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INTERPRETATION OF $\pi \rightarrow \pi^*$ ELECTRONIC TRANSMISSIONS IN THE ABSORPTION SPECTRA OF FLAVONE AND ITS HYDROXY DERIVATIVES

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The electronic spectra of flavone and its 4'-, 3-, 5-, and 7-monohydroxy derivatives have been calculated by the standard Pople-Pariser-Parr method. The contributions of the fragments to the total molecular excitation have been calculated. It has been shown by computer modeling that the electronic transitions of the flavone spectrum can be reduced to the corresponding transitions of the spectrum of chromone, but not of chalcone. A graphical analysis has been performed of the experimental absorption curves. A four-component system of individual bands in the 230-400 nm region is proposed. Their mutual superposition or resolution is responsible for the features of the spectra of hydroxy-substituted flavones.

The absorption characteristics of flavones in the UV and visible regions of the spectrum are widely used for identifying and quantitatively determining these important biologically active natural compounds [1]. However, in spite of a number of special experimental and theoretical investigations [2-5], the question of the nature of the $\pi \rightarrow \pi^*$ electronic transitions in the spectra of flavone and its derivatives cannot apparently be regarded as having been solved. In the present paper to describe the electronic transitions a new theoretical approach is used [6], according to which the contribution of an atom (μ) or fragment (Fr) of a molecule to the $\Psi_0 \rightarrow \Psi_1$ excitation is characterized by the so-called localization number $L_{\mu}^{0 \rightarrow 1}$, %, or $L_{Fr}^{0 \rightarrow 1}$, %. For any transition, the sum of the values of L_{μ} over all the atoms of the molecule is, by definition equal to 100%. A study of the distribution of L_{μ} is, in our view, the most natural theoretical basis for the widely used empirical "fragmentation approach," according to which absorption bands are assigned to particular parts of the molecule.

The calculation of the energies and intensities of the transitions was performed by the standard Pople-Pariser-Parr (PPP) method according to a published program [7]. The localization numbers were determined with the aid of a special extension.* The molecule of flavone and its hydroxy derivatives were assumed to be planar and the interatomic distances (r_{μ}) were taken to be equal to the average tabulated lengths of the C-C, C=O, C-O bonds [8]. The "spectroscopic" system of parameters generally adopted was used: $W_C = -11.16$ eV, $W_O = -17.70$ eV, $W_{\dot{O}} = -34$ eV, $\gamma_C = 11.13$ eV, $\gamma_{\dot{O}} = 15.23$ eV, $\gamma_{\ddot{O}} = 23$ eV, $\beta_{\text{benz}} = -2.4$ eV, $\beta_{C-C} = 2.11$ eV, $\beta_{C=C} = -2.53$ eV, $\beta_{C=\dot{O}} = -3.3$ eV, $\beta_{C-\ddot{O}} = -2.5$ eV. The integrals $\gamma_{\mu\nu}(r_{\mu\nu})$ were calculated by means of the Mataga-Nishimoto formula. A total of 49 single excited configurations was calculated.

The calculated π -electronic spectrum of flavone is shown in Fig. 1. The energy sequence of the transitions and the qualitative ratio of the intensities that are given are stable with a variation in the semiempirical parameters within wide limits. An analysis of the distribution of the localization numbers permits the direct identification of the low-intensity 0-3 transition as a "benzene" transition localized in ring B. For the other transitions analyzed, the contribution of ring A to the corresponding excitations is always considerable ($L_A \cong 35-60\%$), while the contribution of ring B is relatively small ($L_B \cong 10-25\%$). Even this result casts doubt on the assignment of one of the long-wave $\pi \rightarrow \pi^*$ transitions of the spectrum of

