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Investigations on the interaction of several chromophores in the same molecule.

By Á. Kiss, G. FODOR and A. LÓZSA.

In an earlier communication (1) the ultraviolet absorption spectra of α -aryl- β -N-acylamino-propanols: $\text{Ar-CHOH-CH}(\text{CH}_3)\text{-NH-CO-R}$ were measured and the problem of the additivity of light absorption for several chromophores investigated. The group $\text{Ar-CHOH-CH}(\text{CH}_3)\text{-NH-CO-}$ was here regarded as one chromophore, and R containing occasionally an aromatic radical also, as another. In case of $\text{R} = \text{homoaryl}$, the extinction curves calculated by summation of the extinction coefficients for the single chromophores are in good agreement with experimental data; if $\text{R} = \text{aryl}$ was present, a discrepancy could be observed. Another line of approach is to regard the molecule of the same type as to be composed of the following chromophores: $\text{Ar-CHOH-CH}(\text{CH}_3)$ and $\text{H}_2\text{N-CO-R}$. The considerations for the interaction of the chromophores were made, with regard to the resonance theory, especially, considering mesomeric and inductive effects due to the chromophores.

The mechanism of the absorption of light by benzene derivatives.

The excitation of the electrons of benzene molecule gives rise to two absorption bands (Fig. 1. curve 1), these are present, although deformed and shifted, in the spectra of all benzene derivatives (4). Some benzene derivatives show a third band also. The substituents of the benzene molecule have an inductive and electromeric effect upon the absorption spectrum of benzene. These effects are considered as a polarisation of the binding electrons of benzene (5), resp. as a participation of the π -electrons of the conjugated substituent in the mesomeric system of benzene (6).

The electromeric effect upon the absorption of light for benzene is larger than the polar inductive effect caused by the substituents. These two effects are not separable, a rather complicated superposition of both takes place. The inductive effect influences the degree of participation of the single structures in the ground state of the molecule, resulting indirectly in an electromeric effect also. Reciprocally, the electromeric effect is connected with a varying inductive effect. Moreover, if the substituent did not contribute to the mesomeric system in the ground state, its influence could take place even then in the excited state.

Discussion.

In the molecule of *phenylacetic acid* (II) the distribution of π -electrons in the benzene ring is inductively influenced by the carboxymethyl group. The mesomeric systems for the benzene nucleus and for the carboxyl group (for the sake of simplicity the resonating forms are not formulated) remain unaffected, being isolated by a methylene group. The inductive effect is estimated by comparison of absorption curve for II (Fig. 1. curve 2) with that for benzene (Fig. 1. curve 1). The band contained in II corresponds to the main band for benzene. Where structure IIb is present, the extension of the π -electron system

that for II (Fig. 1, curve) toward longer wave lengths and increased the extinction coefficient.

In the structure of *veratric acid* (VII) the methoxyl groups (cf. IIIb—III d) and the carboxyl group both participate in the aromatic nucleus. A larger increase of the extinction and a simultaneous shift toward the visible of the curve for VII (Fig. 1, curve 7), compared with that for VI (Fig. 1, curve 6) are both attributed to the resonance among the mesomeric hybrids and to the extinction for the system of π -electrons. Comparing the extinction curve for VII (Fig. 1, curve 7) with that for III (Fig. 1, curve 3) the inductive, resp. the electromeric effect of the carboxyl group could be estimated.

The possible mesomeric forms for *piperonylic acid* (VIII) are similar to those for VII (VIIIa—VIII d). The increase of the first band is probably due to a strain effected by the entrance of a methylenedioxy group in the molecule of benzoic acid (Fig. 1, curve 8).

