in portions at 50° in the course of an hour to a mixture of 1.6 g (0.01 mole) of 2-acetylbenzofuran, 50 ml of chloroform, and 10 ml of concentrated sulfuric acid, after which the mixture was stirred at 50° for 3 h. It was then cooled, the organic layer was separated, and the aqueous phase was extracted with chloroform. The combined chloroform extracts were dried with sodium sulfate, and the solvent was removed by distillation to give 1.4 g (80%) of methylamide V with mp 107-108° (from aqueous alcohol) [5] and R_f 0.57. IR spectrum: 1658 (C=O) and 3270 cm^{-1} (N-H). UV spectrum, λ_{max} (log ε): 216 (4.06) and 269 nm (4.03).

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PECULIARITIES OF THE MANIFESTATION OF THE K ABSORPTION BANDS IN THE UV ABSORPTION SPECTRA OF AZOMETHINE BASES

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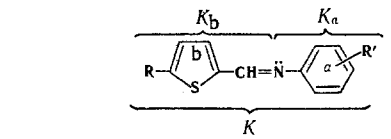
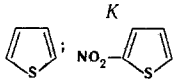
The structure of the UV spectra of azomethine bases of the thiophene and dithienyl series was examined on the basis of the concept of the nonplanar structure of azomethine bases. A peculiarity of the manifestation of the K absorption bands associated with stabilization of the wavelengths of the K bands, which is determined by an increase in the angle of acoplanarity of the azomethine system above 30°, was revealed.

In the present research we investigated the structure of the UV absorption spectra of azomethine bases of the general formula



R = H; Br; NO_2;  ;

R' = H; p,m-CH_3; p-OH; p-OCH_3; p,m-Cl; p,m-Br; p,m-COOH; m-NO_2

Their interpretation became possible after the assumption on the basis of UV absorption spectra, of the nonplanar structure of benzylideneaniline [1] as a result of rotation of the *a* ring about the bond with the nitrogen atom at a certain angle θ [2-5]. The acoplanarity of this molecule was recently confirmed by the results of x-ray diffraction analysis [6]. The long-wave absorption band in the spectra of the azomethines usually corresponds to the $\pi \rightarrow \pi^*$ electron transition of the entire conjugated system of the azomethine (the K band) [1, 2, 4,

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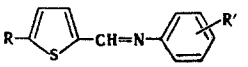
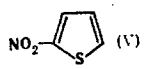
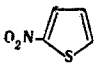
TABLE 1. K Absorption Bands of Azomethine Bases

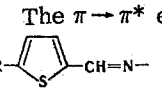


R / R′	H(I)		Br(II)		NO_2(III)		 (IV)		 (V)	
	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε	λ_{max}, nm	ε
H	323	15260	335	16000	374	14500	370	29000	415	32500
p-CH_3	334	14000	340	16400	390	14200	370	28500	420	28970
m-CH_3	326	13130	335	16000	378	13740	370	29000	415	32500
p-OH	345	12550	355	14460	418	15500	395	39610	435	27500
p-OCH_3	338	16600	350	11500	408	15000	385†	29680	430	30000
p-Cl	325	10200			375	12500	370†	24750†		
p-Br	325	14500	335	12500	375	15080	369†	19740†		
m-COOH	325	14200	335	16500	375	12800	370	23810	415	26250
p-COOH	326	13400	335	12200	375	13900	370	25000	415	31000
m-NO_2									415	30730

† These values are for the m-Cl- and m-Br-substituted compounds.

TABLE 2. Calculation of Angle θ in Azomethine Molecules from the Braude Formula

R	R′	λ, nm	ε	λ_0, nm	ε_0	θ
H (I)	H	323	15260	370	17120	32°30
Br (II)	*m*-CH_3	335	16000	383	21300	30°
O_2N (III)	H	374	14500	395	20000	31°30
 (IV)	*p*-CH_3	370	28500	438	34700	25°
 (V)	*m*-CH_3	415	32500	464	39600	25°

