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Spectral Properties and Photochemical Activity of Chalcone Derivatives

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Abstract — A relationship is found between spectral–luminescent and photochemical properties for mono- and disubstituted chalcone derivatives $R^1CO–CH=CHR^2$ [R^1, R^2 = Ph, 4-FC_6H_4, 4-BrC_6H_4, 2-furyl, 2-thienyl, 4-$(PhCONH)C_6H_4$, 4-$NH_2C_6H_4$, 4-$Me_2NC_6H_4$].

Earlier we showed [1] that the spectral–luminescent and photochemical properties of chalcone derivatives are much dependent on the nuture of substituents in the styryl moiety. On the other hand, we found that the benzamide and nitro groups in the ketone moiety exhibit inhibiting effect, and this finding is consistent with data of Tsukerman *et al.* [2, 3] who reported that the CO group in α,β-unsaturated ketones does not completely destroy conjugation.

In this connection we considered it worthwhile to compare the optical properties and the photochemical activity of a series of monosubstituted chalcones with similar substituents either in the ketone or in the stylbene moiety, and also to examine the behavior of disubstituted analogs, including corresponding structural isomers. The choice of substituents was determined not only by their donor–acceptor ability, but also by their feasibility, like, for example, with amide chalcone derivatives, for functionalization, which would aid in introducing chalcone chains into polymers. Practically, such investigations allow modeling properties of new chalcone polymers. It should be noted that no data on the effect of the structure of the ketone moiety on the luminescence of chalcone derivatives are still available, except for some information for disubstituted chalcones derived from dimethylaniline (295 K) [3, 4], whereas investigations on the effect of the same factor on *trans–cis* isomerization have been restricted to heterocyclic analogs [5].

The objects for study were compounds **I**–**XXIII**, both previously unknown and earlier studied, such as heterocyclic chalcone analogs, for which we obtained new information.

$R^1CO–CH=CHR^2$
I–**XXIII**

I, $R^1 = R^2$ = Ph; **II**, R^1 = 4-BrC_6H_4, R^2 = Ph; **III**, R^1 = 2-furyl, R^2 = Ph; **IV**, R^1 = 2-thienyl, R^2 = Ph; **V**, R^1 = 4-$(PhCONH)C_6H_4$, R^2 = Ph; **VI**, R^1 = 4-$NH_2C_6H_4$, R^2 = Ph; **VII**, R^1 = Ph, R^2 = 4-BrC_6H_4; **VIII**, R^1 = Ph, R^2 = 2-furyl; **IX**, R^1 = Ph, R^2 = 2-thienyl; **X**, R^1 = Ph, R^2 = 4-$(PhCONH)C_6H_4$; **XI**, R^1 = Ph, R^2 = 4-$NH_2C_6H_4$; **XII**, R^1 = 4-BrC_6H_4, R^2 = 4-$(PhCONH)C_6H_4$; **XIII**, R^1 = 2-furyl, R^2 = 4-$(PhCONH)C_6H_4$; **XIV**, R^1 = 2-thienyl, R^2 = 4-$(PhCONH)C_6H_4$; **XV**, R^1 = 4-FC_6H_4, R^2 = 4-$NH_2C_6H_4$; **XVI**, R^1 = 4-BrC_6H_4, R^2 = 4-$NH_2C_6H_4$; **XVII**, R^1 = 2-furyl, R^2 = 4-$NH_2C_6H_4$; **XVIII**, R^1 = 2-thienyl, R^2 = 4-$NH_2C_6H_4$; **XIX**, R^1 = 2-thienyl, R^2 = 4-$Me_2NC_6H_4$; **XX**, R^1 = 4-$(PhCONH)C_6H_4$, R^2 = 4-BrC_6H_4; **XXI**, R^1 = 4-$(MeCONH)C_6H_4$, R^2 = 2-furyl; **XXII**, R^1 = 4-$(MeCONH) \cdot C_6H_4$, R^2 = 2-thienyl; **XXIII**, R^1 = 4-$NH_2C_6H_4$, R^2 = 4-BrC_6H_4.

The experimental results are given in Tables 1 and 2. As solvent at 295 K we most frequently used *N*,*N*-dimethylacetamide. With amides and amines, measurements in ethanol and heptane–toluene were also performed.

In terms of structure, the compounds can be divided into 3 groups: 3-(aryl, heteryl)-1-phenyl-1-propen-3-one derivatives (**II**–**VI**) (1st group), 1-(aryl, heteryl)-3-phenyl-1-propen-3-one derivatives (**VII**–**XI**) (2nd group), and disubstituted chalcone derivatives **XII**–**XXIII** (3rd group).

Monosubstituted chalcones I–XI. In the series R^1, R^2 = 4-bromophenyl–2-furyl–2-thienyl–*N*-benzoyl–4-aminophenyl–4-aminophenyl the frequency shift (Δν) of the long-wave π,π^*-absorption band with

Table 1. Spectral-luminescent properties and photochemical activity of chalcone derivatives in *N*,*N*-dimethylacetamide at 295 K (in air)[a]