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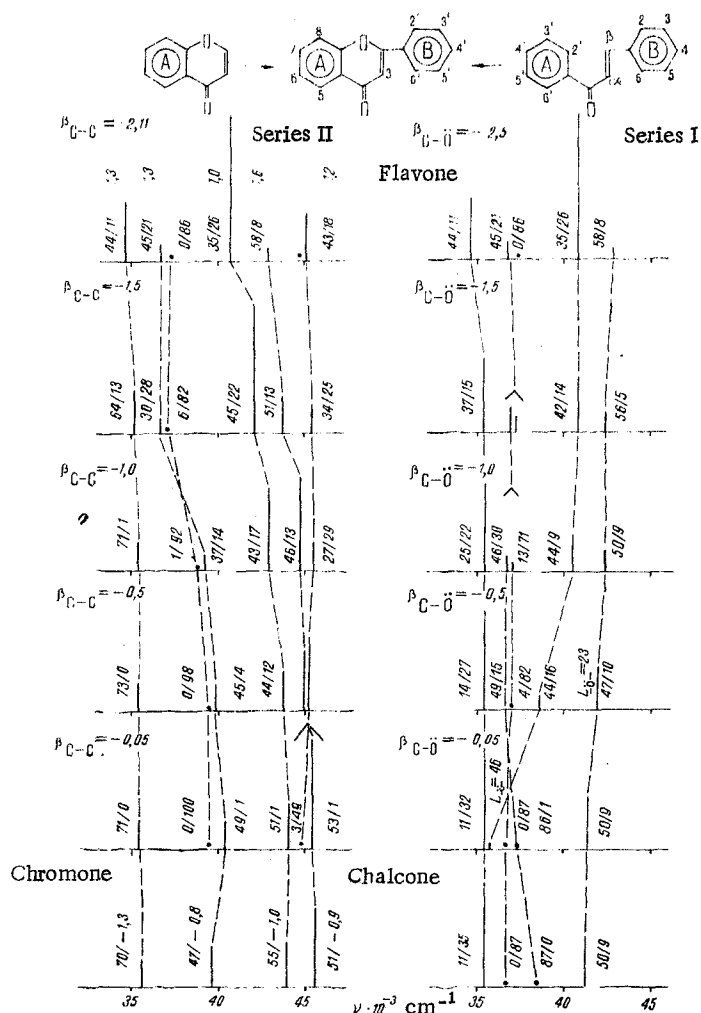


Fig. 1. Relationship of the electronic transitions in the calculated spectra of chalcone and chromone to the transitions of the flavone spectrum. Series I - variation in the resonance intervals of the C-Ö bonds, $\beta_{C-\ddot{O}} = -0.05$ to -2.5 eV. Series II - variation of the resonance integral of the C-C bond in the benzene ring B, $\beta_{C-C} = -0.05$ to 2.1 eV. For each transition in the ratio of the localization numbers of the excitation in ring A and ring B, $L_A\%/L_B\%$ is given. For the transitions of the chromone and flavone spectra the levels of excitation in ring A (K_A) are given in fractions of a unit. The points denote the positions of low-intensity transitions with $f \leq 0.02$. The L_{Fr} values are not shown for "pseudodegenerate" transitions close in energy.

flavone to the "cinnamoyl" ($\text{Ph}-\text{CH}=\text{CH}-\text{C}=\text{O}$) fragment adopted in the literature [2-4].

In the present paper, the question of the correspondence of the spectra of flavone, chromone, and chalcone is resolved by the "computer experiment" method. In the first series of calculation (Fig. 1) the "transformation" of the planar molecule of trans-S-trans-chalcone into the flavone molecule is modeled, this being achieved by a gradual increase in the resonance integral $\beta_{C-\ddot{O}}$, i.e., by an enhancement of the transmitting influence of the oxygen bridge Ö. It follows from the results of the calculation that in the spectrum of chalcone there is a well-defined localization of the intensive transitions lowest in energy either in ring B and the "cinnamoyl" fragment ($L_{\text{Ph}-\text{CH}=\text{CH}-\text{C}=\text{O}}^{0 \rightarrow 1} \approx 90\%$), or in ring A and the carbonyl group ($L_{\text{Ph}-\text{C}=\text{O}}^{0 \rightarrow 4} \approx 75\%$). This fact has obtained reliable experimental confirmation [9] and is explained by the cross-conjugation nature of the π -system of chalcone.

The introduction of an oxygen bridge between the 2'- and β -carbon atoms of the chalcone molecule leads to the appearance of a new transition, the intensity of which rises with an increase in β_{C-O} , which can be unambiguously assigned to the 0-4 transition of the flavone spectrum (Fig. 1). With a gradual "introduction" of an oxygen bridge, the 0-1 transition of the chalcone spectrum decreases its energy, intensity, and what is most important, changes the nature of its localization (compare the ratio $L_A^{0 \rightarrow 1}, \%$ / $L_B^{0 \rightarrow 1}, \%$ in chalcone (11/35) and flavone (44/11). One of the local "benzene" transitions of the chalcone spectrum ($L_B^{0 \rightarrow 2} = 87\%$) remains the same as in the spectrum of flavone ($L_B^{0 \rightarrow 2} = 86\%$), while the other "benzene" transition "loses" the property of localness ($L_A^{0 \rightarrow 2} = 45\%$, $L_B^{0 \rightarrow 2} = 21\%$, flavone). With respect to the type of localization, the "benzene" 0-4 transition of the chalcone spectrum can be compared with the 0-5 transition of the flavone spectrum.