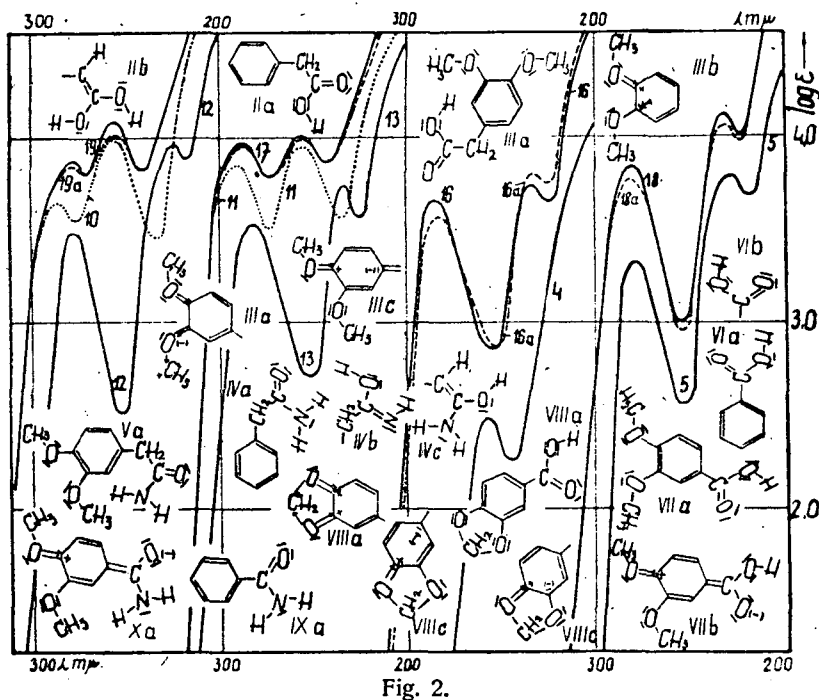


Fig. 2.

The structure of *benzamide* (IX) makes a tautomerism possible among carbonamide and imidohydrine forms (cf. IVa—IVb), both forms being energetically probable (Fig. 1, curve 9). Measurements of extinction, recorded by Hantzsch (7) show the imidohydrine form to be dominant in the ground state, which are at variance with our data.

The mesomeric structures for *veratric acid* (X) are, without regard to the tautomerism between imidohydrine and carbonamide forms (cf. IVa—IVb), the same as supposed for VII (cf. IIIb—III d and Xa). Consequently, the curves for the two compounds are similar (Fig. 2, curve 10 and Fig. 1, curve 7), in good accordance with our considerations made for IX.

The formation of a five-membered hetero ring in *piperonyl amide* (XI) has the same effects (strain and tautomerism and mesomerism) as in VIII.

The spectrum for XI (Fig. 2, curve 11) and that for VIII (Fig. 1, curve 8) show a close resemblance.

In the case of *1-(3', 4'-dimethoxyphenyl)-propanol-1* (XII) the mesomeric effect, suggested by the methoxyl groups is of importance in the ground state (cf. IIIb—IIIId). The similarity between the curves for XII (Fig. 2, curve 12) and for III (Fig. 1, curve 3) indicates a very feeble inductive effect of the alcoholic hydroxyl group upon the mesomeric system of the benzene ring.

The methylenedioxy group participates in the mesomeric system of the aromatic ring, in case of *1-(3',4'-methylenedioxyphenyl)-propanol-1* (XIII) (cf. VIIIb—VIIIId). The discrepancy between the curves for XII (Fig. 2, curve 12) and for XIII (Fig. 2, curve 13) is due to the strain effected by the hetero ring in the latter compound. Comparison of the spectra for XII and XIII (Fig. 2, curves 12 and 13) with those for VII (Fig. 1, curve 7) and for VIII (Fig. 1, curve 8), resp. with those for X and XI (Fig. 2, curve 10 and 11) indicates the methylene group having an enhanced mesomeric effect in case of the benzene nucleus with an adjacent carboxyl group, resp. carbonamido group. This fact could be attributed to the mesomeric tendency of the latter groups.

Introduction of an acylamino group into the β -carbon atom of the propanol side-chain, for instance at α -*(3,4-dimethoxyphenyl)- β -acetamino-propanol* (XIV) is without any influence upon the spectrum (Fig. 1, curve 14) compared with that for XII (Fig. 2, curve 12), the acylamino group behaves evidently as an isolated chromophore. The tautomerism among carbonamido and imidohydrine forms (XVa—XVb) have not influence upon the mesomeric system of the methoxyl groups (cf. IIIb—IIIId). This assumption is supported by the close resemblance of the curves for XII (Fig. 2, curve 12) and XIV (Fig. 1, curve 14).

The spectrum for α -*(3,4-methylenedioxyphenyl)- β -N-acetamino-propanol* (XV) indicates the presence of the mesomeric system of the five membered hetero ring (VIIIb—VIIIId), the strain of which is manifested also by the difference between the curves for XIV from that for XV (Fig. 1, curve 14, resp. 15).

The extinction curve for α -*(3,4-methylenedioxyphenyl)- β -N-phenacetamino-propanol* (XVI) is composed, in case of the mesomeric forms (XVIa—XVIc), from the individual extinction coefficient of three independent chromophores α , β and γ . In case of XVIc the chromophores β and γ possess a common system of π -electrons. Chromophore γ has in both cases less π -electrons as chromophore α ; the former increases the extinction values only at shorter wave lengths as the latter. The extinction caused by the chromophore β being negligible, the absorption of light is made up of the extinction at α and of that of γ .

In confirming this assumption, the extinction coefficients for the compound were calculated from those of XII and II, using the formula: $E = e_1 + e_2$ in which e_1 and e_2 are the extinctions for XIII and for II; E is the extinction for XVI. The calculated curve (Fig 2, curve 16a) is in good agreement with the curve found for XVI (Fig. 2, curve 16), showing a strong additivity of the extinctions of the chromophores.

