ULTRAVIOLET ABSORPTION SPECTRA OF CHALCONE ANALOGS CONTAINING A SELENOPHENE NUCLEUS

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The UV absorption spectra in solutions in hexane and ethanol of chalcone analogs containing, apart from 2-selenienyl, the following heterocyclic radicals—2-furyl, 2-thienyl, 2-pyrryl, 2- and 3-pyridyl, and 2-quinolyl—have been measured and discussed. Considerations on the electronic influence of the heterocycles have been put forward and the Hammett's parameters have been evaluated for some of the radicals.

Continuing a spectrophotometric study of α,β-unsaturated ketones of the selenophene series [1], we have measured the ultraviolet absorption spectra in hexane and ethanol solutions of chalcone analogs containing other heterocyclic radicals apart from 2-selenienyl (table). The characteristic absorption curves, which may be used for identification purposes, are given in Figs. 1 and 2.

As a rule, all the substances concerned have, in the region investigated, three well-defined absorption bands. The absorption maxima of the long-wave bands of all the compounds in ethanolic solution are displaced in the red direction by 3–22 nm in all cases as compared with λ_{max} in hexane solution. This is a consequence of the formation in the first case of more or less stable hydrogen bonds and shows that the long-wave band is due to the occurrence of π-π^* electronic transitions in the conjugated chain including the carbonyl group.

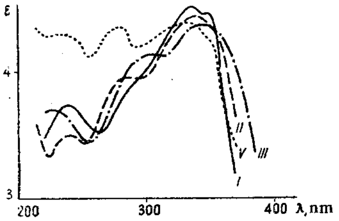


Fig. 1. UV spectra of the ketones I, II, III, and V in hexane.

In the spectrum of a solution of the ketone I in hexane, the long-wave band is split and has two maxima (Fig. 1): a narrow one typical for α,β-unsaturated ketones (λ_{max} 336 nm) and the second with λ_{max} 349 nm; in ethanolic solution, only one broad maximum is observed. As we have found, there is a similar pattern in the absorption spectra of 3-(2-furyl)-1-2-thienyl) propen-1-one and of 1, 3-bis(2-furyl)propen-1-one (333 and 346 nm, and 331 and 346 nm, respectively). It is possible that the appearance of a second maximum in the 346–349 nm region is connected with the appearance of the vibrational structure characteristic for the furfurylidene radical.

For a series of ketones containing the 2-selenienylidene grouping (III, VI–X), the quasi-autonomic absorption in the region 305–310 nm (Fig. 1, 2) that is characteristic for it and which has been mentioned previously [1, 2] is observed.

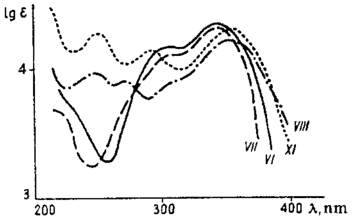


Fig. 2. UV spectra of the ketones VI, VII, VIII, and XI in hexane.

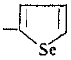
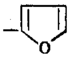
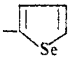
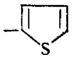
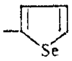
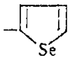
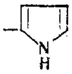
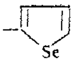
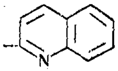
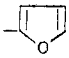
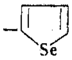
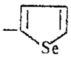
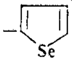
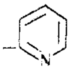
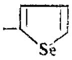
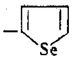
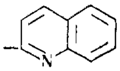
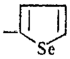
On comparing the UV spectra of chalcone (λ_{max} in ethanol 312 nm [3]) and its heterocyclic analogs (I–III, VI, VII), it can be seen that in the spectra of the latter the long-wave bands are displaced bathochromically by 25–54 nm. This red shift is caused by the fact that five-membered heterocyclic radicals—2-furyl, 3-thienyl, and 2-selenienyl—exhibit an electron-donating effect [4] and, as is well known [3, 5], the replacement of phenyl in α,β-unsaturated ketones by a nucleophilic radical leads to a bathochromic effect which is more considerable where this substitution takes place remote from the carbonyl group.