Comp. no.	Absorption			Fluorescence				Photolysis	
	λ_a	ν_a	ε	ν_f	$\Delta\nu(H1/2)$	$\Delta\nu_{Ss}$	$\varphi_f \times 10^2$	λ_{ex}	$F \times 10^2$
I	312	32.1	2.68					313	29
II	316	31.6	2.99					313	22
III	321	31.2	2.90					313	18
IV	323	31.0	3.06					313	23
V	330	30.3	3.95					334	14
V[b]	334	29.9	3.31					334	15
V[c]	318	31.4	2.77					313	16
VI	365	27.4	2.43	17.2–17.8	7.6	~10.0	0.05	366	2.3
VI[b]	364	27.6	2.41	17.2–17.8	7.6	~10.0	0.06	366	0.9
VI[c]	321	31.1	2.44	26.3–25.6	8.4	~5.0	$<10^{-3}$	334	16
VII	316	31.6	3.09	–	–	–	–	313	23
VIII	342	29.2	2.74	18.9–19.6	8.6	~10.0	0.11	366	3.0
IX	345	29.0	2.19	–	–	–	–	366	3.2
X	353	28.3	3.62	21.7, 19.2	–	6.3	0.18	366	21
X[b]	349	28.7	3.53	20.6	4.2	8.1	0.36	366	22
X[c]	338	29.6	1.92	–	–	–	–	334	19
XI	406	24.6	2.83	19.3	2.9	5.3	17	406	6.8
XI[b]	403	24.8	2.85	18.7	3.0	6.2	1.1	406	1.5
XI[c]	339 sh, 355, 370 sh	29.5 sh, 28.1, 27.0 sh	2.48	23.7 sh, 22.7, 21.5 sh	4.6	5.4	0.01	366	8.3
XII	359	27.9	2.89	21.7, 19.2		6.2	0.10	366	21
XIII	358	27.9	2.83	21.7, 19.2		6.2	0.11	366	11
XIV	360	27.8	3.95	21.7, 19.2		6.1	0.13	366	13
XV	410	24.4	3.15	19.1	2.9	5.3	16	406	6.8
XVI	416	24.0	3.04	18.5	3.0	5.5	23	406	1.1
XVII	412	24.3	3.10	19.4	2.9	4.9	20	406	4.9
XVIII	415	24.1	3.34	18.7	3.1	5.4	29	406	2.1
XIX	424	23.6	3.50	18.0	3.1	5.6	58	406	0.1
XX	334	29.9	3.85					313	15
XXI	348	28.7	3.10					366	1.7
XXII	351	28.5	3.44					366	2.5
XXIII	370	27.0	2.29	17.9	7.2	9.1	0.10	366	2.0

[a] (λ_a, ν_a) Long-wave absorption maximum, nm, $\times 10^{-3}$, cm^{-1}, $\varepsilon \times 10^{-4}$, l mol^{-1} cm^{-1}; ($\nu_f$, $\Delta\nu(H\ 1/2)$, $\Delta\nu_{Ss}$) maximum, fluorescence band half-width, and Stokes' shift, $\times 10^{-3}$, cm^{-1}; (φ_f) fluorescence quantum yield; (F) photoreaction quantum yield at λ_{ex}, nm. [b] In 95% ethanol. [c] In heptane–toluene, 10 : 1. The data for compounds **V** and **X** are taken from [1] and for compounds **X** and **XI** in 95% ethanol, from [6].

respect to chalcone (**I**) is 500–900–1100–1800–5300 and 500–2900–3100–4100–7500 cm^{-1} for the 1st and 2nd groups, repectively. The largest shifts are characteristic of substituents stongly involved in charge transfer, which is consistent with theoretical and experimental data for chalcone and its derivatives [7–9]. As follows from the published data, the first π,π^* band of compounds **VII**–**XI** (2nd group) is formed mostly by the charge transfer from the 1-aryl or 1-heteryl substituent on the propenone moiety and is a bathochromically shifted π,π^* band of 1,3-diphenyl-1-propen-3-one (**I**). Substitution in the ketone moiety of chalcone (compounds **II**–**VI**) results in that the $\pi \rightarrow \pi^*$ transition is mostly contributed by the charge transfer from the 3-aryl or 3-hetaryl substituent on the propenone moiety, i.e. it is a superposition of the π,π^* band of chalcone and a bathochromically shifted band of the corresponding acetophenone (compounds **II**, **V**, and **VI**) or acetylheteryl derivatives (compounds **III** and **IV**). This explains the slightly stronger absorption

Table 2. Luminescent parameters at 77 K in 95% etanol[a]

Comp. no.	ν_f	ν_{ph}	φ_{ph}/φ_f	τ_{ph}	E_S	E_T	ΔE_{ST}
II	–	18.3, 16.7, 15.2	$>10^2$	0.005		18.3	
III	–	18.2 sh, 17.9, 16.9, 15.4	$>10^2$	0.010		18.2	
IV	–	18.3 sh, 18.0, 16.9, 15.4	$>10^2$	0.008		18.3	
V	–	18.4, 17.8 sh, 16.9, 15.3	$>10^2$	0.012	(24.8)	18.4	(6.2)
VI	20.1, 19.3 sh	18.5, 18.0 sh, 17.0, 15.4	1.1	0.013	22.9[b]	18.5	4.4
VII	–	17.8, 16.2, 14.6	>10	0.007	–	17.8	–
VIII	23.7, 22.6, 21.1 sh	16,5, 14.9	1.0	0.010	23.7	16.5	7.2
IX	23.4, 22.4, 21.1 sh	16.4, 14.8	0.6	–	23.4	16.4	7.0
X	23.5, 22.1, 21.0 sh	17.6, 16.1, 14.5	0.1	0.016	23.5	17.6	5.9
XI	21.7 sh, 20.6, 19.5 sh	15.9 sh, 14.3	0.1	0.029	21.7	15.9	5.8
XII	23.2 sh, 21.9, 20.8 sh	17.6, 16.0, 14.5	0.2	–	23.2	17.6	5.6
XIII	23.5 sh, 22.7, 21.5 sh	17.7, 16.1, 14.6	0.1	0.013	23.5	17.7	5.8
XIV	23.5 sh, 22.5, 21.2 sh	17.7, 16.1, 14.6	0.2	0.010	23.5	17.7	5.8
XV	21.7 sh, 20.6, 19.5 sh	[v]	<0.1		21.7	(15.9)	(5.8)
XVI	19.8, 19.2 sh	[c]	<0.1		20.9[b]	(15.1)	(5.8)
XVII	19.8, 18.9 sh	[c]	<0.1		21.7[b]	(15.9)	(5.8)
XVIII	20.1, 19.4 sh	[c]	<0.1		21.2[b]	(15.4)	(5.8)
XIX	19.4, 18.7 sh	[v]	<0.1		20.6[b]	(14.8)	(5.8)
XX	24.4, 23.1, 21.9 sh	18.0, 16.5, 14.9	20	0.007	24.4	18.0	5.6
XXI	24.3, 22.9, 21.7 sh	16.5, 15.7 sh, 14.9	1.5	0.006	24.3	16.5	7.8
XXII	24.0, 22.7, 21.5 sh	16.6, 15.0	0.8	0.007	24.0	16.6	7.4
XXIII	20.2	18.4 sh, 18.0, 16.8, 15.3			22.4[b]	18.4	4.0

