

On the Absorption of Light of Isomeric Derivatives of Benzaniline

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1. Introduction.

In an earlier communication (1) we have shown that the benzene rings A and B (fig. 1, form. I) which are bound to the C and N atom of the azomethine group, respectively behave differently. So the extinction curves of the isomeric pairs which are substituted in the same places relating to the azomethine groups show great differences. The task of this work is to approach to this problem.

Concerning the experimental apparatus and the method we refer to earlier papers (2). The compounds were prepared by procedures described in the literature by Pauncz (3). The compounds were purified thoroughly and their purity was controlled by determining the melting point. The solvent was ethanol the purity of which was controlled spectrographically (4).

2. General Remarks.

By benzaniline (1) in the ground state prevails the Ia structure (fig. 1) on account of the greatest number of double bonds. So the azomethine group can only participate in the excited state in the mesomerism of the phenyl nucleus. The resonance and superposition of many structures (which for the sake of brevity are not formulated) diminish the energy of excitation. Therefore its extinction curve (fig. 1, curv. 1, = 1/1) is shifted compared with that of benzene (1/1a, shifted with $\log \epsilon = 1,0$ upwards) toward longer wave lengths and the extinction increases strongly.

When the structure Ia prevails the absorption of light consists in the excitation of the π -electrons of the benzene ring and that of the azomethine group (1, 5, 6, 7). This assertion is only true as far as we can give the electron arrangement in the benzaniline by electromeric structures. When π -electrons of the benzene ring and of the azomethine group form molecular orbitals which seems to be probable from the form of the extinction curves then this explanation is not satisfactory (5). The question was not to answer by curve analysis because of the overlapping of the absorption regions of the phenyl nucleus and of the azomethine group (5). To solve this problem absorption measurements are carried on by some benzaniline derivatives.

By the derivatives of the benzaniline the trans form is more advantageous from energetic reasons. This seems to be justified by the below discussed mesomeric cases, the hydrogen-bond formation (cf. fig. 1, IIa) by the o-hydroxy derivatives (which cannot develop in the case of cis form IIa), verified by the infrared absorption (8), by the Raman spectra (9) and by the measurement of electric moments (13, 14).

The two benzene rings A and B which are connected directly by the mesomeric capable azomethine group influence one another in dif-

ferent manners (electromerically or inductively) depending on their substituents. These effects are not independent from each other and they are not additive but they mix in a complicated way. Generally the electromeric and the inductive effect operate one against the other. The π -electrons of the A and B benzene rings can enter into mesomerism with the π -electrons of the substituent in different manners depending on the mesomerism ability of the substituent (1).

