} f(x) dx \approx (\beta - \alpha) \cdot f\left(\alpha + \frac{\beta - \alpha}{2}\right)$$

where

$$\beta - \alpha = \frac{L}{2} - \frac{L}{2} + 2a = 2a$$

and

$$\alpha + \frac{\beta - \alpha}{2} = \frac{L}{2} - 2a + \frac{2a}{2} = \frac{L}{2} - a$$

so we have

$$\int_{b-a}^{\frac{L}{2}} \psi_{\text{Stilb.}}^2(x) dx \approx 2a \cdot \psi_{\text{Stilb.}}^2(b).$$

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