[a] (ν_f, ν_{ph}) Fluorescence and phosphorescence absorption maxima, $\times 10^{-3}$, cm^{-1}; (φ_{ph}/φ_f) phosphorescence-to-fluorescence quantum yield ratio; (τ_{ph}) phosphorescence lifetime, s; (E_S, E_T, and ΔE_{ST}) energies of the S_1 and T_1 states, and singlet–triplet splitting, $\times 10^{-3}$, cm^{-1}; values in parentheses are proposed values. [b] Determined by the blue boundary of the fluorescence band. [c] Unresolved band at $(18.0–12.5) \times 10^3$ cm^{-1}.

of 1st group derivatives compared with 2nd group derivatives (cf. **IV**, **IX** and **V**, **X**). The local absorption of benzalacetone shows up in solutions of amine **VI** in polar solvents as the second π,π^* band (ν_a 32700 cm^{-1}) (Fig. 1a, spectra *2* and *3*). Compound **VI** is the only 1st group derivative to fluoresce at room temperature, while with an extremely low quantum yield ($10^{-5} \times 10^{-3}$) (Table 1; Fig. 1a, spectra *4*–*6*). Noteworthy is a broad structureless fluorescence band with a large Stokes' shift $\Delta\nu_{Ss}$ (up to 10^4 cm^{-1} in polar solvents). The parameters of this band and the intensity of fluorescence do not change in going from *N*,*N*-dimethylacetamide to ethanol. The energies of $\pi\rightarrow\pi^*$ transitions in solutions, obtained from Fig. 1a, are ~29000 (heptane) and ~23400 cm^{-1} (*N*,*N*-dimethylacetamide, ethanol). Taking account of the E_S value for the $n\pi^*$ level, $(24 \pm 1) \times 10^3$ cm^{-1} [10], we can conclude that in the first case emission involves the $S_2(\pi\pi^*)$ level, and in the second, as a result of inversion, the $S_1(\pi,\pi^*)$ level. In both cases, apparently, a strong vibronic interaction with the $S(n\pi^*)$ state takes place. It is known [11] that the first π,π^* band of 4-aminoacetophenone which is a model for compound **VI** is a charge-transfer band. The parameters of this band in heptane (283 nm, 35300 cm^{-1}, 1.7×10^4 l mol^{-1} cm^{-1}) and ethanol (318 nm, 31400 cm^{-1}, 2.2×10^4 l mol^{-1} cm^{-1}) suggest that the cross conjugation of the $C_6H_5CH{=}CHCO$ and $4\text{-}NH_2C_6H_4CO$ fragments in aminochalcone **VI** red shifts the lowest $\pi\rightarrow\pi^*$ band by ~4000 cm^{-1}, but the intensity of this band is preserved. The same changes are characteristic of the emission band. The emission band of 4-aminoacetophenone in ethanol is a fairly narrow band at 31200–23800 cm^{-1} (ν_f ~ 27000 cm^{-1}), which corresponds to a $\Delta\nu_{Ss}$ value of $\sim 4.5 \times 10^3$ cm^{-1}. The 0–0-transition energy in alcohol is ~28000 cm^{-1}, i.e. it is higher than that of 3-(4-aminophenyl)-1-phenyl-1-propen-3-one (**VI**) by 4600 cm^{-1}, in agreement of the value of the spectral shift (vide supra).

The 2nd group contains three fluorescing compounds. Replacement of the phenyl group by 2-furyl (compound **VIII**) gives rise to a weak fluorescence similar in parameters and nature to the fluorescence of amine **VI**, but the corresponding band is shifted bathoflorically to the band of the latter by ~2000 cm^{-1}. Benzamide **X** exhibits fluorescence; it is 2–3 times stronger compared with heterocyclic chalcone derivative **VIII** but still remains extremely weak (φ_f ~10^{-3}). The fluorescence band half-width $\Delta\nu(N\ 1/2)$ in ethanol, while having a large Stokes' shift, is half that of compound **VIII**. In *N,N*-dimethylacetamide a two-band fluorescence is observed, resulting, according to speculations in [1], from torsion of the phenyl groups about the amide C(O)NH bond in the excited state. The strongest fluorescing 2nd group compound is amine **XI** (Table 1; Fig. 1b, spectra *4*–*6*). Earlier we studied the luminescence of this compound in ethanol solutions [6]. Our present data on the luminescence in *N,N*-dimethylacetamide and heptane reveal both macroscopic and microscopic solvent effects on the properties of the fluorescent state. In heptane the $S_0 \rightleftarrows S_1$ bands are notably structured, while the emission band half-width is half that of compound **VI** (4600 and 8400 cm^{-1}, respectively). Therewith, the luminescence intensity increases by an order of magnitude. Apparently, the localization of the excitation energy in the styrene π system weakens the perturbing effect of the n,π^* state. In going from the hydrocarbon to a more polar solvent, the ν_a absorption maximum of compound **XI** shifts red, 3300 (ethanol) and 3500 cm^{-1} (*N,N*-dimethylacetamide), and the fluorescence band undergo a bathofloric shift by 4000 and 3400 cm^{-1}. In going from ethanol to an aprotic solvent (*N,N*-dimethylacetamide), the latter band preserves its shape but shifts blue by 600 cm^{-1} (Fig. 1b, spectra *5* and *6*), and, what is more, the quantum yield (φ_f) increases 15 times. Obviously, the quenching in ethanol is associated with protolytic reactions in the S_1 state, which are favored by ≡N···HO intramolecular bonding [12].