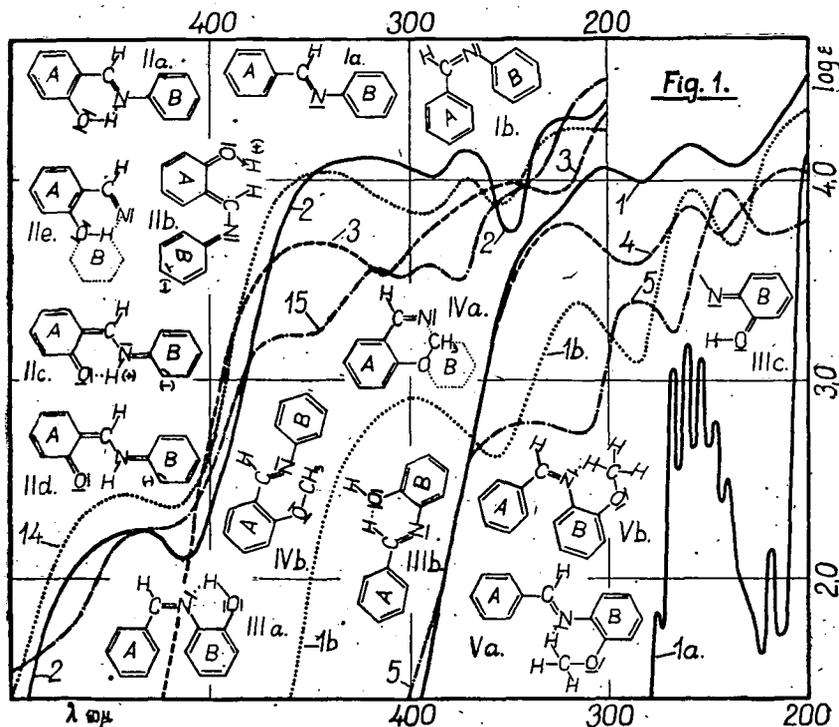


Fig. 1. Curves. 1a: benzene, shifted with $\log \epsilon = 10$ upwards. 1b: 2-hydroxybenzal-ethylamine, shifted with $\log \epsilon = 0,4$ downwards. 1: benzalaniline. 2: 2-hydrobenzal-aniline. 3: benzal-2-hydroxyaniline. 4: 2-methoxybenzal-aniline. 5: benzal-2-methoxyaniline. 14: 2-hydroxybenzal-2-hydroxyaniline. 15: 3-hydroxybenzal-2-hydroxyaniline.

From the three not sharp bands of benzalaniline (1/1) the first should belong to the azomethine group, the second and the third to the phenyl nucleus (1, 5). To prove this assertion we can mention that by azobenzene and by stilbene the first band belongs to the azo- and to the ethylene group, respectively (10, 11). The above mentioned three bands are present in the spectra of all derivatives of benzalaniline. By the derivatives containing an HO-group in the ortho or para position, appears further, fourth band at longer waves (1). The position and the intensity of the bands by the singular derivatives varies strongly depending on the energy of excitation and the probability of transition. This influences to a high degree the shape of the extinction curve. When the π -electrons of the A or of the B benzene ring are influenced by the inductive effect differently or if the π -electrons of these benzene rings are in other mesomeric structures in consequence of the electromeric effect of the substituent, then we receive the shifting or the

splitting of the bands. Therefore the number of bands changes by the investigated derivatives of benzaniline.

Because of the strong solvent effect, the following differences of the extinctions curves are only valid in ethanol solvent. In an other solvent the situation is different and this will be the subject of a later paper.

We give a survey of the mesomerism of hydroxy derivatives of benzaniline. By the meta derivatives the hydroxy group is in mesomerism only with the substituted A and B ring, respectively (cf. fig. 2, form. VIa to VI d). By the ortho and para derivatives, the mesomerism starting from the substituted A and B rings, respectively spreads through the whole molecule (cf. fig. 1, form. IIa-II d, resp. IIIc, and fig. II, VIIIa-VIIIc, resp. IXa).

3. Discussion of the Experimental Data.

By 2-hydroxybenzaniline (II) the HO-group in the ortho position increases the possible mesomeric structures in the ground (1/IIa-d) and in the excited state. In the ground state both the quinoidal (1/IIb-c) and the benzenoidal (1/IIa) structures are possible moreover the hydrogen bond (1/IIa) which can hinder the development of other mesomeric structures because of mesomerism short closing (1). The resonance of the structures diminishes the energy of excitation and therefore the extinction curve (1/2) is shifted toward longer wave lengths, compared with that of benzaniline (1/1). The participation of ionic structures already in the ground state causes the transfer of electronic charge by the excitation whereby the extinction increases (1, 15). The appearance of the first band shows that the quinoidal mesomeric structure (1/IIb-d) participates in the ground state. This question will be discussed more detailed in a later paper in connection with the solvent effect.

As we pointed out the hydrogen bond (1/IIa) can only develop in the case of trans form. It is omitted by the cis form (1/IIe). By IIe the HO-group and the B-ring, respectively is driven out from the plain of the molecule. In the first case the mesomerism of the HO-group is repressed. So we must regain the extinction curve of the benzaniline (1/1). In the second case we expect the extinction curve of the 2-hydroxybenzalethylamine (1/1b). To both cases contradicts the extinction curve of the 2-hydroxybenzaniline (1/2), thus this compound must be in the trans form. As we shall see from the followings the steric relation cannot be surely decided alone from the extinction curve. Comparing the extinction curves of the investigated derivatives of benzaniline with those of cis and trans stilbene (II) we may assume that by the derivatives of benzaniline the trans form is prevailing.

