SYNTHESIS AND SPECTROPHOTOMETRIC STUDY OF SOME AMINO DERIVATIVES OF THIOPHENE ANALOGS OF CHALCONE

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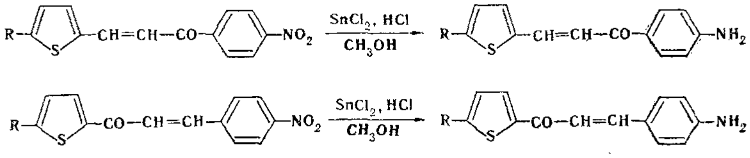
Eight amino derivatives of thiophene analogs of chalcone were obtained by reduction of the corresponding nitro derivatives with stannous chloride in concentrated hydrochloric acid, and their UV absorption spectra in dioxane were measured. The long-wave band was assigned to the corresponding fragments of the molecule on the basis of a comparison of the absorption curves of the investigated compounds with the curves of simpler compounds – aminoacetophenone, aminobenzalacetone, acetothienone, etc.

Continuing our research on the synthesis and study of the physicochemical properties of heterocyclic analogs of chalcones of the thiophene series [1] we synthesized two series of amino derivatives containing substituents with different electronic natures in the 5 position of the thiophene ring and an amino group in the 4 position of the benzene ring and measured their electronic absorption spectra in dioxane.

The synthesis of the compounds was accomplished by reduction of the corresponding nitro derivatives with stannous chloride in concentrated hydrochloric acid via the scheme [2]



where R = H, CH_3, OCH_3, and Br.

All of the derivatives that we synthesized are crystalline substances that are quite soluble in benzene and dioxane.

The structures of the compounds were confirmed by a study of their IR spectra. We observed three absorption bands in the region of the stretching vibrations of the amino group at 3240-3250, 3340-3350, and 3430-3450 cm^{-1} instead of the usual two bands.

It is known [3] that the empirical relationship $\nu_{sym} = 345.53 + 0.876\nu_{as}$ exists between the symmetrical and asymmetrical stretching vibrations of the amino group. In our case it is satisfied between the 3430-3450 and 3340-3350 cm^{-1} absorption bands. However, the vibrations at 3240-3250 cm^{-1} should evidently be assigned as in [4] to the intermolecular interaction between the amino and carbonyl groups.

The fact that the measurement of the IR spectra of potassium bromide pellets of the compounds shows a pronounced lowering of the carbonyl frequency (1623-1640 cm^{-1}) as compared with the frequencies observed for other chalcone derivatives (1660-1675 cm^{-1}) also speaks in favor of this assumption.

The presence of an amino group was also confirmed by diazotization.

The electronic spectra of heterocyclic analogs of chalcone have been repeatedly studied [5-7], but no one has studied the spectra of the amino derivatives.

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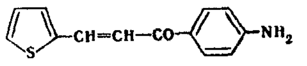
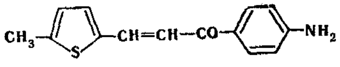
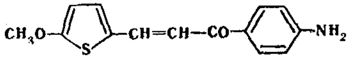
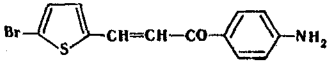
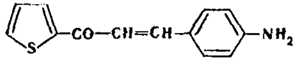
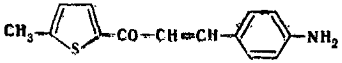
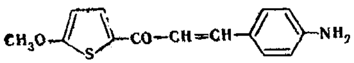
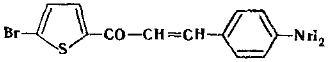
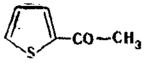
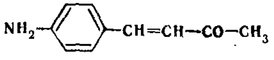
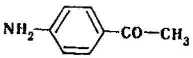
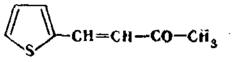
TABLE 1. Results of Measurements of the UV Spectra in Dioxane

