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SPECTRA AND HALOCHROMISM OF QUINOLINE NUCLEUS-CONTAINING CHALCONE ANALOGS

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The electron absorption spectra of 14 quinoline analogs of chalcone are measured in concentrated sulfuric acid. It is shown that not all the compounds studied in that solvent exhibit halochromism because protonation of the quinoline ring system greatly decreases ketone basicity. It is established that replacement of phenyl in the quinoline chalcone molecules by furyl-2, thienyl-2, and 4-chlorophenyl causes a bathochromic shift. Similar replacement of phenyl by 5-nitrofuryl-2, 5-nitrothienyl-2, and 4-nitrophenyl gives rise to a hypsochromic shift, and there is no halochromic coloration.

A previous paper [1] dealt with the results of a study of the electronic absorption spectra of acid solutions of 1-(quinolyl-2)-3-arylpropenones with electron-donating substituents in the aromatic ring, and the carbonyl group occupying various positions in the conjugated chain. The present paper deals with a spectrophotometric study of 95% sulfuric acid solutions of certain chalcone analogs containing the quinoline group, and also furyl-2 (I, II), thienyl-2 (III, IV), pyridyl-4 (V), quinolyl-2 (VI), as well as electron-accepting substituents with I substituents, 4-chlorophenyl (VII, VIII), 4-nitrophenyl (IX, X), 5-nitrofuryl-2 (XI, XII), and 5-nitrothienyl-2 (XIII, XIV).

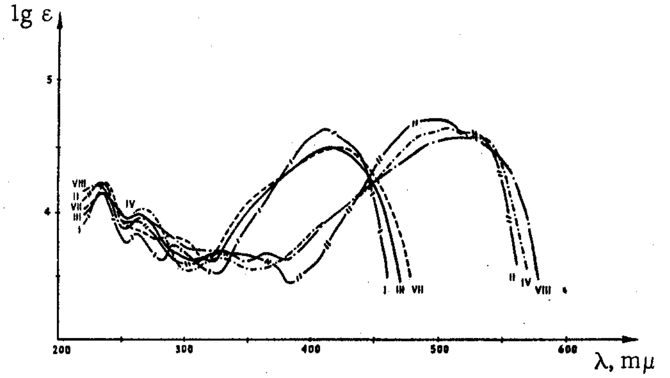


Fig. 1. Absorption curves of ketones I-IV, VII-VIII in concentrated sulfuric acid.

Figures 1 and 2 show the visible and ultraviolet absorption curves, and the basic spectral characteristics are given in the table. For comparison the end of the table gives previous data for 1-(quinolyl-2)-3-phenylpropenones (XV, XVI).

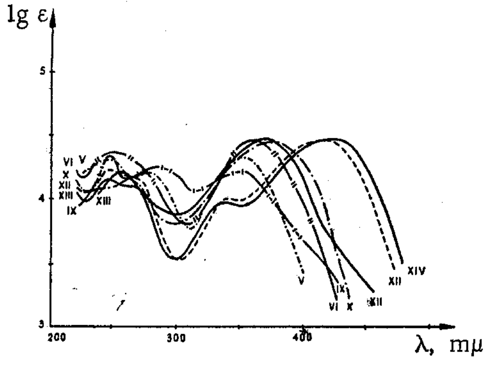


Fig. 2. Absorption curves of ketones V, VI, IX, X, XII-XIV in concentrated sulfuric acid.

Comparison of absorption curves I-XIV in concentrated sulfuric acid solution with the corresponding curves obtained in neutral solvents (carbon tetrachloride, alcohol) [2], shows that not all the compounds investigated exhibit halochromic coloring. A new intense absorption band in the long wave region appears in the spectrum curves of ketones I-IV, VII and VIII, while the intensities of the other bands decrease appreciably, and the color deepens by 80-180 mμ, due to formation of conjugated carbenium ions. Actually the curves of solutions of ketones V, VI, IX-XIV in concentrated sulfuric acid differ comparatively little from the curves of alcohol solutions, but their long wave band maxima are shifted by 20-60 mμ. It can be assumed that in the latter case the phenomenon of halochromy is not manifested, but there is some doubt about this with the ketones XII and XIV, whose λ_{max} are displaced by 63 and 56 mμ, respectively. Since halochromic coloring is conditioned by the presence of carbenium ions in the solution, in unclear cases the presence of acid-base equilibrium should be considered as evidence supporting manifestation of halochromy, and it can be detected by an isobestic point on a series of absorption curves, determined at different acid concentrations, for the particular compound. Actually such a point exists for compounds I-IV, VII and VIII (e. g., Fig. 3), but it is lacking for the others. The ketones' lack of halochromic properties indicates a low basicity for the carbonyl group, and that carbenium ions cannot be formed. As it is known that analogs of the ketones V-XIV in which the quinolyl-2 group is repaced by phenyl, exhibit