α -*(3,4-methylenedioxy-phenyl)- β -N-piperonylamino-propanol* (XVII) contains independently the chromophores for XIII and for XI, α -*(3,4-methylenedioxy-phenyl)- β -N-homoveratroylamino-propanol* (XVIII) those

for XII and for V; α -(3,4-dimethoxy-phenyl)- β -N-veratroylamino-propanol (XIX) the chromophores for XII and V. The very good agreement of the experimental curves (Fig. 2, curves 17, 18 and 19) with those calculated (Fig. 2, curves 17a, 18a and 19a) from the extinction coefficients for compounds XIII and XI, resp. XII and V, resp. XIII and V, proved that the mutual inductive effect between the chromophores of XVII, XVIII and XIX is small. The mesomeric structures of the radicals R_1 and R_2 were already discussed. These experimental results give evidence for the additivity of the extinctions of the chromophores even in case of organic molecules of more complicated structure, attention should be called, however, to mesomeric and inductive effects.

Experimental.

The measurements of absorption spectra were carried out by A. Lózsa (2) during his dissertation. The method used was the same as reported in recent papers (3). The compounds employed were in part commercial preparations of analytical purity, in part they were prepared by Lózsa, by procedures described in the literature. All compounds were recrystallised, resp. distilled to constant melting point, resp. boiling point. All determinations were made using ethanol, the purity of which was controlled spectrographically.

Summary.

The absorption of light for the benzene nucleus is influenced inductively by the adjacent non-absorbing groups only to a small extent. In this case, the structure of the compound cannot be determined from its absorption spectrum.

The selective absorption of chromophoric groups is preserved, if they are isolated from the benzene nucleus by a group, unable to participate in the mesomeric system of the chromophores.

If the benzene nucleus is conjugated with chromophoric groups which are able to form a mesomeric system, both lose their selective absorption depending of the degree of their mesomeric tendency. It is not possible to find simple correlation of structure with absorption spectra in the latter case. The mesomeric effect of the substituents, generally, surpasses the intensity of their inductive effect.

A theoretical discussion of the probability of protomeric and electromeric structures of the investigated compounds as well in the ground state as in the excited state was made. An explanation of the absorption curves was, therefore, possible. Moreover, the effect of the substituents on the absorption of benzene derivatives could be predicted.

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Über die Mesomerie der Sulfogruppe.

(Vorläufige Mitteilung.)

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Einleitung.

Die physikalischen und chemischen Eigenschaften der Benzolsulfoderivate möchten die Forscher allgemein derweise erklären, dass die Sulfogruppe sich nicht in der Mesomerie des Benzolringes beteiligt. Sie unterbricht das System der konjugierten Doppelbindungen, so kann sich kein einheitliches System von π -Elektronen ausbilden. Die mit ihr verbundenen zwei Molekülhälften beeinflussen sich gegenseitig nur schwach induktiv (1a, 1b). Dieser Frage näher zu kommen wurden die Extinktionskurven einiger Benzolsulfosäure- und Diphenylsulfon-Derivate ausgemessen.

Die Derivate der Benzolsulfosäure.

Die übliche Struktur (1a) der Benzolsulfosäure (1) mit 12 äusseren Elektronen beim Schwefelatom ist möglich, da das Schwefelatom auch in der Verbindung SF_6 von 12 äusseren Elektronen umgeben ist, weiterhin ist der Schwefel kein Element der ersten Periode, wo die Elemente nur 8 äussere Elektronen haben können. Viel wichtiger ist, dass die SO_2 -Gruppe sich charakteristisch verschieden verhält, als die $C=O$ oder $C=C$ Gruppe. Es ist bis jetzt keine organische Verbindung bekannt, deren Eigenschaften für die Existenz von wahren Doppelbindungen in der SO_2 -Gruppe sprechen (1a, 2). Dies bestätigt die starke Durchlässigkeit von Dimethylsulfon, welches merklich unterhalb $180 m\mu$ absorbiert (3).

Bei der Grenzform 1b hat das Schwefelatom weder Doppelbindungen, noch einsame Elektronen. Beherrscht diese Grenzform den Grundzustand von I, so besteht die Lichtabsorption in der Anregung der in der benzoidalen Grenzstruktur befindlichen π -Elektronen des Benzolringes. Die grosse Ähnlichkeit der Extinktionskurve von I (Kurve 2) zu dieser des Benzols (Kurve 1 mit $\log \epsilon = 1$ nach oben verschoben) bekräftigt die Richtigkeit dieser Annahme. Die Verschiebung der Extinktionskurve von I nach den langen Wellen spricht für die schwache induktive Wirkung der SO_2 -Gruppe. Da die Extinktionskurven des ionisierten und nicht ionisierten