In the ground state of benzal-2-hydroxyaniline (III) the mesomeric structures (1/IIIa-b) are similar to those of II (1/IIa-d) with the difference that the mesomerism starts from the B-ring. But since the first band is not present (1/3) the quinoidal structure participates in the ground state only scarcely. This should mean that the quinone-imine structure (1/IIIc) owing to its greater energy is much less favourable than the quinone-methine (1/IIId) structure. It is remarkable that by III compared to II, all the mesomeric structures are possible in the cis form (1/IIIa) too. By IIIa we can imagine a hydrogen bond with a six-membered ring.

By 2-methoxybenzaniline (IV) the methoxy group interrupts the

H-bonds in both cases (1/IVa-b). Neither in the in the cis (1/IVa) nor in the trans (1/IVb) form can the methoxy group be placed in the plain of the molecule, whereby its mesomerism will be tied up from steric reasons. So the mesomerism of IV will be analogous to that of I and in accordance with this the extinction curve of both compounds will be similar (1/4 and 1/1, resp.). The little differences are caused by the inductive effect of the methoxy group. The steric hindrance is underlined by the fact that by anisol the etherification does not hinder the mesomerism of the oxygen atom (12).

By benzal-2-methoxyaniline (V) the mesomerism is similar to that of IV. There is possible a H-bond with a six-membered ring both in the cis (2/Va) and in the trans (2/Vb) form, and this may be the cause by mesomerism short closing of the different shape of the extinction curve of V (1/5) and of IV (1/4), respectively.

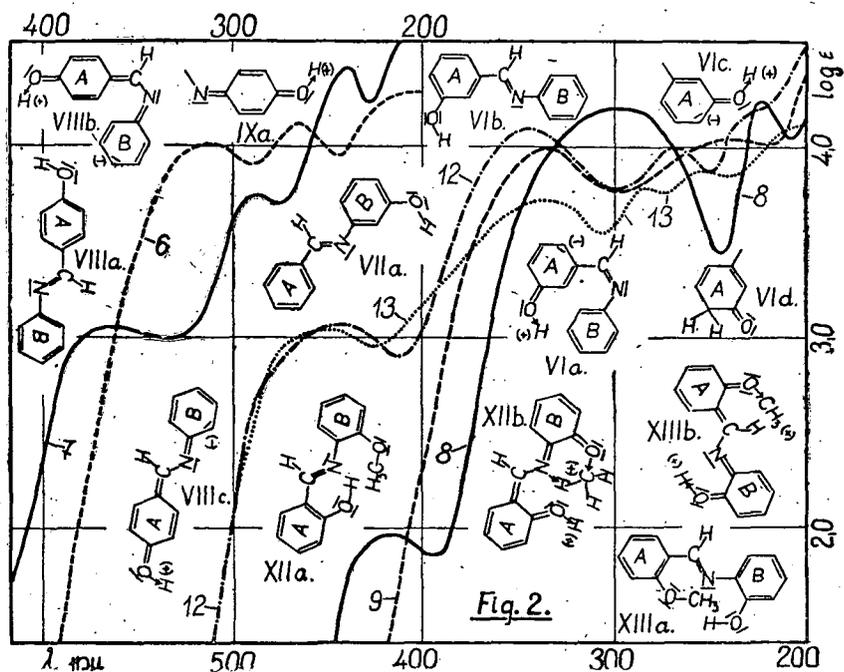


Fig. 2. Curves: 6: 3-hydroxybenzal-aniline. 7: benzal-3-hydroxyaniline. 8: 4-hydroxybenzal-aniline. 9: benzal-4-hydroxyaniline. 12: 2-hydroxybenzal-2-methoxyaniline. 13: 2-methoxybenzal-2-hydroxyaniline.

In the ground state of 3-hydroxybenzal-aniline (VI) the VIa-b mesomeric structures are possible both in the cis (2/VIa) and in the trans (2/VIb) form. Because of the meta position of the HO-group, the quinoidal structure cannot develop by the A-ring in the ground state (2/VIa and VIc). Since its extinction curve (2/6) is very similar to that of I (1/1), the VIb structure can hardly participate in the ground state. The little differences are due to the inductive effect of the HO-group in the meta position.

By benzal-3-hydroxyaniline (VII) the mesomerism is analogous to that of VI (2/VIa-d) with the difference that here the B-ring is in the mesomerism (2/VIIa). We cannot explain satisfactorily the fact that the

whole extinction curve is shifted toward the longer waves and the intensity of the first two bands diminishes (2/7):

In the ground state of 4-hydroxybenzalaniline (VIII) both in the cis (2/VIIIb) and in the trans (2/VIIIa) form are quinoidal and benzenoidal structures (2/VIIIa-VIIIc) which is shown by the appearance of the first band (2/8). The stronger appearance by II (1/2) would mean, that the H-bond influences the intensity of this band in some way.

