ELECTRONIC SPECTRA OF ISOMERIC para-DICHALCONES AND para-DICHALCONE ANALOGS

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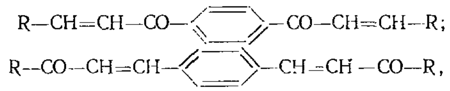
UDC 541.651:547.572

The electronic absorption spectra of chalcones have been rather carefully studied. Szmant and Basso [1] established the relationship between the position of the absorption maximum of the long-wavelength band and the electronic nature of the substituents introduced into one of the chalcone aromatic rings. Recently, we have shown [2] that the shift in λ_{max} for chalcones expressed in wave numbers which occurs on account of electron-donating substituents on the benzene ring located away from the carbonyl group is satisfactorily correlated by Hammett σ-constants of the substituents. We decided to study the electronic spectra of para-dichalcones and find the influence of substituents of various chemical types on these spectra as well as the effect of substituting the phenyl ring by some multicyclic aromatic and heterocyclic groups as such data are lacking in the literature.

To this end we measured spectra of isomeric para-dichalcones in dioxane and chloroform*:



in which R = phenyl (I, II), 4-tolyl (III, IV), 4-anisyl (V, VI), 2,4-dimethoxyphenyl (VII, VIII), 2,4,6-trimethoxyphenyl (IX, X), 4-dimethylaminophenyl (XI, XII), 4-chlorophenyl (XIII, XIV), 4-bromophenyl (XV, XVI), 4-nitrophenyl (XVII, XVIII), 4-p-biphenyl (XIX, XX), β-naphthyl (XXI, XXII), 9-anthryl (XXIII, XXIV), 2-pyrryl (XXV, XXVI), 2-furyl (XXVII, XXVIII), 2-thienyl (XXIX, XXX), and 2-selenienyl (XXXI, XXXII). The spectral data obtained are presented in Table 1.

The preparation of diketones I-XXXII has been described by us earlier [3] except for compounds VII, IX, XX, XXI, XXIII-XXV which were obtained analogously by crotonic condensation of 1,4-diacetylbenzene or terephthalic dialdehyde with the corresponding carbonyl compounds (Table 2). Recrystallization was performed from chlorobenzene (VII, IX, and XX), dimethylformamide (XXI, XXIII), or acetic acid (XXIV, XXV).

The absorption spectra were taken on an SF-4A spectrophotometer at solution concentrations from 2 to $5 \cdot 10^{-5}$ mole. The solvents were purified according to methods described in the literature [4].

The luminescence spectra were taken on the apparatus consisting of a monochromator, ISP-51 spectrograph, and FÉP-1 photoelectric attachment. Luminescence was excited by UV radiation at 365 nm separated from the spectrum of a DRSh-500 mercury quartz lamp by a UFS-3 light filter. Corrections were introduced for the spectral sensitivity of the apparatus. The relative quantum yield was determined according to Cherkasov [5].

In the near UV region, chalcone in dioxane and chloroform solutions has an absorption band with maxima at 305 and 310 nm, respectively. It is possible to represent para-dichalcone I or II as a double chalcone in which two identical chromophores are connected to each other through the central benzene ring.

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*The solvents were selected taking into account that one of these solvents forms hydrogen bonds with the diketones studied and the other does not.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 12, No. 1, pp. 91-96, January, 1970. Original article submitted December 23, 1968; revision submitted May 12, 1969.