5, 7]. In addition, absorption bands of the structural components, the amine and aldehyde rings (the K_a and K_b bands), also appear in the spectra of azomethines in connection with their nonplanar structure [1, 2, 4, 5, 7]. In establishing the origin of the absorption bands in the spectra of the investigated azomethines we used the method of comparison of the absorption bands in their spectra with the absorption bands of the starting compounds, the method of artificial addition of the starting compounds to the investigated solution of the azomethine, and spectrophotometric monitoring of the hydrolysis of the azomethines over the entire range of wavelengths. The absorption bands of the structural components of the molecule are clearly revealed in this case, and the K bands are identified from their disappearance during decomposition of the investigated azomethine. The K_a and K_b absorption bands frequently show up in the form of shoulders or overall absorption bands of both systems and are only slightly sensitive to a change in the substituents within the limits of the investigated series. As seen from the results, the K band is very sensitive to variation of the substituents (Table 1). Correlation of the K bands with the Hammett σ constants revealed the following regularity. In systems with electron-donor substituents in the amine component of the molecule, the change in the wavelengths corresponds to the σ substituent constants (Fig. 1). When the electron-acceptor properties of the substituent are intensified, the wavelength of the K band stops changing. A stable K band value for various series of the investigated compounds is reached over the range of transition from electron-donor substituents to electron-acceptor substituents. Thus for 2-thienalanilines and 5-nitro-2-thienalanilines this transition corresponds to the point for the unsubstituted compound, whereas for 2,2′-dithienyl-5-methylidyneanilines it corresponds to the point for the p-CH_3 group of the substituted compound and for 5-bromo-2-thienalanilines and 5′-nitro-2,2′-dithienyl-5-methylidyneanilines it corresponds to the point for the m-CH_3 group of the substituted compounds (Fig. 1). It may therefore be assumed that when electron-acceptor substituents are introduced, the transmission of their effects through the conjugated system of the aniline ring to the conjugated π system of the remaining portion of the molecule weakens maximally. The $\pi \rightarrow \pi^*$ electron transition, the fundamental component of which is the $\pi \rightarrow \pi^*$ electron transition of the  fragment, is recorded as the K band in this case. The thorough-

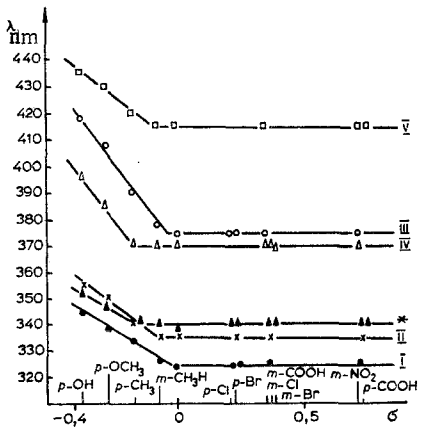


Fig. 1. Correlation of the wavelengths of the K absorption bands of azomethine bases (the line with the asterisk was constructed from the data in [8]).

ly analyzed data on the K absorption bands of salicylalanilines [8], the amount of which was sufficient for correlation treatment, confirm the dependences obtained for the investigated compounds.

The fact of stabilization of the wavelengths of the K bands is a consequence of the increase in the angle of the electron-acceptor properties of the substituents. Since the tendency of the change in the angles of acoplanarity in azomethine systems as the character of the substituents changes has been demonstrated in a number of studies [3-5, 7-9], it was of interest to thoroughly analyze the angle of acoplanarity for compounds beginning with which, as demonstrated by the discovered regularity, changes in the wavelengths of the K bands are not observed. It can be seen from the data in Table 2 that the angle of acoplanarity determined from the Braude formula [4, 5, 10] $\cos^2 \theta = \varepsilon/\varepsilon_0$, where ε and ε_0 are the molar extinction coefficients of an azomethine with nonplanar and planar structures, lies in the 30° range for the isolated compounds. The protonated (in concentrated sulfuric acid) starting azomethines were used as the standard compressed structures [2, 11, 12]. In a series of salicylalanilines [8] stabilization of the wavelengths of the K bands is achieved in the case of the p-CH_3-substituted compound (Fig. 1), and the angle of acoplanarity is 37°. It should be noted that the small difference between the angle of acoplanarity determined in this research and the angle noted in [8] can be explained by the fact that in the determination of the angle of acoplanarity of the azomethine system one must take into account the nonplanar orientation and the certain freedom of rotation of the aldehyde ring. In salicylalanilines the aldehyde ring is stabilized in the plane of the molecule due to the formation of an intramolecular hydrogen bond of the OH group with the unshared electron pair on the nitrogen atom. The protonated form of these compounds can be regarded as a completely planar system. In the case of a loose aldehyde ring its complete compression is probably not achieved. The intensity of the K band of the compressed structure is therefore somewhat reduced, and this is reflected in the decreased angle of acoplanarity. Thus, variation of the substituents in the aldehyde component demonstrated that replacement of the hydrogen atom in the 5 position of the thiophene ring by bromine and a nitro group gives rise to a bathochromic shift of the K band (Fig. 1). The bathochromic effect may be due to the increase in the chain of the conjugated system that is achieved by involvement of the unshared electron pairs of the substituents in the conjugation system and by the increase in the planarity of the aldehyde ring. In addition, the lowered values of the angles of acoplanarity of 2,2'-dithienyl-5-methylidyneanilines and 5'-nitro-2,2'-dithienyl-5-methylidyneanilines may be due to superimposition on the K absorption band of the azomethine system of the long-wave absorption band of the aldehyde components, which show up in the 350 nm range ($\varepsilon \sim 10{,}000$). Thus it may be stated that for the investigated systems the effect of the substituent in the amine ring on the conjugated system of the remaining portion of the molecule is considerably weakened at and above acoplanarity angles of 30°.