In the ground state of benzal-4-hydroxyaniline (IX) the same mesomeric structures are possible both in the cis and in the trans form as by VIII, with the difference that here the mesomerism starts from the B-ring (2/IXa). The missing of the first band (2/9) shows that the quinoidal form hardly participate in the ground state. This should mean, as we mentioned by III, that the quinone-methine structure because of its lower energy is more probable than the quinon-imine structure.

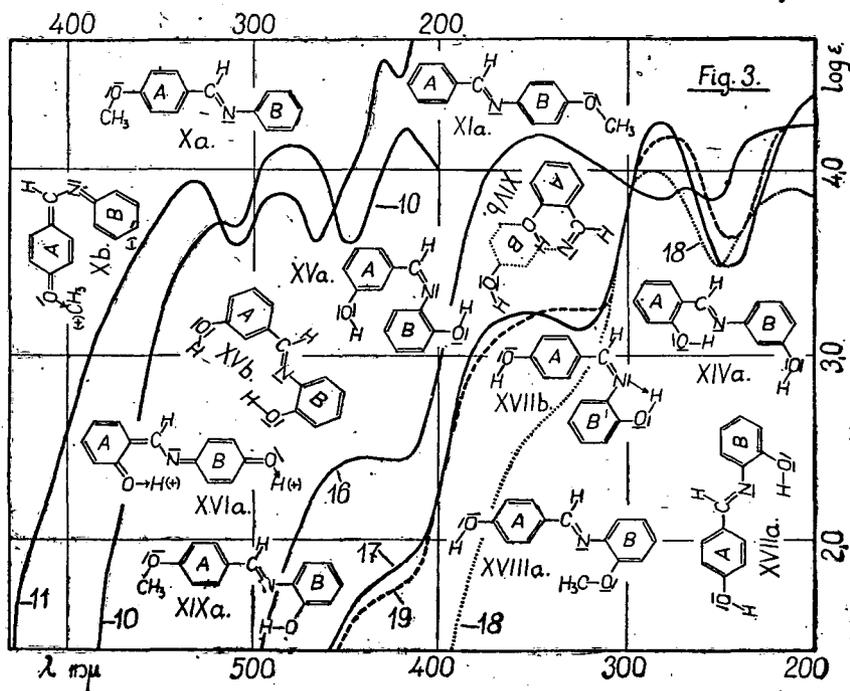


Fig. 3. Curves: 10: 4-methoxybenzalaniline. 11: benzal-4-methoxyaniline. 16: 2-hydroxybenzal-4-methoxyaniline. 17: 4-methoxybenzal-2-hydroxyaniline. 18: 4-hydroxybenzal-2-methoxyaniline. 19: 2-methoxybenzal-4-hydroxyaniline.

By 4-methoxybenzalaniline (X) the methoxy group neither by the cis (3/Xb), nor by the trans (3/Xa) form hinders the mesomerism (cf. 2/VIIIa-c). The absence of the first band (3/10) and the similar shape of the extinction curve to that of I (1/1) shows that the etherification causes much greater obstacle to the mesomerism by the derivatives of benzal-aniline than by the phenols (12). The structure differences between the extinction curves of X (3/10) and I (1/1) are due to the inductive effect of the methoxy group.

By benzal-4-methoxyaniline (XI) the mesomerism is the same as by X (cf. 3/Xa-b) with the difference that here the B-ring is in the me-

somerism (3/XIa). So we cannot satisfactorily explain the shifting of the extinction curve (3/11) toward the longer wave lengths.

By 2-hydroxybenzal-2-methoxyaniline (XII) the mesomerism is similar to that of 2-hydroxybenzal-2-hydroxyaniline (1) and of II (cf. 1/IIa-d) apart from the steric hindrance of the methoxy group (2/XIIa). In the case of trans form, it is diminished cf. XIIb. In the case of cis form cf. 1/IIb. So we could expect an extinction curve (2/12) of a similar structure to that of II (1/2), what the shape of the two curves proves. The structure differences are due to the fact that the quinoidal structure XIIb is in some way more advantageous.