The difference in the luminescent properties of 1st and 2nd group compounds is most evident in ethanol glasses at 77 K (Table 2). Compounds **II**–**V** in these conditions, like at 295 K, do not fluoresce but exhibit weak short-lived phosphorescence whose band and 0–0 transition are only slightly affected by the structure of the ketone moiety. The overall emission spectrum of amine **VI** was independent on λ_{ex} (313, 366, and 406 nm) and contained two bands of comparable intensity (Fig. 2a). The overall luminescence quantum yield was ~0.1. Notable is the fact that such a stong electron donor as NH_2 only slightly affects parameters of the $T \rightarrow S_0$ transition. The phosphorescence spectrum of this compound (Fig. 2a, spectrum *3*) is similar, both in position and vibrational structure (500, 1000, and 1600 cm^{-1}), to those of the other compounds of this group (Table 2) but shifted red relative to the corresponding band of 4-aminoacetophenone (ν_{00} 22 700 cm^{-1}) [11] by ~4000 cm^{-1}. The energies of the *T* states (E_T) for compounds **II**–**VI** can be estimated at $(18.3 \pm 0.2) \times 10^3$ cm^{-1}, which is close a value proposed for chalcone (18.0×10^3 cm^{-1} [10]). Note that our estimates for compounds **III** and **IV** are much lower than those of Reinhardt *et al.* [5], based on the results of quenching of photochemical *trans*–*cis* isomerization in solutions at room temperature (~21 000 cm^{-1}). The small *S*–*T* splitting for amine **VI** (4400 cm^{-1}) is presumably associated with the anomalous bathofloric shift of the fluorescence band on freezing, which has been observed, for instance, with 4-aminoacetophenone (shift ~2000 cm^{-1}) [11]. Probably, such a behavior is explained by appearance in these conditions of a more planar conformation, which is explained by a contribution of charge transfer into the S_1 state.

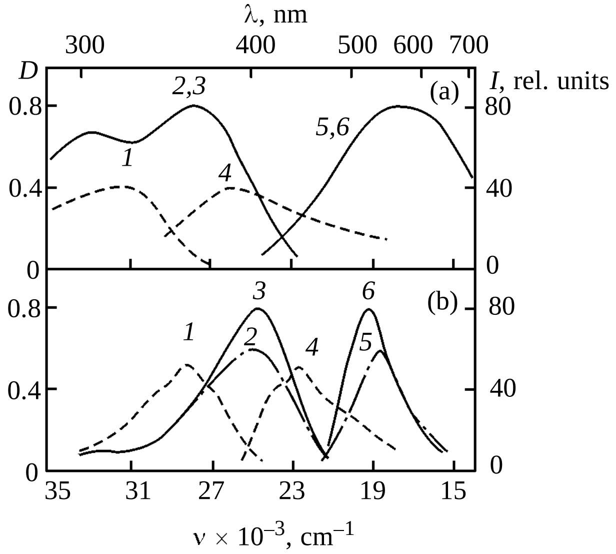

Fig. 1. Absorption (long-wave band) and fluorescence spectra in (*1, 4*) heptane, (*2, 5*) ethanol, and (*3, 6*) *N,N*-dimethylacetamide at 295 K. (a) 3-(4-Aminophenyl)-1-phenyl-1-propen-3-one (**VI**) and (b) 1-(4-aminophenyl)-3-phenyl-1-propen-3-one (**XI**).

The luminescent properties of compounds **VII**–**XI** at 77 K are quite diverse (Table 2). The compounds all, except for 4-bromophenyl derivative (**VII**), exhibit both fluorescence and phosphorescence. Compound **VII** exhibits phosphorescence only, with the parameters of the $T \rightarrow S_0$ transition and the φ_{ph}/φ_f values close to those characteristic of 1st group compounds. With **VIII**–**XI**, the fraction of the long-lived component changes from 0.5 to 0.1. The phosphorescence spectrum is less structured than the fluorescence spectrum. The vibration quantum energies for the latter are

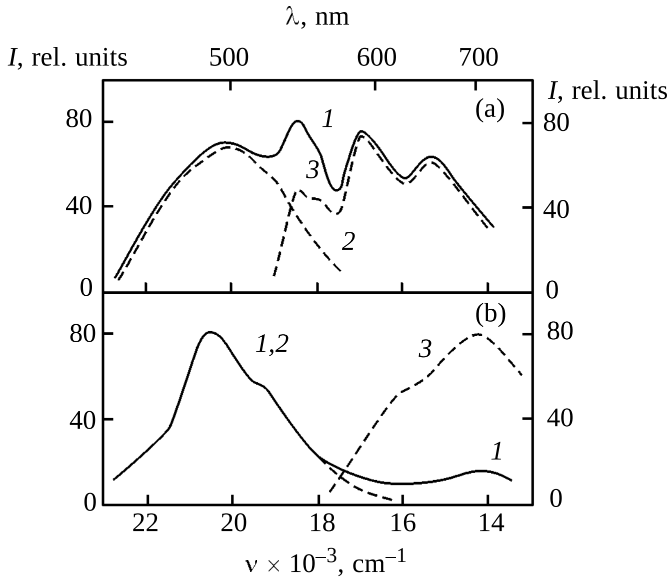

Fig. 2. Emission spectra in ethanol glasses (77 K): (*1*) overall spectrum, (*2*) fluorescence, and (*3*) phosphorescence, λ_{ex} 366 nm (for a and b, see the legend to Fig. 1).

1100, 1300, and 1400 cm^{-1} ($\nu_{C=C}$, ν_{C-H}), whereas the long-lived luminescence spectrum contains two prevailing frequencies: 1500 and 1600 cm^{-1} (ν_{C-O}). The *S–T* splitting is 6000– 7000 cm^{-1}, which corresponds to lower $S_1(\pi\pi^*)$ and $T_1(\pi\pi^*)$ states but is hardly consistent with the proposed localization of the triplet energy on the carbonyl moeity. The emission bands of amine **XI** are least structured and correspond to least energy transitions for all 1st and 2nd group compounds (Fig. 2b, spectra *1–3*). The φ_f for compound **XI**, measured using a new reference (see Experimental) was 0.65, which is close to the previously measured value of 0.56 [6]. Thus, about 40% of compound **XI** molecules at 295 K in the absence of any other competing processes pass to the *T* level. The overall luminescence quantum yield for the other compounds of the series was lower by an order of magnitude.

As follows from data in Table 2, the E_T values for 2nd group compounds, unlike those for **II**–**VI**, are much structure-dependent and vary by ~2000 cm^{-1}: from 17800 (**VII**) to 15900 cm^{-1} (**XI**). The E_T values for heterocyclic chalcone analogs **VIII** and **IX** (Table 2) are close to previously reported values (16700 and 16900 cm^{-1}, respectively [5]).

