ELECTRONIC SPECTRA OF α,β-UNSATURATED KETONES – INDOLE DERIVATIVES

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UDC 547.756:543.422.6

The electronic spectra of (3-indolyl)-, (1-methyl-3-indolyl)-, and (6-nitro-3-indolyl)-substituted α,β-unsaturated ketones were measured and interpreted. 3-Indolyl and N-methyl-3-indolyl substituents have a considerable bathochromic effect as compared with the phenyl group in the investigated systems as a consequence of the electron-donor effect, which surpasses that for 4-anisyl, 2,4-dimethoxyphenyl, 2-furyl, 2-thienyl, and 2-selenienyl and differs only slightly from 2-pyrrolyl. The introduction of electron-donor substituents into the p position of the benzene ring of 1-(3-indolyl)-3-phenyl-1-propenone causes a red shift of the long-wave absorption band, the difference in frequencies of which correlates with the Hammett σ substituent constants. Except for compounds containing a nitro group, 1-(3-indolyl)-3-aryl-3-propenones and their N-methyl derivatives fluoresce well in alcohol with $\lambda_{max} > 475$ nm.

The electronic spectra of α,β-unsaturated ketones that contain an indole ring have received very little study. Only quite recently a paper [1] appeared in which the UV spectra of several indole analogs of chalcones and the effect of the introduction of a methyl group in the α position of the heteroring and lengthening of the conjugation chain by one vinylene group were discussed.† Some fragmentary information on the spectra of unsaturated carbonyl compounds of the indole series is contained in [2-4].

We undertook a systematic investigation of the absorption and fluorescence spectra of isomeric 1-(3-indolyl)-3-arylpropenones with carbonyl groups in various positions in the aliphatic chain as a function of their chemical structure. In particular, the effects of N-methyl substitution, the introduction of a nitro group into the 6 position of the heteroring, and of groups that differ with respect to their electronic nature were evaluated. In the process, the spectra of 2,5-di(3-indolylmethylene)cyclopentanone and 2,6-di(3-indolylmethylene)cyclohexanone and some indole analogs of p-dichalcone were also studied.

The principal spectral characteristics of the indole analogs of chalcones in alcohol and dioxane solutions are presented in Table 1, while the spectral characteristics of their N-methyl derivatives are given in Table 2. In the overwhelming majority of cases, two well-expressed and extremely intense bands (ε 13,000-30,000), which are quite specific for each compound and can be used to identify them, appear on the spectral curves. On the basis of their high intensities and behavior toward solvents, they can be assigned to the $\pi-\pi^*$ electron transitions in the major chromophore – the basic conjugation chain, which includes a carbonyl group, since the latter is not a complete insulator of conjugation [5] – and in the quasiautonomous portion of the molecule (the benzoyl or analogous heterocyclic chromophore). On passing from dioxane solutions to alcohol solutions, the absorption maximum of the long-wave band of the indole chalcones is shifted to the red region by 12-25 nm, and this shift is considerably greater (almost double) for 3-propenones than for the isomeric 1-propenones (Tables 1 and 2). A similar phenomenon was also observed for other α,β-unsaturated ketones [6]. The reason for this phenomenon apparently consists in the fact that indole chalcones to a considerable degree recall merocyanines, for which positive solvatochromism is ob-

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†This study became known to us after our research had been completed.

A. M. Gorkii Kharkov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 949-953, July, 1972. Original article submitted June 25, 1971.

TABLE 1. Spectral Characteristics of Indole Analogs of Chalcones

Aryl (hetaryl)	1-(3-Indolyl)-3-aryl(hetaryl)-1-propenones			1-(3-Indolyl)-3-aryl(hetaryl)-3-propenones			Lumines., λ_{max}, nm (alcohol)
	comp.	λ_{max}, nm (ε)		comp.	λ_{max}, nm (ε)		
		ethanol	dioxane		ethanol	dioxane	
Phenyl	I	342 (22700), 280 (20180)	328 (15800), 280 (18300)	II	389 (23830), 260 (14690)	365 (21300), 265 (10470)	502
4-Tolyl	III	348 (23800), 281 (16300)	333 (24280), 280 (19350)	IV	388 (22000), 279 (15060)	365 (22190), 272 (12770)	500
4-Anisyl	V	353 (21230), 268 (12590)	338 (27670), 281 (13860)	VI	387 (22800), 285 (25700)	362 (24700), 282 (11940)	492
2,4-Dimethoxyphenyl	VII*	358 (14440), 255 (13640)	346 (17550), 248 (14940)	VIII	385 (25000), 281 (12270)	359 (17000), 279 (11720)	490
4-Dimethylaminophenyl	IX*	397 (33230), 320 (13900), 256 (17820)	386 (28870), 322 (11540), 255 (14800)				
4-Chlorophenyl	X	344 (20940), 281 (20070)	330 (21380), 280 (21640)	XI	395 (24340), 272 (16000)	369 (22500), 268 (15860)	510
4-Nitrophenyl	XII	360 (18000), 298 (22800)	348 (16370), 298 (18750)	XIII	416 (19170), 275 (19870)	395 (18440), 275 (20300), 255 (25700)	—
4-Xenyl	XIV	348 (13800), 280 (12900)	341 (33100), 280 (20100)	XV	396 (27400), 286 (19800)	372 (25320), 285 (19500), 255 (16500)	520
2-Furyl	XVI	357 (25390), 272 (20300)	342 (26300), 278 (10230)	XVII	396 (26700), 285 (14250)	372 (26680), 282 (12800)	510
2-Thienyl	XVIII	358 (26300), 273 (13000)	345 (26500), 272 (12800)	XIX	398 (26000), 280 (13150)	375 (24000), 277 (12800)	532
2-Selenienyl				XX	402 (26250), 286 (14060), 265 (10700)	379 (22900), 282 (13150), 255 (21000)	525
4-Pyridyl				XXI	408 (21960), 274 (11530)	380 (20400), 281 (11420)	539