TABLE 1. Spectral Characteristics of Dichalcones

$R{-}C_6H_4{-}CH{=}CH{-}CO{-}C_6H_4{-}CO{-}CH{=}CH{-}C_6H_4{-}R$ (para-dichalcones)			$R{-}C_6H_4{-}CO{-}CH{=}CH{-}C_6H_4{-}CH{=}CH{-}CO{-}C_6H_4{-}R$ (para-isodichalcones)		
compound	λ, nm, (ε)		compound	λ, nm, (ε)	
	dioxane	chloroform		dioxane	chloroform
I	320 (38020)	321 (37150) 275 (20240)	II	350 (47150) 270 (12300) 235 (14790)	355 (44670) 275 (13490)
III	334 (44670) 275 (18620)	334 (33110) 251 (23440)	IV	350 (47860) 235 (17380)	357 (46770) 295 (16220)
V	352 (41690) 278 (20420)	357 (37150) 277 (25120)	VI	354 (47860) 240 (18200)	358 (57540)
VII	369 (31620) 275 (22910)	375 (37150) 280 (22390)	VIII	325 (30200) 270 (13800)	362 (45710) 267 (12120)
IX	370 (36310) 278 (21380)	379 (31620) 280 (22390)	X	336 (40470) 265 (6310)	345 (32360)
XI	427 (51290) 314 (16600) 273 (20890)	437 (47860) 320 (14130) 275 (21480)	XII	394 (44670) 310 (26300)	407 (35480)
XIII	320 (33110) 272 (17780) 235 (14790)	321 (31620) 265 (24240)	XIV	355 (44670) 285 (16220) 235 (17780)	358 (43650)
XV	317 (25120) 262 (23990)	324 (30900) 267 (24270)	XVI	345 (33110) 290 (17380) 235 (17380)	345 (30900) 270 (18620)
XVII	322 (41690) 267 (30900)	318 (29350) 270 (30410)	XVIII	362 (39810) 270 (25120)	365 (29510) 273 (21380)
XIX	343 (39810) 273 (30900)	349 (34670) 252 (36810)	XX	357 (47860) 232 (20890)	353 (36310) 318 (32360)
XXI	363 (22910) 270 (30200)	365 (19050) 273 (31620)	XXII	347 (47860) 250 (56230)	350 (41690)
XXIII	420 (14130) 255 (125000)	435 (14130) 255 (125000)	XXIV	385 (28180) 365 (43650) 255 (125000)	385 (42660) 365 (3981) 255 (125000)
XXV	390 (39810) 273 (28840)	393 (25200) 289 (19500)	XXVI	362 (40710) 243 (11220)	367 (33880)
XXVII	353 (43650) 277 (18200)	358 (43550) 280 (19860)	XXVIII	360 (56220) 237 (13180)	364 (55480)
XXIX	353 (41690) 280 (20890)	360 (41590) 281 (23320)	XXX	360 (50120) 238 (12880)	365 (54950)
XXXI	363 (37150) 320 (19950) 290 (20890)	370 (34040) 285 (19590)	XXXII	362 (39810) 305 (17380) 218 (13800)	367 (46770)

Kiprianov and Mushkalo have drawn attention to the fact that a separation of two absorption bands is observed in the case that there is interaction of the two chromophores absorbing similar quanta. Indeed, the long-wavelength absorption maximum of dichalcone I is red-shifted by 11 to 15 nm, while the maximum of isodichalcone II is red-shifted by 45 nm, and, furthermore, a shorter wavelength absorption band at 270-275 nm is observed (Fig. 1). The fact that dichalcones I and II absorb at longer wavelengths than does chalcone also supports the opinion earlier put forward by us that the carbonyl group does not act as a complete isolator of conjugation in the α,β-unsaturated ketones [7].

Introduction of substituents of various chemical types into the benzene ring located at the distal ends of the molecules do not affect the long-wavelength band maxima of dichalcones and isodichalcones equally. Thus, donor groups (methyl, methoxy) in the case of I, III, and V lead to a significant red shift while in the case of isodichalcones (II, IV, and VI), these donor substituents do not have a significant effect on the spectral data. The dimethylamino group in dichalcones (see XI) leads to a red shift of 107-116 nm while in the case of isodichalcones, the shift is only by 44-52 nm (XII). Analogously, the replacement of the phenyl

TABLE 2. Dichalcones

Compound	mp	Appearance	Found, %	Formula	Calculated, %	Yield, %
VII	205	Bright yellow needles	C 73,30 H 5,74	$C_{28}H_{26}O_6$	C 73,35 H 5,72	68
IX	262	"	C 69,20 H 5,80	$C_{30}H_{30}O_8$	C 69,48 H 5,83	60
XX	286—287	Light yellow plates	C 88,0 H 5,33	$C_{36}H_{26}O_2$	C 88,30 H 5,34	80
XXI	266	"	C 87,3 H 5,05	$C_{32}H_{22}O_2$	C 87,65 H 5,05	75
XXIII	270—271	Orange plates	C 89,1 H 4,8	$C_{40}H_{26}O_2$	C 89,19 H 4,86	75
XXIV	276	"	C 89,08 H 4,78	$C_{40}H_{26}O_2$	C 89,19 H 4,86	66
XXV	218	Golden plates	N 8 ,86	$C_{20}H_{16}N_2O_2$	N 8,86	72

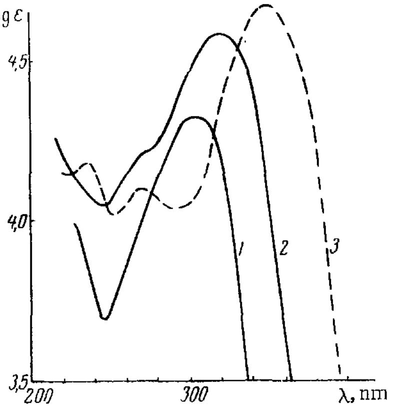

Fig. 1

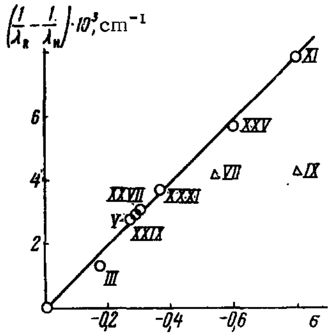

Fig. 2

Fig. 1. Absorption curves in dioxane: 1) chalcone; 2) para-dichalcone; 3) para-isochalcone.

