

ELECTRONIC SPECTRA OF α, β -UNSATURATED DIKETONE
DERIVATIVES OF THIOPHENE

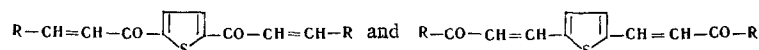
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The electronic absorption spectra of α, β -unsaturated diketone derivatives of thiophene of the p-dichalcone type have been studied. As a rule, these compounds have deeper colors than the monoketone thiophene analogs of the chalcones corresponding to them. Electron-donating substituents in the aromatic nucleus of 2,5-dicinnamoylthiophene and also the replacement of the phenyl radicals in them by heterocyclic radicals cause a bathochromic shift of the long-wave absorption maximum (frequency) which correlates satisfactorily with Hammett's σ constants. Some ketones with strong electron-donating groupings fluoresce under UV irradiation.

In preceding papers [1, 2] we have described the synthesis of α, β -unsaturated diketones from 2,5-diformyl- and 2,5-diacetylthiophenes which are heterocyclic analogs of p-dichalcone. The electronic absorption spectra of such systems have not so far been studied. Nevertheless, they are of interest not only for identification purposes but also for the theory of color, especially in view of recent investigations by A. I. Kiprianov and I. L. Mushkalo [3] on dyes with two chromophores present in more or less strong conjugation.

In the present work we have measured the absorption spectra in the UV and visible regions of unsaturated diketones of the type of



The measurements were carried out in dioxane and ethanolic solutions. The main spectral characteristics of the compounds studied and of some other substances for comparison are given in Tables 1 and 2, and characteristic absorption curves in Figs. 1 and 2.

All the unsaturated diketones studied (I-XXXI) are characterized in the spectral regions above 220 nm studied by two or three strong absorption bands ($\log \epsilon \geq 4$). In ethanolic solution the absorption maxima are displaced somewhat (from 1 to 30 nm) in the red direction as compared with dioxane solutions. This compels us to ascribe the corresponding absorption to $\pi - \pi^*$ electronic transitions in the individual chromophores.

As is well known [4], the long-wave absorption in α, β -unsaturated ketones has the nature of a transfer of charge from the ethylene orbital to the carbonyl π^* -orbital, and the red shift observed in ethanol is a consequence of the formation of a hydrogen bond of the type $>C=O \dots HO-$. It is a characteristic feature that in the diketones with donor substituents, V-IX, XII, because of their high basicity at the carbonyl group this long-wave shift is maximal. We have observed no $n - \pi^*$ electronic transitions due to the passage of unshared electrons from the orbital of the carbonyl oxygen or the sulfur of the heterocycle, and they are possibly masked by the $\pi - \pi^*$ bands.

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TABLE 1. Spectral Characteristics of the Unsaturated Diketones

$$R-CH=CH-CO-\text{S}-CO-CH=CH-R \quad \text{and} \quad R-CO-CH=CH-\text{S}-CH=CH-CO-R$$

