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LITERATURE CITED

1. D. Taverier and M. Anteunis, Tetrahedron, 27, 1677 (1971).
2. V. P. Lezina, A. U. Stepanyants, F. A. Alimirzoev, S. S. Zlotskii, and D. L. Rakhmankulov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 792 (1976).
3. M. Goodman and F. Morehouse, Organic Molecules in Action, Gordon (1973).
4. E. Eliel, Angew. Chem., 24, 779 (1972).
5. M. Anteunis, Heterocycles, 4, 293 (1976).
6. F. A. Alimirzoev, A. A. Lapshova, V. V. Zorin, A. U. Stepanyants, V. P. Lezina, F. N. Latypova, S. S. Zlotskii, and D. L. Rakhmankulov, Zh. Prikl. Khim., No. 4, 911 (1980).
7. M. Van Gorcom and G. E. Hall, Quart. Rev., 22, 14 (1968).
8. R. Keskinen, A. Nikkila, and K. Pihlaja, Tetrahedron, 28, 3943 (1972).
9. G. V. Lagodzinskaya and A. A. Fomichev, Zh. Strukt. Khim., 8, 695 (1967).

SYNTHESIS AND SPECTRAL AND LUMINESCENT PROPERTIES OF 4-(5-ARYLOXAZOYL-2)BENZOIC ACIDS AND THEIR DERIVATIVES

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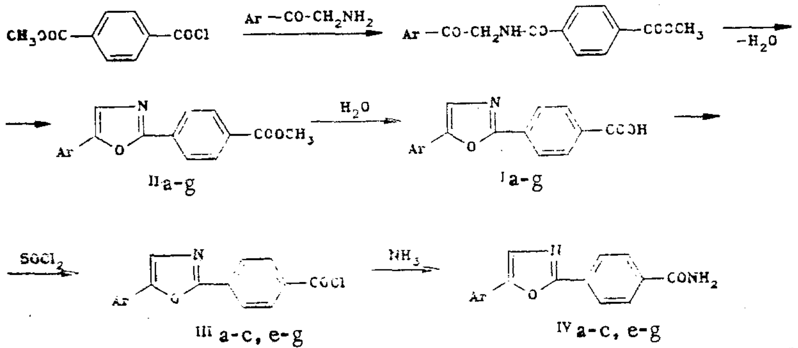
Condensation of acid chloride of monomethyl terephtalate with ω-aminomethylarylketones and subsequent cyclodehydration of the resulting amides in sulfuric acid or phosphorus oxychloride give rise to methyl 4-(5-aryloxazolyl-2)benzoates which led to the corresponding acids, acid chlorides, and amides. The effect of electron-withdrawing groups on the spectral and luminescent properties, as well as on the stability of substituted 2,5-diaryloxazoles toward UV irradiation has been investigated.

As a continuation of our studies [1-3], we have investigated the effect of structural transformations related to the replacement of the hydrogen atom in the aldehyde group by a hydroxyl, methoxyl, or amino group, or a chlorine atom on the spectral and luminescent properties of substituted 2,5-diaryloxazoles. From acid chloride of monomethyl terephthalate [4] and ω-aminomethylarylketones, we obtained in the Robinson–Gabriel reaction methyl 4-(5-aryloxazolyl-2)benzoates (II), and then by their hydrolysis, the corresponding carboxylic acids (I). From the latter, we obtained their acid chlorides (III) and amides (IV) (Table 1).



I—IV a Ar=C_6H_5; b Ar=4-CH_3—C_6H_4; c Ar=4-CH_3O—C_6H_4; d Ar=4-$(CH_3)_2N$—C_6H_4; e Ar=4-Cl—C_6H_4; f Ar=4-C_6H_5—C_6H_4; g Ar=1—$C_{10}H_7$

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TABLE 1. Physicochemical Properties of Compounds I-IV