By 2-methoxybenzal-2-hydroxyaniline (XIII) the mesomerism is similar to that of 2-hydroxybenzal-2-hydroxyaniline (1) and of III (cf. 1/IIIa-c) apart from the steric hindrance of the methoxy group both in the case of cis and of trans (2/XIIIa-b) form. So we should expect to obtain by XIII (2/13) and by III (1/3) curves of a similar shape. The appearance of the first band by XIII (2/13) shows that the quinoidal structure is in some way more advantageous (2/XIIIb). The extinction curves of both compounds are very similar to that of 2-hydroxybenzal-2-hydroxyaniline (1). The difference is due to the etherification of the one hydroxy group.

By the 2-hydroxybenzal-3-hydroxyaniline (XIV) the mesomerism of the HO-group in 2-position dominates the mesomerism of the ground state (cf. 1/IIa-e), to what refers the similarity of its curve (1/14) to that of II (1/2). The HO-group in the meta position has inductive effect and hinders the development of the quinoidal structures, what is to prove by drawing diagrams. In the case of cis (3/XIVb) the steric hindrance of the mesomerism is similar as by II (cf. 1/IIb and 3/XIVb). By the trans form (3/XIVa) it is not hindering.

By 3-hydroxybenzal-2-hydroxyaniline (XV) the steric hindrance falls out both in the cis (3/XVa) as in the trans (3/XVb) form. The mesomerism is a counterpart of XIV. The increase of the number of the bands (1/15) refers to the similar mesomerism of the HO-groups in the 2' and in 3 position, respectively, and to that, that the structures of different energy have separate excitation.

By 2-hydroxybenzal-4-hydroxyaniline (XVI) the mesomerism is hindered in the case of cis form just as by II (cf. 1/IIb). By the trans form this hindrance falls out (3/XVIa). The mesomerism is more complicated than by the former compounds (1). In the ground state the structures (cf. 1/IIa-d and 2/IXa) beginning from the ring A and B, respectively and moreover 3/XVIa) are possible. So we should expect an extinction curve of a similar shape to II (1/2) and really we obtain such one (3/16).

By the 4-hydroxybenzal-2-hydroxyaniline (XVII) the steric hindrance of the HO-group falls out both by the cis (3/XVIIb) and by the trans (3/XVIIa) form. The mesomerism is a counterpart of XVI. The different form of the extinction curve (3/17) compared with that of VIII (2/8) shows that the two HO-groups participate in the mesomerism approximately in the same manner. Comparing the extinction curves of XVI (3/16) and XVII (3/17) we see that the intensity of the first two bands is strongly different.

By the 4-hydroxybenzal-2-methoxyaniline (XVIII) the methoxy group in the 2-position shows the same steric hindrance (3/XVIIIa) as by V (cf. 1/va-b). Apart from this the mesomerism is similar to that of VIII (cf. 2/VIIa-c). So we expect a similar curve. The great structure differen-

ces (2/8 and 3/19, resp.) among them the missing of the first band is due perhaps to the short closing of mesomerism due to the H-bond. (cf. 1/Va-b) or the steric hindrance of the mesomerism.

By the 4-methoxybenzal-2-hydroxyaniline (XIX) 3/XIXa) the steric hindrance falls out both in the cis (cf. 1/IIIa) and in the trans (cf. 1/IIIb) form. The mesomerism is similar to that of III (cf. 1/IIIa-c) or of XVII (cf. 3/XVIIa-c). The great structure differences (1/3) are due to that, that by XIX (3/19) both group participate in the mesomerism as by XVII (3/17).

Summary.

The appreciation of the possible structures of the ground and of the excited state allows generally the explaining of the structure differences by the extinction curves of the derivatives of benzalániline.

The phenyl nucleus bound to the C and to the N atom of the azomethine group respectively behaves differently with regard to its mesomerism.

By the 2 and 4 hydroxy derivatives appears a first band on the limit of the visible. Since this band is missing by the 2' and 4' derivatives, the quinone-imine structure is much less represented in the ground state than the quinone-methine structure.

According to the extinction curves, the investigated benzalániline derivatives are present in the trans form.

The free rotation of the radicals is generally restricted, their probable situation is given in the figures.

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