R	Com- pound	λ_{max} , nm (ϵ)		Com- pound	λ_{max} , nm (ϵ)	
		dioxane	ethanol		dioxane	ethanol
Phenyl	I	345 (33880)	355*	II	396 (33880)	405 (43650)
		240 (11750)			282 (17380)	284 (19950)
4-Tolyl	III	358 (28180)	365*	IV	398,5 (36310)	407 (40740)
		275 (12300)			290 (19500)	291 (20420)
		242,5 (12590)				
4-Anisyl	V	372 (29500)	390*	VI	401 (38900)	409 (50120)
		287 (14800)			318 (15490)	327 (19950)
		246 (11750)			288 (15140)	292 (17380)
2,4-Dimethoxyphenyl	VII	376 (19950)	405*	VIII	402,5 (35480)	409 (44670)
		298 (18620)			284 (15850)	288 (18620)
		229 (15850)				
4-Hydroxyphenyl	IX	381 (26900)	402*	X	406 (36300)	416 (52480)
		287 (10470)			317 (14800)	325 (21380)
		247,5 (9770)			288 (15500)	290 (20420)
4-Dimethylamino-phenyl	XI	437 (31600)	456 (29180)	XII	422 (47860)	440 (54950)
		308 (25700)	311 (23660)		309 (25700)	315 (21880)
		228 (7943)	258 (13940)		227 (15850)	
4-Fluorophenyl	XIII	346 (33880)	346*			
		236 (15490)				
4-Chlorophenyl	XIV	346 (28840)	347*	XV	403 (34670)	407 (44670)
		237 (16220)			289 (29900)	292 (25700)
					233 (18620)	233 (19500)
4-Bromophenyl	XVI	347 (33880)	349*	XVII	404 (36300)	410 (38900)
		257 (16600)			292 (23400)	295 (24000)
					236 (17780)	238 (16980)
4-Nitrophenyl	XVIII	320*	320*	XIX	360 (22900)	362 (28840)
					280 (19950)	272 (25120)
					235 (13200)	236 (13800)
Pyrrol-2-yl	XX	432 (30200)	425 (32630)	XXI	413 (35500)	420,5 (46770)
		301 (16980)	305 (18240)		285 (14450)	287,5 (18200)
		227 (11750)	242,5 (5518)		227 (8128)	235 (12000)
2-Furyl	XXII	371 (30900)	373,5 (46770)	XXIII	400 (25480)	411,5 (44670)
		287 (14800)	295 (19950)		295 (16600)	300 (20900)
			239 (17780)		225 (8320)	234 (11750)
2-Thienyl	XXIV	375 (35480)	384 (39800)	XXV	402 (34670)	413 (37150)
		288 (14450)	295 (21880)		295 (16600)	301 (17000)
		257 (9772)	236 (19500)		233 (9550)	230 (16220)
2-Selenienyl	XXVI	385 (29500)	395 (46770)	XXVII	404 (38000)	418 (36300)
		304 (15140)	314 (30900)		299 (17400)	303 (16220)
		258 (10720)	235 (23440)			
2-Quinoly	XXVIII	303 (14500)	304*			
		247 (23400)				
2-Pyridyl				XXIX	403,5 (34670)	411 (30200)
					282 (13500)	282 (14130)
3-Pyridyl				XXX	398 (33100)	401 (34670)
					283 (13800)	281 (15140)

*In view of the low solubility of these compounds, the measurements are only qualitative.

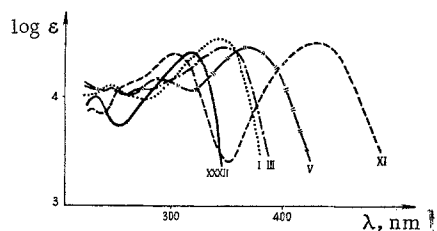


Fig. 1. UV spectra (in dioxane).

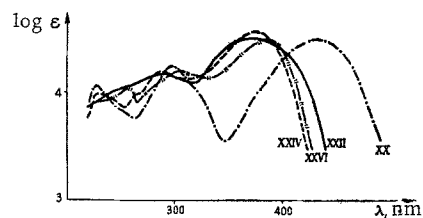


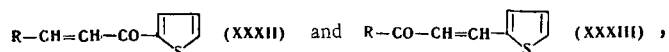
Fig. 2. UV spectra (in dioxane).

TABLE 2. Spectral Characteristics of Chalcones, Dichalcones, and Their Heterocyclic Analogs

Com- pound	Formula of the ketone	λ_{max} , nm (ϵ)	
		dioxane	ethanol
XXXI		315 (22000) 265 (17000)	—
XXXII		318 (25120) 229 (10470)	325* 228*
XXXIII		338 (19500) 271 (10000)	342*
XXXIV		352	275*
XXXV		322	320
XXXVI		305 228	270 312* 225*

* According to the literature [5].