The ability of chalcone and its derivatives to photochemical *trans–cis* isomerization, as we proposed in [1], depends both on “physical” and “chemical” factors. The first factor is directly related to spectral-luminescence properties and assumes three sequences of levels (in the order of growing energy) [schemes (1)–(3)]:

$$S_0\text{–}T(\pi\pi^*)\text{–}T(n\pi^*)\text{–}S(n\pi^*)\text{–}S(\pi\pi^*), \tag{1}$$

$$S_0\text{–}T(\pi\pi^*)\text{–}T(n\pi^*)\text{–}S(\pi\pi^*)\text{–}S(n\pi^*), \tag{2}$$

$$S_0\text{–}T(\pi\pi^*)\text{–}S(\pi\pi^*)\text{–}T(n\pi^*)\text{–}S(n\pi^*). \tag{3}$$

Reactive is the $T(\pi\pi^*)$ level. Our estimates for the energies of the $S(n\pi^*)$ and $T(n\pi^*)$ states, in the absence of the possibility of direct measurements, are 23000–25000 and 21500–23000 cm^{-1}, respectively [5, 10].

The quantum yield of the photochemical *trans–cis* isomerization (*F*) of 1st and 2nd group compounds in *N,N*-dimethylformamide varies tenfold: from 0.23 (**IV**) to 0.02 (**VI**) (Table 1). It is important to note that the most sensitive to photolysis are compounds **II**–**V**, **VII**, and **X**, which have $E_T \geq 17600$ cm^{-1} (Table 2). The fact that compounds **II**–**V** and **VII** do not fluoresce suggests realization in them, like in parent chalcone **I**, of scheme (1).

The low value of τ_{ph}, the values of vibration frequencies in the phosphorescence spectra of compounds **II**–**XI**, and also, as judjed the low intensity of luminescence, the higher rate of the $T \rightsquigarrow S_0$ transition are likely to result from the nonplanar molecular structures of chalcone [10] and its derivatives and the perturbing effect of the C=O group [6]. Concerning the latter factor, we suppose that such a perturbation is produced by the vibronic interaction of the $T(\pi\pi^*)$ and $T(n\pi^*)$ levels, resulting from from overlap of their potential surfaces. This effect, as follows from the theoretical and experimental evidence for azanaphthalene molecules [13, 14], is stronger than those associated with dipole and spin–orbital interactions. In our case this conclusion is indirectly evidenced by the fact that the highest τ_{ph} value is characteristic of amine **XI** which has the lowest $T(\pi\pi^*)$ level in the series in question (Table 2). The fairly strong fluoresce of compound **XI** in *N,N*-dimethylacetamide suggests realization of scheme (3). Benzoylation of compound **XI** increases E_S (energy of the S_1 state) by 2000 cm^{-1}, quenches the fluorescence by 2 orders of magnitude, and increases *F* three times, implying realization of scheme (2) for compound **X**.

Further investigations (Tables 1 and 3) revealed two more features of the photoreaction. First, in going from *N,N*-dimethylacetamide to heptane the *F* value for inactive amine **VI** increased several times, whereas for most other compounds in the **II**–**XI** series it remained invariable. Specifically, the *F* values for heterocyclic chalcone analogs **III** and **IV** in heptane

Table 3. Rate of photochemical *trans–cis* isomerization as a function of medium and dissolved gas[a]

Solvent	$[O_2]$	k_q	Comp. no.	E_S	φ_{ST}	F (Ar)	$F(O_2)$	τ_T	k_r	k_d
			VI	29.0	1.0	23	14	2.9	7.9×10^7	2.6×10^8
			X	26.8	1.0	19	19	–	–	–
			XI	25.3	1.0	14	7.2	4.2	3.3×10^7	2.1×10^8
95% ethanol	6.4×10^{-3}	5.4×10^9	**V**	27.8	1.0	18	15	5.8	3.1×10^7	1.4×10^8
			VI	23.4	–	1.9	0.8	40.0	–	–
			X	24.0	0.9^b	22	22	–	–	–
			XI	21.4	–	1.8	1.2	15	–	–
N,N-Dimethylacetamide[c]	4.9×10^{-3}	7.7×10^9	**V**	28.2	1.0	18	14	7.5	2.4×10^7	1.1×10^8
			VI	23.4	–	4.2	2.2	24	–	–
			X	24.3	0.9^b	21	18	4.5	5.2×10^7	1.7×10^8
			XI	21.5	0.4	14	9.0	15	2.4×10^7	4.4×10^7

[a] ($[O_2]$) Concentration of dissolved oxygen, M [15]; (k_q) diffusion reaction rate constant, l mol^{-1} s^{-1}, calculated from the viscosity [16]; (E_S) energy of the $S(\pi\pi^*)$ level in solution, $\times10^{-3}$, cm^{-1}, from Fig. 1 and Table 1; (φ_{ST}) quantum yield of population of T states; [F(Ar), $F(O_2)$] quantum yields of photoreaction in Ar and O_2, $\times10^2$; (τ_T) lifetime of the T state in solution, ns; (k_r, k_d) rate constants of photoreaction and of energy degradation of electron excitation on the T level, respectively, s^{-1}. [b] From data of [6].
[c] Data for $[O_2]$ and k_q in dimethylformamide.