Fig. 2. Dependence of λ_{max} on Hammett σ-parameters for a series of para-dichalcones ($r = 0.99$, $\rho = 19.9$, $S = \pm 0.5$).

group by electron-donating heterocyclic groups such as 2-pyrryl, 2-furyl, 2-thienyl, and 2-selenienyl (see XXV-XXXII) lead to a red shift while the red shift for dichalcones is much greater than for isodichalcones. The bathochromic effect of these heterocyclic groups increases in the series furyl < thienyl < selenienyl < pyrryl and corresponds to the σ-parameters determined earlier by us [8].

The red shift observed for the series of dichalcones (type I) under the influence of electron-donating substituents correlates well with Hammett σ-parameters according to the equation

$$\left(\frac{1}{\lambda_H}-\frac{1}{\lambda_R}\right)\frac{Nch}{2.3RT} = \sigma\rho$$

(Fig. 2). 2,4-Dimethoxyphenyl and 2,4,6-trimethoxyphenyl groups in isodichalcones as in the case of chalcones [9] create steric hindrance and force the molecule out of coplanarity. This is seen from the fact that the corresponding points do not lie on the correlation curve for dichalcones and in the isodichalcone series, VI, VIII, and X show a drop in absorption intensity and X is even blue-shifted.

Electron-acceptor groups (Cl, Br, NO_2), on the other hand, do not have a significant effect on the long-wavelength absorption of dichalcones while for isodichalcones, chloro and nitro groups lead to a relatively small red shift (5-10 nm).

TABLE 3. Diketone Luminescence

Compound	λ, nm		Quantum yield (chloroform)	Compound	λ, nm		Quantum yield (chloroform)
	crystalline	in chloroform solution			crystalline	in chloroform solution	
V	520	—	—	XXIII	590	583	0,50
VII	515	490	0,22	XXVI	497	—	—
IX	530	490	0,19	XXIX	493	—	—
XI	610	593	1,0	XXX	520	—	—
XXI	530	—	—				

Lengthening the conjugation chain by introduction of a second benzene ring (see XIX-XXII) (biphenyl or naphthyl systems) in dichalcone I lead to a significant bathochromic effect corresponding to 23-28 nm and 43-44 nm. The same groups in isodichalcones have a slight bathochromic shift not exceeding 10 nm. Replacement of the phenyl group by the 9-anthryl group also has a greater effect for dichalcones than for isodichalcones. The absorption intensity decreases rather sharply indicating steric effects and a very pronounced vibrational structure characteristic for naphthalene and anthracene spectra [10] is observed in the spectral curves.

The long-wavelength absorption in isodichalcones as in the case of ordinary chalcones should be assigned to $\pi-\pi^*$ electronic transitions related to charge transfer from the double bond orbital to the carbonyl π^* orbital.

The red shift for λ_{max} observed in going from dioxane solutions to chloroform solutions is the result of hydrogen bond formation between the solvent and carbonyl groups increasing the polarity of the latter and thus lowering the energy for electronic transition. The red shift characteristically resulting from a change in solvent is greater for those ketones which contain donor moieties, that is, which should form more stable hydrogen bonds.

Dichalcones I and II under conditions of UV irradiation do not luminesce in the visible region of the spectrum. On the other hand, 1,4-distyrylbenzene fluoresces rather well [11]. Thus, introduction of carbonyl groups into 1,4-distyrylbenzene leads to a loss of luminescence. However, there is no reason to assume that this effect is related to vibrational deactivation and apparently, arises by the fact that singlet and triplet $n-\pi^*$ levels are unsuitably placed relative to the $\pi-\pi^*$ levels for luminescence [12] and by the singlet–triplet interconversion processes which occur.

The introduction of strong electron-donating groups into para-dichalcones (I) (VII, IX, and XI) or increase of the conjugation system by replacement of the phenyl group by an anthryl group (XVIII) leads to the more rapid decrease of $\pi-\pi^*$ transition energy than the decrease in $n-\pi^*$ transition energy [13] and the corresponding compounds begin to luminesce (see Table 3). Thus, dichalcones VII, IX, and XI luminesce in both the solid state and in solution. We have already noted that upon an increase in the donor–acceptor interaction in α,β-unsaturated ketones, luminescence quantum yields increase [14]. Dichalcone XI luminesces especially well while the quantum yield falls sharply for compounds VII and IX. Luminescence in chloroform is characteristically stronger and red-shifted relative to dioxane solution (for example, for XI, λ_{max} = 563 nm) because chloroform forms hydrogen bonds with carbonyl groups, thus increasing the polarity of the carbonyl groups which leads to an increase in donor–acceptor interactions. Thus, in dioxane solution, only diketones XI and XXIII (λ_{max} = 563 and 565, respectively) of the diketones studied shows significant luminescence. Some of the diketones studied luminesce only in the solid state (Table 3).

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