In our systems we are dealing with two identical chromophores $-\text{CO}-\text{CH}=\text{CH}-$ connected by a thiophene ring which prevents conjugation between them to some degree or other. A. I. Kiprianov and I. L. Mushkalo [3] have drawn attention to the fact that "if each chromophore individually absorbs a similar number of quanta, then, when they are in conjugation, they influence one another in such a way that the frequency of one is raised and that of the other is lowered." We have explained this phenomenon by means of perturbation theory. In actual fact, I-XXX absorbed at longer wavelengths than the monoketones corresponding to them of the type [5]



and, in addition to this, have strong absorption in the short-wave region (Fig. 1). Thus, I absorbs in dioxane at 345 nm, while the monoketone XXXII (Table 2) has λ_{max} 319 nm (26 nm red shift). The long-wave shift of the absorption maximum of the diketone II is considerably greater than that of monoketone XXXIII, amounting to 58–63 nm.

Such a considerable red shift in I and compounds of similar structure (III, V, VII, etc.) as compared with corresponding monoketones also confirms the conclusion arrived at by two of us that the carbonyl group is not a complete insulator of conjugation in α, β -unsaturated ketones [5, 6], otherwise the absorptions of I and XXXII would be identical.

In XXXI, the two chromophores present are joined to one another through positions 3 and 5 of a thiophene ring, conjugation between them is interrupted (it is known that such positions in thiophene corresponds to the meta isomers in benzene [7, 8]), and the long-wave absorption scarcely differs from the absorption of the monoketones (there is even a slight blue shift of 4–8 nm). It is also easy to see that the two chromophores are conjugated better in positions 2 and 5 of the thiophene ring than in the 1,4 (para) positions of the benzene ring. Thus, I and II absorb at a longer wavelengths than their aromatic analogs XXXIV and XXXV, and the passage from the chalcone XXXVI to dichalcones XXXIV and XXXV involves a smaller red shift than the analogous transition among the thiophene derivatives (Tables 1 and 2). Thus, it is confirmed that the thiophene ring polarizes more readily than the benzene ring, as has been pointed out previously [9].

A comparison of λ_{max} of the long-wave bands of diketones of types I and II shows that a shift in the carbonyl group to the end of the conjugated chain deepens the coloration by 20–60 nm. This is, of course explained by the increased length of the chain of conjugation between the main chromophores – the carbonyl groups. An exception is formed by ketones containing powerful electron donors – the dimethylamino and pyrrol-2-yl groups (XI, XII, XX, XXI).

TABLE 3. Fluorescence of Some Diketones in Toluene

Compound	λ_{max} , nm		Stokes shift, cm ⁻¹	I*
	absorption	fluorescence		
VII	382	480	5350	0,16
XI	440	546	4460	0,74
XII	412	530	4880	0,08
XX	433	535	4400	0,24
XXI	410	485	3770	0,07

* Relative intensity with respect to anthracene.

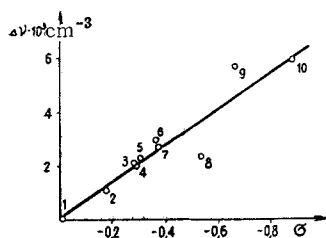


Fig. 3. Relationship between $\Delta\nu$ and σ : 1) H (1); 2) CH₃ (III); 3) OCH₃ (V); 4) 2-furyl (XXII); 5) 2-thienyl (XXIV); 6) 2-seleniyl (XXVI); 7) OH (IX); 8) 2,4-(OCH₃)₂ (VII); 9) pyrrol-2-yl (XX); 10) N(CH₃)₂ (XI).