were 0.20 and 0.23, i.e. they are close or coincide with those in isooctane (0.21 and 0.23 [5]). Second, the quantum yield of photolysis of inactive compounds **VI**, **VIII**, **IX**, and **XI** increased 1.5–3-fold in the absence of oxygen. In particular, the F values for heterocyclic chalcone analogs **VIII** and **IX** in *N,N*-dimethylacetamide saturated with argon were 0.08 and 0.09, respectively, against 0.03 in air. Consequently, the reactivity depends not only on E_T, but also on the lifetime of the T state in the solution (τ_T). Probably, the two values are interrelated, as it follows from the above comparative estimates for amine **XI** at 77 K. Table 3 compares the photochemical activity of amines **VI** and **XI** and their benzoyl derivatives **V** and **X** in various solvents saturated with argon or oxygen. Data on photoreaction quenching with oxygen were used to calculate τ_T values and the corresponding constants of photoreactions. The following assumptions were made: O_2 has no effect on φ_{ST} (φ_f is independent of the presence of absence of O_2); the latter value for compound **XI** in *N,N*-dimethylacetamide is the same as in ethanol at 77 K; and reaction with the singlet oxygen $^1O_2$ formed by quenching of T states can be neglected [17]. It was found the rate of photoisomerization of amides **V** and **X**, unlike amines, only slightly depends on solvents and dissolved gases. For all the four compounds in heptane and for benzoylamine **V** in polar solvents, $E_S(\pi,\pi^*) > E_S(n,\pi^*)$, i.e. scheme (1) is realized: φ_{ST} and F have limiting values. The fact that amine **VI** falls out of the series of 1st group compounds **II**–**VI** in terms of F in *N,N*-dimethylacetamide (vide supra) can now be explained by that in this solvent its E_S is about 6000 cm^{-1} lower than in heptane, i.e. scheme (2) is realized. As can be noted the τ_T values in the hydrocarbon are the lowest and the rate constants of competing photoreactions are the highest compared with ethanol and *N,N*-dimethylacetamide. The slightly reduced photochemical activity compared with the parent chalcone, whose F is equal to 0.30 and is independent of oxygen content, is associated with increased ratio k_d/k_r (rate constants of energy degradation of electron excitation and of photoreaction), probably, as a result of the “chemical” effect.

For amine **XI** in *N,N*-dimethylacetamide, where scheme (3) is realized and the quantum yield of intersystem crossing is no higher than 0.4, the probability of photochemical reaction proved the same as in heptane. To explain this fact, it will suffice to compare the k_d values in the two solvents. The rate of the $T \rightsquigarrow S_0$ transition in *N,N*-dimethylacetamide is 5 times lower than in heptane, which probably results from >NH···O–R< intermolecular hydrogen bonding. With amides **X** and **V**, this factor is obviously less important. Estimation of this factor for amine **VI** (the most stable in N,N-dimethylacetamide) is prevented by the lack of data on the φ_{ST} value, since, if scheme (2) is realized, absorbed energy can be lost at steps *a* and *b* [scheme (4)] [18].

$$S(\pi\pi^*) \overset{a}{\rightsquigarrow} T(n\pi^*) \overset{b}{\rightsquigarrow} T(\pi\pi^*). \qquad (4)$$

In going from *N,N*-dimethylacetamide to ethanol, F for both amines reduces manyfold, most strongly for 2nd group amine **XI**. The lack of correlation of this effect with τ_T suggests that the energy is dis-

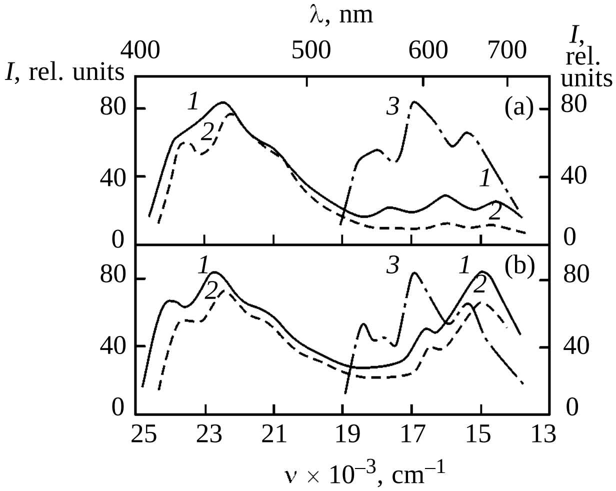

Fig. 3. Overall emission spectra of (*1*) disubstituted and (*2, 3*) monosubstituted chalcones in ethanol glasses (77 K), λ_{ex} 320–380 nm. (a): (*1*) 1-[4-(Benzoylamino)-phenyl)-3-(2-thienyl)-2-propen-3-one (**XIV**), (*2*) 1-(4-(benzoylamino)phenyl)-3-phenyl-2-propen-3-one (**X**), and (*3*) 1-phenyl-3-(2-thienyl)-2-propen-3-one (**IV**); and (b): (*1*) 3-[4-(acetylamino)phenyl)-1-(2-thienyl)-2-propen-3-one (**XXII**), (*2*) 3-phenyl-1-(2-thienyl)-2-propen-3-one (**IX**), and (*3*) 3-[4-(benzoylamino)phenyl)-1-phenyl-2-propen-3-one (**V**).

sipated before the molecule passes to the *T* level. On the other hand, in view of the above-noted features of luminescence in this solvent (Table 1; Fig. 1b), we can suppose that the processes that compete with fluorescence and the $S_1 \rightsquigarrow T$ transition are quenching of the S_1 state both by cleavage of an ≡N···HO intermolecular hydrogen bond and by adiabatic proton phototransfer [12]. With amine **XI**, the latter process is obviously prevailing.

The rate of the photochemical *trans–cis* isomerization for 1st and 2nd group compounds generally depends on E_S, E_T, and φ_{ST}, and on the environment which strongly affects both τ_T and the overall photoreaction pattern.

Separation of the “chemical” factor from the variety of photophysical parameters affecting *F* and depending, in their turn, the “chemical” structure of R^1 and R^2, seems not quite correct. The only substituent that exerts a minimal effect on the photochemical parameters is 4-Br in each of the chalcone phenyl rings (Tables 1 and 2). The *F* values for structurally similar monosubstituted compounds **II** and **VII** are almost equal to each other, i.e. here the “chemical” factor is also not obvious.