In the second series of calculations (see Fig. 1) the gradual "introduction" of ring B into conjugation (a variation of the corresponding β_{C-O} integral), i.e., the "conversion" of chromone into flavone is modeled. Analysis of the contribution of the fragments to the excitation taking into account the substantial difference in the number of atoms in the molecules of chromone and flavone shows that for the 0-1 transition the level of excitation* in ring A in the spectra of the two systems is the same ($K_A \approx 1.3$). In addition, the contribution of ring B to the 0-1 transition of the flavone spectrum is fairly small ($L_B^{0 \rightarrow 1} = 11\%$). The 0-2 transitions in the spectra of chromone and flavone differ more considerably. The level of excitation in ring A rises from $K_A^{0 \rightarrow 2} = 0.8$ (chromone) to $K_A = 1.3$ (flavone). The contribution of the benzene ring B introduced into conjugation proves to be considerably greater than for the 0-1 transition (compare $L_B^{0 \rightarrow 1} = 11\%$ and $L_B^{0 \rightarrow 2} = 21\%$). The "appearance" in the spectrum of flavone of a local low-intensity "benzene" transition $L_B^{0 \rightarrow 3} = 86\%$ is completely explicable while the origin of the allowed 0-4, 0-5, and 0-7 transitions is difficult to treat unambiguously. It is most likely that 0-4 is a disturbed transition of the chromone spectrum, and of the two transitions 0-5 and 0-7 transitions one is "new" in relation to the spectrum of chromone. Thus, on the basis of the results of the calculation it can be stated that the analogy between the spectra of chalcone and flavone is on the whole incorrect. A closer qualitative similarity is shown by the spectra of flavone and chromone. However, one must take into account both the substantial quantitative differences in the characteristics of the corresponding transitions in the spectra of these molecules and also the existence of new transitions due to the specific π -system of flavone.

In the interpretation of the experimental spectra of flavone and its hydroxy derivatives[†] in the 25,000-45,000 cm^{-1} region, we adopted a four-component system of intense π, π^* absorption bands (Fig. 2). The results of the graphical analysis of the curves performed as described in the literature [12, 13] and also the results of calculation do not contradict this hypothesis.

It is natural to establish the following correspondence between the observed and calculated transitions of the flavone spectrum; I-1, II-2, III-4, IV-5. If we compare the experimental spectra of chromone and flavone, then, taking the calculated figures into account, the following correlation of the bands is also apparently valid: I-I, II-II, III-III, and with a somewhat smaller definiteness, IV-IV.

Figure 2 shows that the absorption curves of 4'-, 3-, 5-, and 7-hydroxy- or -methoxy-substituted derivatives on the whole are displaced only slightly on the energy scale relative to the spectrum of flavone, and only the form of the curves changes greatly. This fact can be explained if it is assumed that on 4'-, 5-, and 7-substitution the individual bands of the flavone spectrum I-IV undergo a relatively small bathochromic shift, but since they are located fairly close to one another, this may lead either to their mutual overlapping or partial resolution. In these circumstances, the intensities of the bands observed either increase

*If the molecules compared contain different numbers of atoms, it is necessary to compare not only L_{Fr} but also the coefficients K_{Fr} characterizing "the level of excitation in the given fragment" [10]. $K_{Fr} = L_{Fr}/L_{mol}$, where $L_{mol} = 100/N, \%$, and $L_{Fr} = L_{Fr}/n, \%$; N and n being the numbers of atoms in the molecule and in the fragment, respectively. As can be seen, K_{Fr} no longer depends on N and n; $K_{Fr} \approx 1$ means that the level of excitation in the fragment is close to the "mean molecular" level.

[†]The UV spectra of compounds (a) and (f) were measured in ethanol and that of (b) in hexane on a Specord UV-Vis spectrophotometer, and the UV spectra of compound (c), (d), and (e) were taken from the literature [11].

