

ELECTRONIC ABSORPTION SPECTRA OF HETEROCYCLIC
ANALOGS OF *trans*-CHALCONE

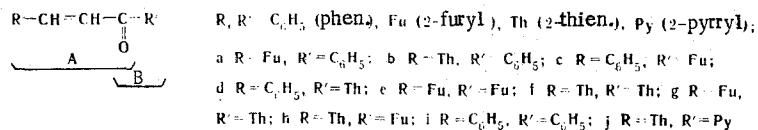
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Thiophene, furan, and pyrrole analogs of *trans*-chalcone have UV spectra consisting of bands belonging to the spectra of the corresponding 2-acetylhetaryl and 2-hetarylideneacetones that are shifted bathochromically as a result of mutual perturbation of these two crossconjugated fragments. The absorption curves of 10 chalcones in hexane solution were measured up to 190 nm, the bands of the individual transitions were isolated graphically, and the degree of localization of the electron excitation on the fragments of the molecules was calculated by a new quantum-chemical method.

The electronic absorption spectra (EAS) of systematic series of heterocyclic analogs of *trans*-chalcone (HAC) were measured in [1-4], and the transitions were assigned to individual portions of the molecules. A subsequent "fragmentary" approach to the analysis of the EAS, which was confirmed by the results of quantum-chemical calculations and data from the graphical analysis of the absorption curves, showed that the interpretation of the bands of the spectra of the HAC requires fundamental refinements and supplements. With this in mind we measured the absorption curves of thiophene and furan analogs of *trans*-chalcone (Fig. 1), 2-acetylthiophene, 2-acetyl furan, 2-thienylideneacetone, and 2-furfurylideneacetone (Fig. 2) in hexane solutions. The energies and intensities of the transitions were calculated by the standard Pariser-Parr-Pople method, and a new method [5] in which the contribution of each atom (μ) to the total molecular excitation is characterized by the localization number L_μ in percent and the summation $\sum_\mu L_\mu$ over all of the atoms of the molecule is always 100% was used for the evaluation of the localization of the π -electron excitation on the fragments of the molecule.

In the analysis of the spectra of the HAC it was assumed that they can be conceived of as a set of bands present in the spectra of the 2-hetarylideneacetone (A) and 2-acetylhetaryl (B) with allowance for the perturbations caused by consolidation of the π systems of the molecule "fragments" (A and B) in the HAC molecule of the following general formula



The spectra of the HAC molecule "fragments" (acetophenone and benzylideneacetone are included here), which are shown in Fig. 2, are in themselves rather complex. According to the results of the calculation, the long-wave π, π^* absorption of 2-acetylhetaryl (240-300 nm) and 2-hetarylideneacetones (250-310 nm) is due to two transitions, which appear on the experimental curve in the form of overlapped I and II bands that are comparable in intensity only for the thiophene derivatives. In this case localization of the excitation in the hetero-ring (L_R) for one of these transitions (the I type) decreases sharply as the number (n) of vinylene groups in the 2-hetarylpolyenone increases ($63 \rightarrow 44\%$ and $68 \rightarrow 43\%$, Fig. 2), whereas it amounts to only 20% for $n = 3$. On the other hand, transitions of the II type are characterized by high localization of the excitation on the hetero-ring ($L_R^{\text{II}} \approx 70-80\%$, Fig. 2) even when $n = 3$ ($L_R^{\text{II}} \approx 60\%$). Thus here, as in the case of phenylpolyenones [6], one can speak either of "polyene" or "ring" character of the two long-wave transitions under consideration.

The experimental data presented in [7] also indicate the "polyene" character of the intense long-wave absorption.