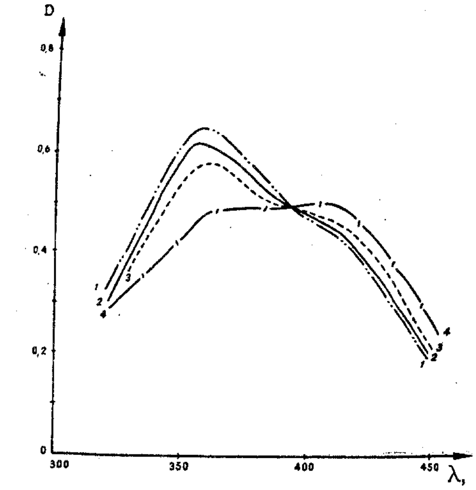
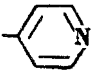
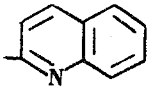
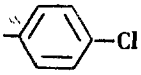
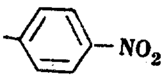
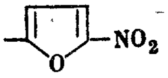
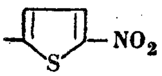
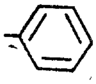


Fig. 3. Absorption curves of ketone VII in sulfuric acid: 1 – 86%, 2 – 87%, 3 – 88%, 4 – 90%.

a well-defined halochromic color in concentrated sulfuric acid (see, for example, [3, 4]) it follows that in its protonated form, quinolyl-2 very considerably lowers the electron density at the oxygen of the carbonyl, and hence the basicities. There the electron accepting effect of the quinoline group exceeds that of the 4-nitrophenyl one. Thus, for example, if the quinoline nucleus of ketones XI, XII, is replaced by the 4-nitrophenyl group (see [5, 6]), the ketones give a halochromic color in concentrated sulfuric acid. Marked lowering of the basicities of the ketones is also brought about by 4-nitrophenyl, 5-nitrofuryl-2, 5-nitrothienyl-2, and the protonated pyridyl-4 group.

The position of the carbonyl group in the compounds under investigation significantly affects the degree of halochromic coloring. All the compounds in which the carbonyl group is next to the quinoline ring system (II, IV, VIII) give a color which is about 90 mμ deeper than in the isomers (I, III, VII). The deeper halochromic coloring of ketones II, IV, and VIII (having furyl, thienyl, and p-chlorophenyl substituents β to the carbonyl group) is connected with formation, in those cases, of a longer donor-acceptor system, where the acceptor is the protonated carbonyl group with the adjacent quinoline portion, while the groups in the β-position can function as donors.

Spectral Characteristics of Quinoline Analogs of Chalcones in 95% Sulfuric Acid

R_1	R–CH=CH–CO–R_1*			R–CO–CH=CH–R_1		
	Compound No.	λ_{max}, mμ	ε	Compound No.	λ_{max}, mμ	ε
	I	412/42200 290/5700	260/6800 234/15600	II	504/52800 330/4800	261/8400 234/16800
	III	413/31200 312/4400	263/9900 234/14500	IV	506/45800 328/4400	266/10900 235/17000
	V	351/22400	277/16300 242/20600	—	—	—
	—	—	—	VI	362/29300	252/24300
	VII	420/30800	287/6800 238/17400	VIII	519/38400	268/9300 231/11700
	IX	351/17100	284/17700 247/23500	X	376/30100	263/14800
	XI	368/28800	248/16700	XII	420/30100 340/10400	248/17700
	XIII	368/30800	254/17100	XIV	421/31300 340/9730	248/15300
	XV	402/25000 300/10000	235/15400	XVI	492/36400 350/5500	258/10700 228/16400

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*R_1 = quinolyl-2.

It is characteristic that furyl-2 and thienyl-2 have the same effect on the coloring of quinoline chalcones. Replacement of these heterocyclic groups by phenyl gives rise to a bathochromic effect of 10-12 mμ (compare I-IV with XV, XVI).

Introduction of an atom of chlorine into the aromatic ring of 1-(quinolyl-2)-3-phenylpropenones does not give rise to loss of halochromic properties. It is found that here there is an 18-27 mμ greater bathochromic effect when chlorophenyl is remote from the carbonyl group, than when it is next to it (compare VII, VIII with XV, XVI). It is of interest that in concentrated sulfuric acid λ_{max} for the ketones IX and X with a 4-nitrophenyl group in their molecules, scarcely differs from that for the analogous ketones, with an amino- or dimethyl amino- groups in place of the nitro-one (see [1]).

It should be mentioned that introducing electron accepting groups in place of phenyl in the quinoline chalcones increases the keeping stability of their sulfuric acid solutions.

Experimental

The spectrophotometric measurements were made in the way previously described [1]. Synthesis of the quinoline chalcones has also been previously described [7].

REFERENCES

1. S. V. Tsukerman, Ch'ang Quoc Shuon, and V. F. Lavrushin, ZhOKh, 35, 1965.
2. S. V. Tsukerman, Ch'ang Quoc Shuon, and V. F. Lavrushin, Zh. priklad. spektr., 1, 1965.
3. P. Pfeifer, Organische Molekülverbindungen, Stuttgart, 1922.
4. M. Dilthey, L. Neuhaus, and W. Schomer, J. Pract. Chem., 123, 235, 1929.
5. V. M. Nikitchenko, S. V. Tsukerman, and V. F. Lavrushin, ZhOKh, 33, 2563, 1963.
6. A. I. Artemenko, S. V. Tsukerman, and V. F. Lavrushin, ZhOKh, 34, 487, 1964.
7. S. V. Tsukerman, Ch'ang Quoc Shuon, and V. F. Lavrushin, ZhOKh, 34, 832, 2881, 1964.

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