* For VII, λ_{max} of luminescence is 470 nm compared with 538 nm for IX.

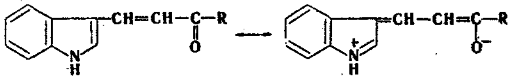
TABLE 2. Spectral Characteristics of N-Methylated Indole Analogs of Chalcones

Aryl (hetaryl)	1-(N-methyl-3-indolyl)-3-aryl(hetaryl)-1-propenones			1-(N-Methyl-3-indolyl)-3-aryl(hetaryl)-3-propenones			Lumines., λ_{max}, nm (ethanol)
	comp.	λ_{max}, nm (ε)		comp.	λ_{max}, nm (ε)		
		ethanol	dioxane		ethanol	dioxane	
Phenyl	XXII	346 (21960), 282 (20000)	336 (16430), 283 (18600)	XXIII	397 (22500), 267 (13050)	379 (22540), 257 (13500)	512
4-Tolyl				XXIV	397 (26500), 283 (18390)	379 (25190), 278 (14800)	506
4-Anisyl	XXV	356 (22560), 318 (14600), 270 (12700)	343 (25190), 256 (21730)	XXVI	396 (21210), 285 (11500)	374 (27700), 284 (31360)	500
2,4-Dimethoxyphenyl	XXVII	362 (20760), 270 (12000)	347 (19640), 255 (14600)	XXVIII	395 (24700), 282 (12040)	371 (55560), 279 (24900)	491
1-Methyl-3-indolyl				XXIX	387 (28470), 272 (16140)	367 (30900), 270 (17080)	477
4-Nitrophenyl				XXX	420 (20000), 275 (19700)	405 (19770), 277 (19500)	—
4-Pyridyl				XXXI	412 (21680), 272 (10680)	400 (18980), 283 (10600)	543

TABLE 3. Spectral Characteristics of Indole Analogs of Chalcones

Comp.	Name	λ_{max}, nm (ε)		Luminesc., λ_{max}, nm (in alcohol)
		ethanol	dioxane	
XXXII	1-(6-Nitro-3-indolyl)-3-phenyl-3-propenone	366 (23100), 268 (14000)	355 (21200), 265 (14400)	—
XXXIII	1-(6-Nitro-3-indolyl)-3-(4-chlorophenyl)-3-propenone	375 (23200), 273 (15160)	362 (21990), 272 (17460)	—
XXXIV	1-(6-Nitro-3-indolyl)-3-(4-nitrophenyl)-3-propenone	399 (24500), 275 (20300)	387 (20300), 282 (18400)	—
XXXV	2,5-Di(3-indolylmethylene)cyclopentanone	445 (5330), 285 (13000)	420 (31690), 279 (13890)	545
XXXVI	2,6-Di(3-indolylmethylene)cyclohexanone	425 (16900), 289 (16620)	395 (15420), 285 (17460)	535
XXXVII	1,4-Bis[β-(3-indolyl)acrylyl]benzene	412 (37250), 281 (27060)	388 (35950), 276 (34580)	—
XXXVIII	1,4-Bis[β-(N-methyl-3-indolyl)-acrylyl]benzene	418 (31090), 280 (21600)	401 (34890), 278 (27480)	414
XXXIX	1,4-Bis[α-(3-indolyl)acrylyl]benzene		363 (48060), 280 (41600), 267 (42500)	

served [7] because of the predominance of a nonpolar structure in the ground state and an increase in the contribution of the dipolar structure in polar solvents:



It is quite apparent from the spectral characteristics of the isomeric 1-(3-indolyl)-3-arylpropenones (I and II, III and IV, etc.) and their N-methyl derivatives (XXII and XXIII, XXV and XXVI) that λ_{max} of the long-wave band for ketones in which the carbonyl group is far removed from the indole ring (3-propenols) is shifted to the red region (by 24-57 nm) as compared with λ_{max} of the isomeric 1-propenones. It was previously established in [5] that the colors of α,β-unsaturated ketones of the aromatic and heterocyclic series are deeper, the further the carbonyl group is from the more electron-donor ring. Consequently, 3-indolyl and 1-methyl-3-indolyl groups in the investigated systems give rise to a considerable electron-donor effect, which exceeds that for 4-tolyl, 4-anisyl, and 2,4-dimethoxyphenyl groups and is only somewhat less than that observed for 4-dimethylaminophenyl. Moreover, methylation generally has a relatively slight effect on the color of the chalcone analogs (see Tables 1 and 2).