In order to make a quantitative evaluation of the electronic influence of these heterocyclic radicals, we made use of the correlation relationship [1] between the absorption λ_{max} and the Hammett's σ constants of the substituents:

$$\left(\frac{1}{\lambda_R} - \frac{1}{\lambda_H}\right)\frac{hc}{2.3\cdot KT} = \rho\sigma.$$

Starting from a value of ρ for 3-aryl-1-(2-selenienyl) propen-1-ones of 20.1 and λ_{max} of the long-wave absorption bands of the ketones I–III, the following values of the σ-parameters were found: for 2-furyl, −0.28; for 2-thienyl, −0.30; and for 2-selenienyl, −0.36. A somewhat lower value of the σ-constant for 2-selenienyl (−0.33) is obtained if the calculation is carried out with the value ρ = 22.4 found for the chalcones [1] and the frequency of the long-wave absorption of 1-phenyl-3-(2-selenienyl)propen-1-one. The values of σ obtained confirm the conclusion drawn on the basis of the measurement of the electronic spectra [4], dipole moments, and infrared spectra of chalcone analogs that, in the static state, the electron-donating properties decrease in the sequence: 2-selenienyl > 2-thienyl > 2-furyl. In addition to this, it follows from data on the proton-accepting capacity of

Ultraviolet Absorption Spectra of Chalcone Analogs of the Type $R_1—CO—CH=CH—R_2$

Compound	R_1	R_2	λ_{max}, nm/ε			
			in hexane		in ethanol	
I			349/27500 290/shoulder	336/31600 238/5500	355/27000 241/5600	295/shoulder
II			338/27500 240/3200	287/9100	357/22900 232/5600	289/9100
III			346/24000 228/5200	305/shoulder	365/21500 237/6900	310/shoulder
IV			—	—	406/24300	288/8100
V			334/23400 235/19500	280/21900	337/27500 232/5600	282/9100
VI			344/22000 235/shoulder	307/15200	363/21400 235/shoulder	316/12900
VII			343/21000	308/13200	365/20000	314/11200
VIII			—	—	364/25400	245/6350
IX			353/16600 272/8000	310/shoulder 247/9500	362/18600 277/7100	310/shoulder 240/shoulder
X			350/15500 275/shoulder	310/shoulder 249/9500	360/18600 275/5600	310/shoulder 240/shoulder
XI			355/20000 252/19500	292/14000	366/20000 255/17000	305/14000

the chalcone analogs [6] that the positive dynamic effect of the conjugation of these heterocyclic radicals changes in a different sequence: 2-furyl > 2-selenienyl > 2-thienyl.

A 2-pyrryl radical remote from the carbonyl group, considered in a study of ketones containing the pyrrole nucleus carried out in cooperation with V. P. Izvekov, has a particularly large bathochromic effect (see IV). This is explained by the fact that in its donor nature pyrryl considerably exceeds the five-membered heterocyclic radicals containing heteroatoms of group VI of D. I. Mendeleev's periodic system [7]. The σ parameters calculated for 2-pyrryl from the values of the ρ constants given above are, respectively, -0.66 and -0.60.

Of the two ketones with a quinoline radical (V and XI), that in which the 2-quinolyl group is adjacent to the carbonyl group has a deeper coloration. Consequently, in this case the quinoline radical exhibits an electron-accepting influence, which is in agreement with information on the study of quinoline analogs of the chalcone [8]. The 2- and 3-pyrridyl radicals (cf. IX and X) also behave as negative substituents, since when the phenyl in 1-phenyl-3-(2-selenienyl)-1-propenone (λ_{max} in ethanol 325 nm [1]) is replaced the absorption shifts in the red direction.

EXPERIMENTAL

The synthesis of the heterocyclic analogs of chalcone with the exception of X has been described in a previous paper [9].

1-(3-Pyridyl)-3-(2-selenienyl)propen-1-one (X). A solution of 1 ml of diethylamine in 300 ml of water was added to a solution of equimolecular amounts (0.15 mole) of 2-selenophenealdehyde and 3-acetylpyridine in 3 ml of pyridine. After a day, the precipitate that had deposited was filtered off and recrystallized from aqueous ethanol. Yield 50%. Light yellow plates with mp 102–103° C. Found, %: Se 29.73, 29.80. Calculated for $C_{12}H_9NOSe$, %: Se 30.11.

The UV absorption spectra were measured in an SF-4 quartz spectrophotometer at concentration of the substances of $2-4 \cdot 10^{-5}$ M.

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