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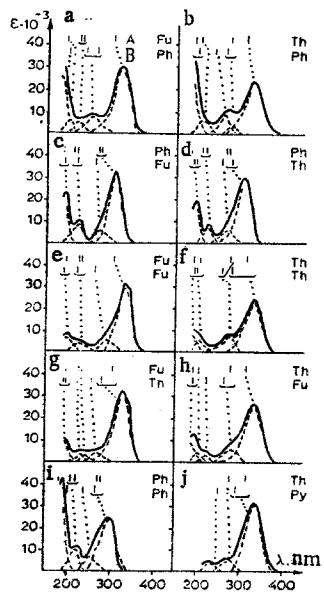


Fig. 1

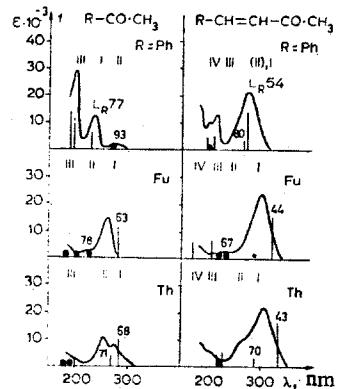


Fig. 2

Fig. 1. Electronic absorption spectra of heterocyclic analogs of chalcone $\text{RCH}=\text{CHCOR}'$ ($\text{R}, \text{R}' = \text{Ph}, \text{Fu}, \text{Th}, \text{Py}; \text{R} = \text{R}'$; $\text{R} \neq \text{R}'$) in hexane. The position of the bands in the experimental spectra of the $\text{RCH}=\text{CHCOCH}_3$ (A) and $\text{R}'\text{COCH}_3$ (B) molecule "fragments" is shown schematically in the upper portion of spectra a-j. The position of the intense bands of the I type is designated by the heavy lines. The brackets indicate the complex character of the isolated bands.

Fig. 2. Experimental and calculated UV spectra of 2-acetyl-hetaryls and 2-hetarylideneacetones: I, II ... is the numbering of the bands of transitions of the same type, L_R are the numbers of localization of the excitation in the ring, f is the calculated oscillator force, and \bullet indicates transitions with $f \leq 0.1$.

According to the traditional "configurational analysis" of the results of calculation of the EAS of 2-hetarylpolyenones, the configuration formed by promotion of an electron from the upper filled MO (φ_1) to the lower vacant MO (Q_1) makes the principal contribution ($> 90\%$) to the Ψ_I state. The state of the Ψ_{II} type is characterized by a substantial contribution of the $\varphi_2 \rightarrow \varphi_1'$ configuration ($\approx 75\%$). In addition, but the $\Psi_0 \rightarrow \Psi_I$ and $\Psi_0 \rightarrow \Psi_{II}$ transitions can be characterized by the magnitude of intramolecular charge transfer (ICT), for example, from the heteroring to the polyene chain: $\sum_{\mu \in R} \Delta q_{\mu} \approx 0.3-0.5 \text{ e}^-$. However, the appreciable charge transfer (CT) between the atoms of the heteroring itself or the polyene fragment is not taken into account in this case. Evidently none of the usual approaches gives a numerical characteristic of the "contribution" of the fragment to the overall molecular excitation as convenient as L_R .

The high-frequency region of the spectrum (up to 190 nm) consists of two to three bands (III, IV, and V), the intensity of which is several times lower in the case of 2-hetarylpolyenones than for phenylpolyenones.

According to the results of the calculation, there are several electron transitions with close energies in this region of the spectrum; this hinders their unambiguous assignment. We propose that the III band in the EAS of the compounds of the furan series is due primarily to a transition with "polyene" character. The corresponding band in the EAS of the thiophene analogs can be ascribed to a transition of the "ring" type; the experimentally manifested band evidently has a complex structure and includes a transition of the "polyene" type, similar to the transition in the EAS of furan compounds.

Band IV in the spectra of 2-hetarylideneacetones is due to a new relatively intense transition localized mainly in the propenone chain.