It was found to be impossible, within the framework of this research, to examine the effect of substituents on the change in the intensity of the K absorption bands. However, it should be noted that the tendencies, indicated in the literature, toward a decrease in the intensity of the K bands as the electron-acceptor properties of the substituents increase are not manifested sufficiently clearly and are not always confirmed. This follows from both the data in Table 1 [for example, in compounds of the I type (R = H), when R' = p-OH, ε = 12,550, whereas in the case R' = p-COOH, ε = 14,200; in compounds of the II type (R = Br), when R' = p-OCH_3, ε = 11,500, whereas in the case R' = p-COOH, ε = 16,500] and from some literature data. Thus ε = 15,300 for salicylal-p-toluidine [13], whereas ε = 13,600 for salicylal-p-aminophenol, ε = 11,500 for salicylalaniline [8], and ε = 12,400 for salicylal-p-aminobenzoic acid. This problem evidently requires special examination.

EXPERIMENTAL

The synthesis and isolation of the investigated compounds have been previously described [14-16]. The

UV absorption spectra of methanol solutions of the compounds were recorded with SF-4 and Spektromom-203 spectrophotometers. The use of other solvents was hindered by the very poor solubility of some of the compounds even in such solvents as dioxane and dichloroethane. In addition, as seen from the data in [11], replacement of the solvents has practically no effect on the character of the spectra of the azomethines. Hydrolysis was carried out in methanol containing concentrated hydrochloric acid at pH 1.5.

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EFFECT OF PROTONATION OF 2,2'-DITHIENYL CARBONYL COMPOUNDS ON THE DIRECTION OF SUBSTITUTION DURING NITRATION

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The nitration of 5-formyl- and 5-acetyl-2,2'-dithienyls by the action of potassium nitrate in 60-95% sulfuric acid solutions was studied. An increase in the acidity of the medium and a decrease in the reaction temperature from +30°C to −30°C lead to an increase in the percentage of the 5'-nitro isomer in the mixture.

The problems involved in the change in the direction of orientation during electrophilic substitution in the thiophene series have been previously elucidated [1]. In particular, Ya. L. Gol'dfarb and co-workers [2, 3] have studied the effect of protonation of the carbonyl group on the direction of substitution during the nitration of 2-formylthiophene and 2-acetylthiophene and have shown that the percentage of the 4-nitro isomer increases as the sulfuric acid concentration increases.

In the case of 5-substituted 2,2'-dithienyls the typical electrophilic substitution reactions take place in the 5' and 3' positions [4], and the ratio of the resulting isomers depends to a considerable extent on the character of the substituent. Thus nitro isomers (5'-NO_2/3'-NO_2) are formed in ratios of 1.58:1 and 1:2, respectively, in the nitration of 5-formyl-2,2'-dithienyl (I) [5] and 5-acetyl-2,2'-dithienyl (II) [6] with copper nitrate in acetic anhydride at 8-10°C.

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