The introduction of donor substituents into the aromatic nucleus of I leads to a considerable red shift of λ_{max} of the long-wave absorption and as a rule the intensity of the absorption of the adjacent band rises (Table 1). The shift in the frequency of absorption under the influence of donor substituents in I correlates with McDaniel and Brown's σ constants [10] according to the equation [11]

$$\left(\frac{1}{\lambda_{max}^R} - \frac{1}{\lambda_{max}^H} \right) \frac{N \cdot h \cdot c}{2,3 \cdot K \cdot T} = \rho \cdot \sigma,$$

where λ_{max}^R and λ_{max}^H are, respectively, the wavelengths of the absorption maxima of the long-wave band of the diketones having a substituent in the aromatic nucleus and without it, N is Avogadro's number, h is Planck's constant, c is the velocity of light, K is Boltzmann's constant, and T is the absolute temperature (Fig. 3). Only the point for VII departs appreciably from the correlation. This must probably be ascribed to steric hindrance [12], which is also confirmed by the fall

in the molar absorption coefficient. The replacement of the phenyl radicals in I by the heterocyclic radicals 2-furyl, 2-thienyl, 2-seleniyl, and pyrrol-2-yl also leads to an increase in the red shift in this sequence and confirms their electron-donating nature. If the σ parameters defined in [13] are used for the heterocyclic radicals mentioned, the corresponding points satisfactorily obey the equation of the correlation curve of Fig. 3.

So far as concerns electron-accepting substituents such as, for example, fluorine, chlorine, and bromine, they scarcely affect the position of λ_{max} . On the other hand, the introduction of a nitro group into I (XVIII) leads to a fairly considerable blue shift (by 25-35 nm). A hypsochromic effect is also observed when the phenyls in I are replaced by 2-quinolyl radicals (XXVIII), which can also be ascribed to the electron-accepting influence of the latter [14].

Substituents introduced into the aromatic nucleus of the diketone II show a comparatively slight influence on the long-wave absorption. Only a dimethylamino group (XII) leads to a bathochromic shift of 26-35 nm. It is also interesting that a nitro group (XIX) leads to a blue shift (by 36-43 nm), although under similar circumstances a considerable red shift is found in the monoketones (XXXIII) [5]. The replacement of the phenyls in II by heterocycles also has very little influence on the spectra. Only such a strong electron-donor as pyrrol-2-yl causes a bathochromic shift of 15-17 nm.

Previously, two of us [15] found that when in α, β -unsaturated ketones there was a marked shift of the electron density along the chain of conjugation from electron-donating groups to the carbonyl groups, photoluminescence was observed. It was found that this situation is preserved in a series of diketones studied. Compounds VII, XI, XII, XXIV, and XXVII, containing the powerful electron-donating groupings 2,4-dimethoxyphenyl, 4-dimethylaminophenyl, and pyrrol-2-yl fluoresce fairly well under the influence of UV light in toluene solution (Table 3). The Stokes shift is fairly considerable, amounting to 3770-5350 cm⁻¹. The intensity of the fluorescence increases markedly with an increase in the donor nature of the radicals and when the carbonyl group shifts in the direction of the thiophene ring. The maximum fluorescence is found for XI, but the fluorescent properties disappear in an acid medium because of the blocking of the diethylamino group.

EXPERIMENTAL

We have described the synthesis of the diketones I-XXX previously [1, 2].

3,5-Di(benzylidenediacetyl)-2-ethylthiophene (XXXI). With stirring, 1.5 ml of 40% potassium hydroxide solution was added dropwise to an ethanolic solution of 3,5-diacetyl-2-ethylthiophene [16] (0.01 mole) and benzaldehyde (0.02 mole). The crystals that deposited on the following day were filtered off, washed with ethanol, and recrystallized from acetic acid to constant melting point. Light yellow needles with mp 162°C. Yield 70%. Found, %: S 8.54. $C_{24}H_{20}O_2S$. Calculated, %: S 8.61.

The absorption spectra were measured on an SF-4A spectrophotometer with solutions having concentrations of from 1.5 to $3.5 \cdot 10^{-5}$ M. The solvents were purified by methods described in the literature [17].

The fluorescence spectra were recorded in an apparatus consisting of an ISP-51 spectrograph monochromator and a FEP-1 photoelectric attachment. The fluorescence was excited by UV rays at 365 nm isolated from the spectrum of DRSh-500 mercury lamp by means of UFS-3 filter. The measurements were corrected for the spectral sensitivity of the apparatus. The relative quantum yield was determined as described by Cherkasov [18].

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