Disubstituted chalcones XII–XXIII. Replacement in 1-[4-(benzoylamino)phenyl]-3-phenyl-2-propen-3-one (**X**) of the phenyl substituent by 4-bromophenyl (compound **XII**), 2-furyl (compound **XIII**), and 2-thienyl (compound **XIV**) has almost no effect on the optical properties of the solutions at 295 K, except for a slight reduction of the φ_f value (Tables 1 and 2). The fluorescence and phosphorescence bands of compound **XIV** in ethanol glasses (77 K) (Fig. 3a) correspond to radiation transitions in monosubstituted derivative **X**, i.e. the excitation energy is localized mostly on the styryl moiety. However, the slightly changed pattern of the $S_1 \rightarrow S_0$ band and doubled relative efficiency of the $T \rightarrow S_0$ transition (Fig. 3a, spectra *1* and *2*), as well as reduced τ_{ph} value for the first of the listed compounds compared with the second point to perturbing effect of 2-acetylheteryl, i.e. to interaction of the amide group and 2-thienyl in compound **XIV**. The slightly reduced *F* values for compounds **XIII** and **XIV** compared with **X**, which have nothing to do with fluorescence quenching (cf. **XII** and **XIII**) (Table 1), are also associated with this interaction.

Compounds **XX**–**XXII** are derivatives of 3-[4-(benzoylamino)phenyl)-1-phenyl-2-propen-3-one (**V**) and structural isomers of compounds **XII**–**XIV**. Spectrally and photochemically, compounds **XXI** and **XXII** with a heterocyclic radical R^2 are generally similar to compounds **XIII** and **XIV**, i.e. the key chromophoric system is heterylmethylene–acetone. Thus, the emission bands (77 K) of compound **XXII** are similar to those of monosubstituted **IX** but not of compound **V** (Table. 2; Fig. 3b, curves *1*–*3*). Interaction between R^1 and R^2 shows up in a red shift (600 cm^{-1}) of the $S_1 \rightarrow S_0$ band and a blue shift (200 cm^{-1}) of the $T \rightarrow S_0$ band, as well as in a slightly increased φ_{ph}/φ_f value compared with **IX**. Absorption bands of disubstituted **XXI** and **XXII** are shifted bathochromically (500 cm^{-1}) and are 1.1–1.5 times stronger compared with monosubstituted **VIII** and **IX**. At the same time, the photochemical activity decreases 1.3–1.7 times (Table 1).

If the styryl moiety of a disubstituted chalcone contains a weakly electron-donor substituent (R^2 = 4-BrC_6H_4) and the ketone moiety, a benzamide [R^1 = 4(PhCONH)C_6H_4] (**XX**) or an aminophenyl radical (R^1 = 4-$NH_2C_6H_4$) (**XXIII**), the key chromophoric system is acetylaryl which is modeled by the corresponding monosubstituted compound, i.e. amide **V** and amine **VI**. As a result, the spectral–luminescent properties and the photochemical activity of both pairs of compounds are similar (Tables 1 and 2). The fluorescence band of compound **XX** at 77 K can be used to estimate E_S for its nonflurescing model compound **V**, which leads to a reasonable estimate for the *S*–*T* splitting, ΔE_{ST} (6200 cm^{-1}) (Table 2). Apparently, for compound **XX**, like for **V**, scheme (1) is realized with the highest φ_{ST} and F values.

The key π system in the fluorescing disubstituted chalcones **XV**–**XIX**, derivatives of 1-(4-aminophenyl)-3-phenyl-2-propen-3-one (**XI**), is the styrene π system. In their optical and photochemical properties they fit scheme (3), which shows up in strong fluorescence and a low F value (Tables 1 and 2). Since these compounds exhibit no phosphorescence, in Table 2 we give the E_T values estimated under the assumption that **XV**–**XIX** have the same S–T splitting as parent amine **XI**. The fact that compound **XIX** has the lowest E_T value (14.8×10^3 cm^{-1}) is consistent with our previous results for 1-(4-dimethylaminophenyl)-3-phenyl-2-propen-3-one [1].

The trends in fluorescent properties in the series R^1 = Ph (**XI**)– 4-FC_6H_4 (**XV**)–4-BrC_6H_4 (**XVI**)–2-furyl (**XVII**)–2-thienyl (**XVIII**) in *N*,*N*-dimethylacetamide (Table 1) are similar to those observed earlier [3] in toluene for α,β-unsaturated ketones derived from **N,N**-dimethylaniline. It is suggested [3, 19] that the long-wave band of the latter is formed by intermolecular charge transfer from the NMe_2 group to carbonyl. Therefore, the ability of the disubstitued chalcones to fluorescence depends on whether this process is favored or unfavored by the substituent in the ketone moiety. Halogen characteristically exhibits here acceptor properties; as a result, replacement of phenyl (compound **XI**) by 4-bromophenyl (compound **XVI**) red shifts $S_0 \rightleftarrows S_1$ bands (500 and 800 cm^{-1}) and increases 1.4-fold the intensity of the radiation transition. Therewith, the photochemical activity decreases 6-fold, probably, on account of the heavy atom–induced 4-fold increase in the k_d value. Compounds **XVII** and **XVIII** exhibit similar properties. Thus, with the latter compound, the efficiency of luminescence increases 1.8-fold and the F value decreases 3.2-fold. The strongest fluorescence is characteristic of 1-[4-(dimethylamino)phenyl)-3-(2-thienyl)-2-propen-3-one (**XIX**) which is close in photophysical properties, including the E_T value (vide supra), to the phenyl analog (R^1 = Ph) [1]. However, unlike the latter compound (F 0.03), compound **XIX** undergoes no isomerization on excitation ($F \sim 10^{-3}$), apparently, because of cross conjugation which is stronger on the T level.

The resulting data allow us to conclude that the properties of the disubstituted chalcones depends primarily on the structure of the arylmethylene (heterylmethylene) group of the acetone moiety (further evidence for this conclusion is provided by a 2–3-fold increase in F for all inactive disubstituted chalcones in deaerated solutions) and that the interaction of cross-conjugated chromophores in their molecules exerts a stronger perturbing effect on the T level compared with the S_1 level.

EXPERIMENTAL

The electronic absorption spectra were measured on a Specord M-400 spectrophotometer. The NMR spectra were obtained on a Bruker AC-200 spectrometer.

Luminescence measurements were performed on the apparatus and by the procedures described in [20, 21]. The fluorescence references at 295 K were quinine sulfate in 0.1 N H_2SO_4 (φ_f 0.55) (λ_{ex} 313 and 366 nm) and 3-aminophthalimide in 0.1 N H_2SO_4 (φ_f 0.45) (λ_{ex} 406 nm) [22]. The luminescence reference in measurements in ethanol glasses (77 K) was 6-carboxy-2-(4-aminophenyl)benzothiazole (φ_f 0.85) (λ_{ex} 366 nm) [23]. The relative errors in φ_f were ±10% (295 K) and ±20% (77 K).