It seemed of interest to compare the bathochromic effect of 3-indolyl and 2-pyrrolyl groups in α,β-unsaturated ketones. A comparison of the spectral data obtained in this study with the corresponding data on pyrrole chalcones presented in [6] demonstrates that there is no substantial difference in the color of these compounds.

For the most part, a small hypsochromic shift that does not exceed 10 nm can be noted for indole derivatives. N-Methylated indole and pyrrole derivatives differ just as little from one another. It can be assumed that the 3-indolyl group in the static state has somewhat less of a donor effect than the 2-pyrrolyl group, although according to the pK_a values of the conjugate acids of the pyrrole and indole analogs of chalcones that we determined [8], the reverse pattern is observed when they are protonated.

The introduction of electron-donor substituents into the benzene ring far removed from the carbonyl group (I, III, V, VII, and IX) or replacement of a phenyl group by a 2-furyl or 2-thienyl group (XVI-XVIII) has a considerable effect on the position of λ_{max} of the long-wave band of indole chalcones. In this case, the observed red shifts, expressed in wave numbers (cm^{-1}), correlate satisfactorily with the σ constants in the equation

$$2.3\,\frac{hc}{KT}\left(\frac{1}{\lambda_H}-\frac{1}{\lambda_R}\right)=\rho\sigma \qquad (r=0.98),$$

where λ_H is the absorption maximum of I, and λ_R is the absorption maximum of the substituted chalcone analog. The ρ constant for indole ketones is appreciably smaller than for ordinary chalcones [6]; i.e., the bathochromic effect induced by identical donor groups is much smaller in the first case than in the second. Thus, for example, a dimethylamino group in indole ketones leads to a red shift of 55-58 nm, while the corresponding shift in chalcones reaches 105-116 nm [9]. This can be explained by the fact that under the influence of a strong electron-donor effect of the 3-indolyl group, the carbonyl group is already polarized to a considerable degree, and its further polarization is hindered, which is reflected in the electronic spectra. Electron-donor substituents introduced into the phenyl group adjacent to the carbonyl group (II, IV, VI, and VIII) have almost no effect on the position of the long-wave band. On the other hand, electron-acceptor groups (chloro and nitro groups) (X-XIII) induce a greater bathochromic shift in 3-propenones than in 1-propenones. In addition, the introduction of a nitro group into the 6 position of the indole ring, i.e., transition to 1-(6-nitro-3-indolyl)-3-aryl-3-propenone (compare II and XI with XXXII and XXXIII) (Table 3) leads to a substantial hypsochromic shift of the long-wave band (10-23 nm), which should be ascribed to weakening of the nucleophilic character of the indole ring.

The electronic absorption spectra of 2,5-dibenzylidenecyclopentanone, 2,6-dibenzylidenecyclohexanone, and several of its heterocyclic analogs were previously examined in [10], and it was demonstrated that fixing of the carbonyl group in space by means of a cyclopentanone ring creates better conditions for conjugation than in the case of cyclohexanone derivatives. A similar phenomenon is also observed in a comparison of the spectra of 2,5-di(3-indolylmethylene)cyclopentanone (XXXV) and 2,6-di(3-indolylmethylene)cyclohexanone (XXXVI) (Table 3). The cyclopentanone derivatives are more deeply colored than the cyclohexanone derivatives. However, a comparison of the spectra of 2,6-dibenzylidenecyclohexanone and 2,5-dibenzylidenecyclopentanone with the spectra of indole analogs (XXXV, XXXVI) persuasively demonstrates that the 3-indolyl group in these systems also gives rise to a considerable electron-donor effect, and the observed bathochromic effect amounts to 93-105 nm (in alcohol). The same large bathochromic shift is noted if the phenyl groups at the ends of the molecule in p-dichalcone (λ_{max} 320 nm in dioxane) are replaced by 3-indolyl groups.

Two of us [11] have found favorable conditions for the development of fluorescence in α,β-unsaturated ketones, the chief of which is the presence of a strong donor-acceptor interaction in their molecules for a certain length of the chain of conjugation between the electron-donor group and the electron-acceptor carbonyl group. Proceeding from the data of this study, one should have expected the presence of fluorescence properties for a series of α,β-unsaturated ketones that contain an indole ring. In fact, in accordance with [11], all 1-(3-indolyl)-3-arylpropenones, except for compounds that contain a nitro group (a nitro group generally completely quenches fluorescence), as well as their N-methyl derivatives and XXXV, XXXVI, and XXXVIII fluoresce well in alcohol solution with a rather significant Stokesian shift, while λ_{max} for the fluorescence of the investigated compounds varies from 470 to 545 nm.

EXPERIMENTAL

The synthesis of the unsaturated ketones (indole derivatives) is described in [12].

The spectra of 1-5 $\cdot 10^{-5}$ M solutions were measured with an SF-4A quartz spectrophotometer.

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