No.		Formula	λ_{max} (lg ε), nm; δ, cm^{-1}								
series	compound		experimentally observed				calculated				
I	1				307 (4,03)	357 (4,12)	357 (4,12); 2800	306 (4,16); 3000	262 (3,94); 2100	233 (4,08); 3000	
	2		256 (4,05)			363 (4,50)	364 (4,50); 3700	305 (3,98); 3600	263 (3,94); 2100	246 (4,00); 3500	
	3		254 (3,85)			375 (4,50)	376 (4,50); 3500	307 (4,00); 2600	260 (4,65); 1500	247 (3,60); 3000	
	4		260 (4,25)			364 (4,40)	364 (4,40); 3600	308 (4,00); 3000	261 (4,23); 3800	250 (4,00); 3000	
II	5		250 (4,20)	270 (4,00)	300 (3,85)	390 (4,43)	387 (4,43); 4000	352 (4,00); 2100	313 (3,30); 3200	278 (3,93); 3000	253 (4,0); 3000
	6		250 (4,20)	270 (4,10)	308 (4,00)	390 (4,35)	385 (4,35); 3700	352 (4,05); 1900	308 (4,01); 3500	267 (4,08); 3000	243 (4,1); 4400
	7		250 (3,85)	270 (4,15)	320 (3,85)	384 (4,50)	392 (4,50); 4000	350 (4,45); 2000	317 (4,16); 3000	290 (4,10); 3000	260 (3,9); 3000
	8		260 (4,30)	275 (4,10)	305 (4,15)	394 (4,40)	394 (4,40); 4000	352 (4,95); 2000	305 (4,14); 3200	276 (4,15); 3500	263 (4,1); 3500
III	9		260 (3,88)	285 (3,76)							
	10		240 (3,98)		307 (4,03)	372 (4,44)					
	11		228 (3,89)	285 (4,06)	303 (4,33)						
	12		213 (3,49)		323 (3,80)						

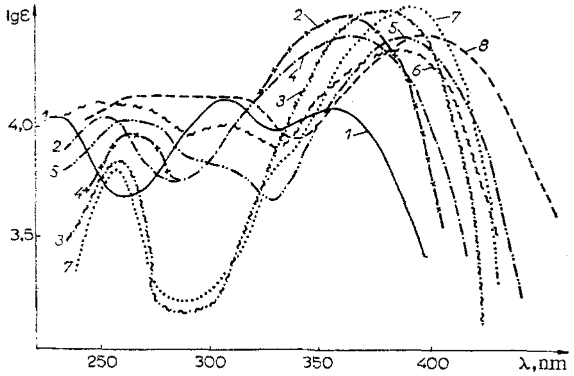


Fig. 1. Absorption spectra: 1) 1-(2-thienyl)-3-(4-aminophenyl)propen-3-one; 2) 1-(5-methyl-2-thienyl)-3-(4-aminophenyl)prop-3-ene; 3) 1-(5-methoxy-2-thienyl)-3-(4-aminophenyl)propen-3-one; 4) 1-(5-bromo-2-thienyl)-3(4-aminophenyl)propen-3-one; 5) 1-(2-thienyl)-3-(4-aminophenyl)propen-1-one; 6) 1-(5-methyl-2-thienyl)-3-(4-aminophenyl)propen-1-one; 7) 1-(5-methoxy-2-thienyl)-3-(4-aminophenyl)propen-1-one; 8) 1-(5-bromo-2-thienyl)-3(4-aminophenyl)propen-1-one in dioxane.

The ketones that we we investigated have complex electronic spectra consisting of mutually overlapping bands. The spectral curves of the individual compounds differ considerably from one another not only with respect to their positions, intensities, or forms of the bands but also with respect to their number. Thus, depending on the position of the carbonyl group in the aliphatic chain, two or four absorption bands are observed in the uv region (Table 1).

In an investigation of 2-thienyl phenyl ketone, Kaper and co-workers [8] assigned the band with a maximum at 282 nm to the $\pi \to \pi^*$ transition of the fragment including the substituted thienyl ring with the carbonyl group and the band with a maximum at 254 nm to the $\pi \to \pi^*$ transition of the arylcarbonyl fragment and the thienyl and aromatic rings.

This assignment is confirmed by the data in [9], in which 5-R-thienyl 2-phenyl ketones were investigated in various solvents. It was noted that the long-wave band undergoes a greater shift to the long-wave region than the short-wave band when substituents with different electronic natures are introduced.

The compounds that we investigated are vinylogs of 2-thienyl phenyl ketone. As seen from Fig. 1, the character of the absorption did not change when a vinylene group was introduced between the thiophene ring and the carbonyl group (compounds 1-4). As before, two absorption bands with maxima at, for example, 306 and 357 nm (curve 1) for 1-(2-thienyl)-3(4-aminophenyl)propen-3-one are observed. When a substituent is introduced in the 5 position of the thiophene ring, the maximum of the long-wave band is shifted bathochromically in conformity with its electronic nature; thus shifts of 6 nm, 18 nm, and 7 nm, respectively, are observed when methyl, methoxy, and bromo substituents are introduced. The observed band has an irregular form, but the shortwave band is not experimentally observed for the disubstituted compounds.