The equipment and technique of the photochemical experiment were described in [6, 17]. The relative error in F was ±15%.

Compounds **I**–**XXIII** were obtained as described in [24, 25] by alkaline condensation of acetophenone and the corresponding aldehydes. Nitro compounds were reduced with $SnCl_2 \cdot 7H_2O$ in HCl. The melting points and the ^1H NMR spectra are given in Table 4.

Table 4. Melting points and ^1H NMR spectra of chalcones **I**–**XXIII**

Comp. no.	mp, °C	^1H NMR spectrum (DMSO), δ, ppm (*J*, Hz)
I	58–59	[26]
II	101–102	8.10 d (2H), 7.95–7.83 m (2H), 7.93 d (1H), 7.79 d (2H), 7.75 d (1H), 7.5–7.40 m (3H)
III	85–86	8.07 d (1H), 7.92–7.78 m (3H), 7.72 d.d (2H, CH=CH, J_{HH} 16.7), 7.6–7.4 m (3H), 6.79 d.d (1H, OCH)

Table 4. (Contd.)

Comp. no.	mp, °C	^{1}H NMR spectrum (DMSO), δ, ppm (*J*, Hz)
IV	82–83	8.33 d (1H), 8.06 d (1H), 7.95–7.8 m (3H), 7.73 d (1H, CH=CH), 7.55–7.4 m (3H), 7.33 d.d (1H, SCH)
V	197–198	10.51 s (1H, NH), 8.2 d (2H), 8.1–7.8 m (7H), 7.73 d (1H, CH=CH, J_{HH} 15.8), 7.68–7.4 m (6H)
VI	107–108	8.0–7.76 m (4H), 7.92 d (2H), 7.76–7.87 m (2H), 7.6 d (1H, CH=CH, J_{HH} 15.9), 7.35–7.50 m (3H), 6.6 d (2H), 6.15 br.s (2H, NH_2)
VII	124–125	8.15 d (2H), 7.98 d (1H, CH=CH, J_{HH} 15.9), 7.76 d (2H), 7.79–7.49 m (6H)
VIII	42–43	8.06 d (2H), 7.92 d (1H, O–CH), 7.75–7.15 m (5H), 7.51 d (1H, CH=CH, J_{HH} 15.3), 7.12 d (1H), 6.69 d.d (1H)
IX	57.5–58.5	8.08 d (2H), 7.91 d (1H, CH=CH, J_{HH} 15.9), 7.79 d (1H, S–CH), 7.74–7.5 m (5H), 7.2 d.d (1H)
X	187–188	10.48 s (1H, NH), 8.15 d (2H), 7.93 d (2H), 7.9 s (4H), 7.8 d (1H), 7.73–7.47 m (7H)
XI	153.5–154	8.08 d (2H), 7.46–7.12 m (7H), 6.59 d (2H), 5.98 br.s (2H, NH_2)
XII	202–203	10.49 s (1H, NH), 8.09 d (2H), 7.97 d (2H), 7.9 s (4H), 7.82 d (2H), 7.8 d (1H, CH=CH, J_{HH} 15.2), 7.73 d (1H, CH=CH, J_{HH} 15.2)
XIII	213–214	10.37 s (1H, NH), 8.03–7.93 m (3H), 7.91 d (2H), 7.77 d (2H), 7.71–7.45 m (6H), 6.71 d.d (1H)
XIV	215–216	10.48 s (1H, NH), 8.31 d (1H), 8.05 d (1H), 7.97 d (2H), 7.9 s (4H), 7.83 d (1H, CH=CH, J_{HH} 15.9), 7.70 d (1H, CH=CH, J_{HH} 15.9)
XV	134–135	8.17 d.d (2H), 7.64 d (1H), 7.56 d (2H), 7.53 d (1H), 7.35 d. d (2H), 6.59 d (2H), 5.92 br.s (2H, NH_2)
XVI	154–155	($CDCl_3$), 7.87 d (2H), 7.76 d (1H, CH=CH), 7.61 d (2H), 7.46 d (2H), 7.28 d (1H, CH=CH), 6.67 d (2H, NH_2)
XVII	142–143	7.88 d (1H), 7.58 d (1H, CH=CH, J_{HH} 15.3), 7.48 d (1H), 7.45 d (2H), 7.25 d (1H, CH=CH, J_{HH} 15.3), 6.66 d.d (1H), 6.58 d (2H), 5.75 br.s (2H, NH_2)
XVIII	174–175	7.81 d (1H, CH=CH, J_{HH} 15.3), 7.49 d (2H), 7.49 d (2H), 7.24 d (1H, CH=CH, J_{HH} 15.3), 6.69 d (2H), 4.03 ush. s (2H, NH_2)
XIX	114–115	8.22 d (1H), 7.98 d (1H, S–CH), 7.7 d (2H), 7.67 d (1H, CH=CH, J_{HH} 16.2), 7.56 d (1H, CH=CH, J_{HH} 16.2), 7.28 d.d (1H), 6.74 d (2H), 3.06 s [6H, $N(CH_3)_2$]
XX	244.5–245.5	10.61 s (1H, NH), 8.21 d (2H), 8.1–7.91 m (5H), 7.87 d (2H), 7.78–7.48 m (6H)
XXI	145–146	10.1 s (1H, NH), 8.25 d (2H), 7.74 d (2H), 7.53 s (2H), 7.01 s (1H), 6.69 d.d (1H), 2.08 s (3H, CH_3)
XXII	164–165	10.33 s (1H, NH), 8.08 d (2H), 7.89 d (1H, CH=CH, J_{HH} 15.4), 7.79 d (1H), 7.56 d (1H, CH=CH, J_{HH} 15.4), 7.18 d.d (1H), 2.08 (3H, CH_3)
XXIII	172–173	7.92 d (2H), 7.90 d (1H), 7.80 d (2H), 7.62 d (2H), 7.56 d (1H), 6.62 d (2H), 6.16 br.s (2H, NH_2)

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