Joint analysis of the curves in Figs. 1 and 2 leads to the assumption that the long-wave intense band in

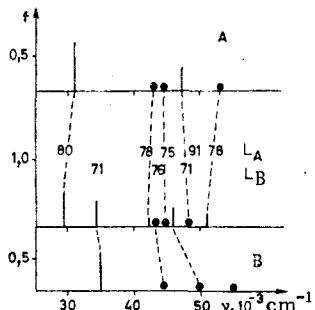


Fig. 3. Origin of the transitions in the calculated spectrum of $\text{Fu}-\text{CH}=\text{CHCO}-\text{Fu}$. The localization of the L_A and L_B transitions on the atoms of fragment A ($\text{Fu}-\text{Cu}=\overset{\text{H}}{\text{CHC=O}}$) and fragment B ($\text{Fu}-\overset{\text{H}}{\text{C=O}}$) is indicated; f is the calculated oscillator force, and denotes transitions with $f \leq 0.1$.

the spectra of HAC is a perturbed band of the I type observed in the spectra of hetarylindeneacetones; different bathochromic shifts [$\Delta\lambda_{\text{pert}} = 17-36 \text{ nm}$, $\Delta\tilde{\nu}_{\text{pert}} = (1.6-4.2) \cdot 10^3 \text{ cm}^{-1}$] are observed as a function of the type of perturbing (phenyl, hetaryl) and perturbable (A) fragment. The subsequent approach necessarily requires the presence in the spectra of HAC of a IB band belonging to the B fragment; perturbation of the 2-acetylhetaryl group by a styryl or 2-hetarylethylene group, in analogy to chalcone [8], will most likely lead to a bathochromic shift of the I band, and $\Delta\tilde{\nu}_{\text{pert}}$ will be close to the value examined above. Experiments show only a few cases in which a distinctly expressed band (Fig. 1a) or a component isolated from the total curve (Fig. 1, spectra b and h) can be confidently assigned to the IB type with $\Delta\lambda = 20-30 \text{ nm}$ and $\Delta\tilde{\nu} = (3-5) \cdot 10^3 \text{ cm}^{-1}$. On the basis of this estimate of $\Delta\tilde{\nu}_{\text{pert}}$, it can be asserted that the IB and IA bands in the remaining curves (Fig. 1, spectra c-g) are markedly overlapped, and an unambiguous assignment is impossible in these cases.

Bands of the II A and II B types evidently appear only in the spectra of thiophene HAC, since in the spectra of 2-acetylthiophene and 2-thienylideneacetone they are comparable in intensity to the bands of the I type. For example, a band that is bathochromically shifted by 15-20 nm [$(2-3) \cdot 10^3 \text{ cm}^{-1}$] relative to bands of the II type of the A and B fragments can be isolated in the spectra presented in Fig. 1 (spectra b, d, and g), while the II A and IB bands on the curve of spectrum h in Fig. 1 merge to give a single band.

The portion of the spectrum below 250 nm, to which little previous study has been devoted in the case of HAC, is extremely complex for demonstrative analysis, since the molecule "fragments" A and B here have a developed system of bands (III-V) and their superimposition is inevitable in the corresponding chalcone. However, there is definite evidence of the fragmentary character of the transitions in this region also. Thus all of the chalcones that contain an "acetophenone" fragment (Fig. 1, spectra a, b, and i) contain an intense band with $\epsilon_{\text{max}} = 30,000$ in the 200 nm region, while those that include a "benzylideneacetone" fragment (Fig. 1, spectra c, d, and i) contain a band with $\epsilon_{\text{max}} = 20,000$. There are no intense bands in the spectra of the heterocyclic fragments in this region (Fig. 2), and the absorption at 200-250 nm does not exceed 10,000-13,000 for any of the purely heterocyclic chalcones.