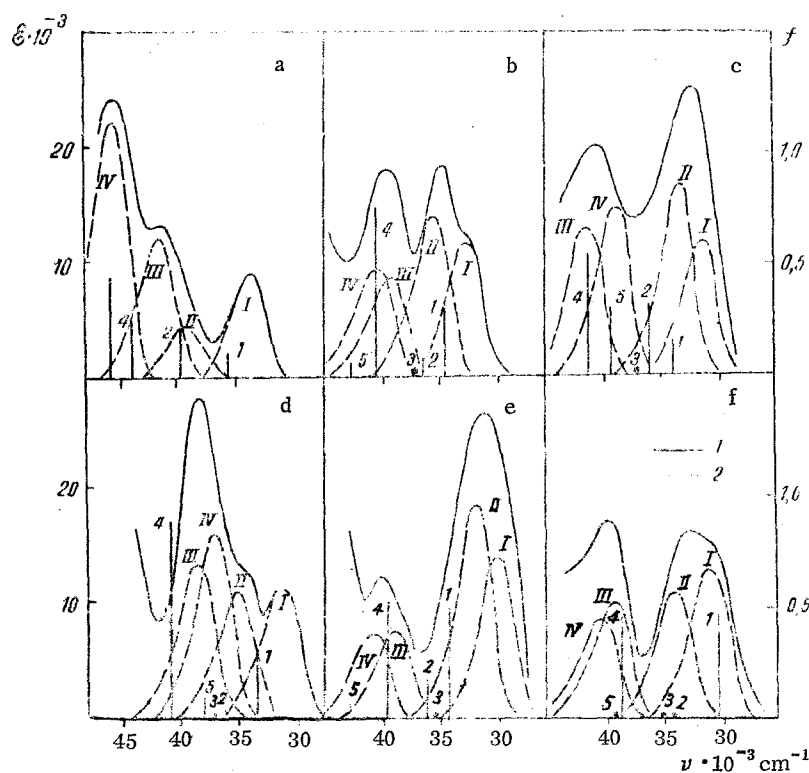


Fig. 2. Experimental and calculated spectra of chromone (a), flavone (b), 7-hydroxyflavone (c), 5-methoxyflavone (d), 4'-hydroxyflavone (e), and 3-methoxyflavone (f): 1) Experimental absorption curves; 2) Bands isolated graphically. The numbers of the bands (I, II, III, and IV) and of the calculated transitions (1, 2, 3, ...) are referred to the flavone spectrum.

or decrease. The hypothesis put forward is confirmed by the results of calculation and of the graphical analysis of the absorption curves (Fig. 2). 3-Methoxyflavone forms a special case. Calculation of the spectrum of a planar model of this molecule predicts a large long-wave shift of all its transitions, while this is not found experimentally. We explain this discrepancy between experiment and calculation by the inadequacy of a planar model of 3-methoxyflavone.

In conclusion, we may note that on comparing the calculated and observed intensities of the transitions, two facts must be taken into account. In the first place, the PPP method, generally speaking, poorly reproduces both the absolute values of the oscillator strengths and their ratio for the transitions of this spectrum. In the second place, the calculation takes no account of electronic-vibrational interaction, while the observed spectra are vibronic. And, in actual fact, in the assignment of the transitions that we have performed it is possible to see a number of inconsistencies. Thus, in the spectrum of flavone, for example, the calculated intensities of the transitions in the pairs 1 and 2, and 4 and 5, differ strongly, while the bands I and II, and III and IV, corresponding to them are close in intensity. In the spectra of the substituted flavones, strong bands are made to correspond to low-intensity calculated transitions and so on. In all such cases, we were guided, in the first place, by the correspondence in the nature of the transitions compared, i.e., in the nature of the electron redistribution on excitation. So far as concerns the graphical analysis of the absorption curves, in some cases the positions of the components of the spectrum isolated and the halfwidths and intensities of the bands must be regarded as rough values. Their stricter evaluation is hardly possible because of the pronounced overlapping of the individual bands.

SUMMARY

A calculation of the energies, intensities, and localizations of transitions in the spectra of chromone and flavone and its 4'-, 3-, 5-, and 7-monohydroxy derivatives has been made by the Pople-Pariser-Parr method. It has been shown that the first four allowed $\pi \rightarrow \pi^*$ tran-

sitions are localized mainly in the chromone fragment of the molecule. In the case of the hydroxy derivatives, the absorption bands of flavone undergo a relatively small bathochromic shift, but because of their closeness the individual components either overlap or, conversely, are resolved. This explains the substantial differences in the form of the spectra of the hydroxyflavones.

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REDUCTIVE AMINATION OF *L*-MENTHOL BY ALIPHATIC NITRILES

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The reductive amination of *L*-menthol with aliphatic nitriles has been studied. A probable scheme of the mechanism of the reaction has been put forward and the stereochemical composition of its products has been determined. It has been established with the aid of the ^{13}C NMR method that the reaction forms a mixture of isomeric optically-active *N*-alkylmenthyl-, -neomenthyl-, -isomenthyl-, and -neoisomenthylamines in a ratio of 54:24:17:5. The absolute configurations of the amines obtained have been determined.

The synthesis of nitrogen-containing compounds in the *p*-menthane series is of considerable interest, since these substances possess a broad spectrum of biological action [1, 2]. Continuing investigations [3-6] on the synthesis of amino derivatives of monoterpenes and their synthetic analogs, we have studied the reductive amination of *L*-menthol (I) with aliphatic nitriles, namely acetonitrile, acrylonitrile, and butyronitrile in a catalytic apparatus of the flow-through type under a pressure of hydrogen in the presence of heterogeneous catalyst.

In spite of the fact that menthol has been known for a long time [7], its chemical transformations have been little studied. This is due to the low reactivity of the hydroxy group in the menthol molecule resulting from the steric effect of the neighboring alkyl groups. Our

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