The second series of isomers differs from the first series with respect to the position of the carbonyl group. It is adjacent to the thiophene ring in this series of compounds. The character of the spectra is somewhat different.

In contrast to the first series, four absorption bands are observed here. It is interesting that the position of the maximum of the long-wave band remains almost unchanged as substituents are introduced. Three other bands appear on the curves in the form of inflections (Fig. 1).

In both the first and second series the observed bands are quite intense (log $\varepsilon \sim 4$ and higher); this is characteristic for the bands of $\pi \to \pi^*$transitions.

The observed absorption bands of the investigated compounds were broken down into individual components by the Yatsimirskii method [10]. Four to five absorption bands were obtained as a result of this analysis.

In order to examine the nature of the observed absorption bands we examined the spectra of simpler compounds — aminoacetophenone, aminobenzalacetone, acetothienone and its vinylogs, and their derivatives — and

TABLE 2. Yields, Melting Points, and Results of Analysis of Amino Derivatives of Thiophene Analogs of Chalcone

No.	Compound	mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
				N	S	N	S	
1	1-(2-Thienyl)-3-(4-aminophenyl)propen-3-one	94	$C_{13}H_{11}ONS$	6,32	14,09 14,07	6,10	13,95	45
2	1-(5-Methyl-2-thienyl)-3-(4-aminophenyl)propen-3-one	108	$C_{14}H_{13}ONS$	5,94	13,20 13,23	5,75	13,15	80
3	1-(5-Methoxy-2-thienyl)-3-(4-aminophenyl)propen-3-one	118	$C_{14}H_{13}O_2NS$	5,69	12,47 12,53	5,39	12,34	37
4	1-(5-Bromo-2-thienyl)-3-(4-aminophenyl)propen-3-one	152	$BrC_{13}H_{10}ONS$	4,82	10,42 10,46	4,54	10,38	79
5	1-(2-Thienyl)-3-(4-aminophenyl)propen-1-one	173	$C_{13}H_{11}ONS$	6,28	14,05 14,10	6,10	13,95	80
6	1-(5-Methyl-2-thienyl)-3-(4-aminophenyl)propen-1-one	160	$C_{14}H_{13}ONS$	5,92	13,15 13,18	5,75	13,15	76
7	1-(5-Methoxy-2-thienyl)-3-(4-aminophenyl)propen-1-one	163	$C_{14}H_{13}O_2NS$	5,70	12,44 12,48	5,39	12,34	50
8	1-(5-Bromo-2-thienyl)-3-(4-aminophenyl)propen-1-one	160	$BrC_{13}H_{10}ONS$	4,76	10,52 10,48	4,54	10,38	80

compared them with the curves of the investigated compounds. On the basis of this comparison it may be concluded that the long-wave band in compounds 5-8 belongs to the aminobenzalacetone fragment, whereas in the case of compounds 1-4 it is affiliated with the corresponding 5-thienyl-substituted fragment.

The data obtained in this study are in agreement with concepts regarding the localization of electronic transitions on individual fragments of molecules [11, 12].

EXPERIMENTAL

The investigated compounds were obtained by reduction of the corresponding nitrothiophene chalcones with stannous chloride in an alcoholic hydrochloric acid medium. For this, 0.5 g of the starting compound was dissolved in refluxing methanol, the reductive mixture consisting of 2.5 g of stannous chloride in 5 ml of concentrated hydrochloric acid was added, and the mixture was refluxed for no less than 2 h. The solution was poured into water, and the aqueous solution was made slightly alkaline with ammonia. It was then treated with benzene until the aqueous layer became colorless. The mixture was then distilled, without drying, to remove the benzene until cyrstals began to precipitate. The product was further purified by recrystallization to constant melting point. The yields, melting points, and results of elementary analysis are presented in Table 2.

The IR spectra of KBr pellets of the compounds (2 mg of the compount in 100 mg of KBr) at 700-3600 cm^{-1} were recorded with a UR-20 spectrometer. The uv spectra of $3-5 \cdot 10^{-3}$ M solutions of the compounds (at various layer thicknesses) were measured with an SF-4A spectrophotometer.

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