In Fig. 1 an attempt was made to show the position in the spectra of the HAC of all of the bands of the A and B fragments. The graphically isolated bands were described by curves of the logarithmic normalized distribution, [9], and the half-width of these bands was assumed to be $(4-5) \cdot 10^3 \text{ cm}^{-1}$; this provided a guarantee against the isolation of "superfluous" anomalously narrow components. It is seen that all of the necessary bands are inscribed in the experimental curve.

The treatment of the spectra of the HAC presented above is not unique. Thus the intense long-wave band in the spectra of HAC was also assigned [3, 4] to the A fragment, while the next distinctly observable short-wave maximum was ascribed to the B fragment. This formal approach has been found to be occasionally successful for a number of spectra (Fig. 1, spectra a, b, h). However, a hypsochromic shift to the 220-250 nm region of the band of the 2-acetylhetaryl fragment when it is included in the HAC molecule was assumed in other cases [3, 4] (Fig. 1, spectra c, d, e, g, and i).

The results of the calculations take on special value for the confirmation of the "fragmentary" treatment of the spectra of HAC. The theoretical spectrum of 1,3-difurylpropenone and of the molecule "fragments" is presented in Fig. 3 as an example. The corresponding transition in the spectrum of one or another fragment can be ascribed to each transition in the spectrum of this chalcone on the basis of the closeness of the energies and from the character of the localization of the excitation. For the remaining HAC the L_A and L_B values range from 70 to 90%, although more delocalized transitions also occur. An analogous interpretation of the spectra of pyrrole analogs of chalcone has also been found to be successful (Fig. 1, spectrum 1). Thus the principles of analysis of the absorption curves tested on some HAC evidently can be used for the interpretation and quantitative prediction of the spectra of crossconjugated molecules that include different heterorings.

EXPERIMENTAL

The absorption curves of hexane solutions of the compounds were measured with an SF-16 spectrophotometer with nitrogen purging of the monochromator. The synthesized (by crotonic condensation) HAC and the commercial reagents were purified by recrystallization or vacuum sublimation; where necessary, they were chromatographed with a column filled with Al_2O_3 .

The spectra were calculated by the Pariser-Parr-Pople method with allowance for 25 singly excited configurations from a known program [10] modified by V. É. Umanskii (Computer Center, Kharkov State University) for the calculation of localization numbers. The molecules were assumed to be planar, having trans-*s-cis* geometry of the propenone chain [11]. It was also assumed that the heterorings exist in the transoid conformation with respect to the adjacent double bonds. The bond lengths were assumed to be the standard values. The semiempirical parameters were calibrated from the experimental spectra of heterocycles: $\gamma_{\mu\nu}$ according to Mataga and Nishimoto: $\gamma_{\text{CC}} = 11.13$, $W_{\text{CC}} = -11.16$, $\beta_{\text{C}=\text{C}} = -2.53$, $\beta_{\text{C}-\text{C}} = -2.11$ eV; $\gamma_{\text{CO}}^{\text{CO}} = 15.23$, $W_{\text{OO}}^{\text{CO}} = -17.7$, $\beta_{\text{C}=\text{O}} = -3.2$ eV; $\gamma_{\text{O}\bar{\text{O}}}^{\text{O}\bar{\text{O}}} = 21$, $W_{\text{O}\bar{\text{O}}}^{\text{O}\bar{\text{O}}} = -34$, $\beta_{\text{C}-\bar{\text{O}}} = -2.0$ eV; $\gamma_{\text{S}\bar{\text{S}}}^{\text{S}\bar{\text{S}}} = -13$, $W_{\text{S}\bar{\text{S}}}^{\text{S}\bar{\text{S}}} = -22$, $\beta_{\text{C}-\bar{\text{S}}} = -1.4$ eV; $\gamma_{\text{N}\bar{\text{N}}}^{\text{N}\bar{\text{N}}} = 18$, $W_{\text{N}\bar{\text{N}}}^{\text{N}\bar{\text{N}}} = -26$, and $\beta_{\text{C}-\bar{\text{N}}} = -1.8$ eV.

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