Compound	Mp, ℃	Found N, %	Empirical formula	Calc. N, %	Yield, %
Ia	247—248	5,2	$C_{16}H_{11}NO_3$	5,3	93
Ib	257—258	5,2	$C_{17}H_{13}NO_3$	5,0	80
Ic	259—260	4,9	$C_{17}H_{13}NO_4$	4,8	81
Id	222—223	8,8	$C_{18}H_{16}N_2O_3$	9,1	70
Ie	269—270	4,8	$C_{16}H_{10}ClNO_3$	4,7	71
If	301—302	4,2	$C_{22}H_{15}NO_3$	4,1	78
Ig	239—240	4,6	$C_{20}H_{13}NO_3$	4,4	89
IIa	170—171	5,2	$C_{17}H_{13}NO_3$	5,0	83
IIb	154—155	5,0	$C_{18}H_{15}NO_3$	4,8	92
IIc	155—156	4,7	$C_{18}H_{15}NO_4$	4,5	89
IId	118—119	8,5	$C_{19}H_{18}N_2O_3$	8,7	47
IIe	193—194	4,6	$C_{17}H_{12}ClNO_3$	4,5	96
IIf	210—211	4,1	$C_{23}H_{17}NO_3$	4.2	92
IIg	117—118	4,4	$C_{21}H_{15}NO_3$	4.5	95
IIIa	156—157	5,0	$C_{16}H_{10}ClNO_2$	4,9	96
IVb	226—227	10,8	$C_{16}H_{12}N_2O_2$	10,6	95
IVc	252—253	10,2	$C_{17}H_{14}N_2O_2$	10,1	96
IVd	234—235	9,7	$C_{17}H_{14}N_2O_3$	9,5	72
IVe	250—251	4,8	$C_{16}H_{11}ClN_2O_2$	4,7	95
IVf	284—285	8,5	$C_{22}H_{16}N_2O_2$	8,2	70
IVg	231—232	9,1	$C_{20}H_{14}N_2O_2$	8,9	80

TABLE 2. Spectral and Luminescent Characteristics of Compounds I-V in Toluene

Compound	Absorption		Luminescence		Compound	Absorption		Luminescence	
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η
Ia	335	4,75	400	0,58	IIe	338	2,85	400	0,54
Ib	341	2,27	405	0,52	IIf	347	3,27	410	0,47
Ic	347	—*	420	0,52	IIg	339	1,90	425	0,43
Id	355	1,78	465	0,26	IIIa	354	2,25	430	0,54
Ie	338	2,60	400	0,48	IVa	327	3,33	395	0,55
If	348	—*	415	0,45	IVb	334	2,25	400	0,46
Ig	340	1,90	425	0,40	IVc	345	2,24	415	0,50
IIa	335	3,15	395	0,56	IVe	333	2,85	395	0,51
IIb	340	2,59	405	0,52	IVf	344	—*	410	0,43
IIc	347	2,30	415	0,47	IVg	336	2,04	415	0,40
IId	353	1,29	460	0,23	V	346	2,50	405	Weak lighting

*Poorly soluble.

Contrary to the formyl-substituted 2,5-diaryloxazoles, compounds I-IV manifest in toluene quite intensive luminescence. They emit light in the region of 400-460 nm with the quantum yield (η) varying in the range of 0.2-0.6 (Table 2). Such an effect is attributed to the mesomeric effect of substituents having lone electron pairs on the distribution of the electron density in the CO group, due to which the energy of the $n \rightarrow \pi^*$ transition increases to a greater degree than that of the $\pi \rightarrow \pi^*$ transition, and the probability of the radiationless losses of electron density decreases.

Replacement of the hydrogen atom in the aldehyde group by the hydroxyl (compound Ia), methoxyl (IIa), or amino group (IVa) results in the hypsochromic shift (11-19 nm) of the long-wave band in the absorption spectra. This effect is the most significant in the case of the amino group which decreases the electron-withdrawing properties of the carbonyl group in these compounds to a greater extent than in the case of the corresponding aldehyde V.

A more complicated relationship was observed in the absorption and luminescence spectra of the acid chlorides, due to the dual character of the halogen inducing both the mesomeric and inductive effects. The absorption and luminescence maxima of IIIa are shifted in the bathochromic and bathofluoric fashion with respect to the spectrum of the analogous compound with the aldehyde group (V). In spite of a strong inductive effect of the halogen, the intensity of luminescence in toluene is not weaker than that of the acid, ester, and amide.

This indicates the importance of the inductive and mesomeric effects of the substituent linked to the carbonyl group in the formation of the spectral and luminescent properties of 2,5-diaryloxazoles.

Introduction of electron-releasing substituents, interacting with the CO group through the system of conjugated bonds, into the 5-phenyl radical of compounds I, II, and IV, leads, similarly as in the case of aldehydes, to long-wave shifts of absorption and luminescence bands. The methyl group (Ib, IIb, IVb) causes small bathochromic and bathofluoric effects, considerably increasing under the influence of stronger electron-releasing substituents, the methoxy and dimethylamino groups (Ic, IIc, IVc, Id, IId). The increase of the Stockes shift in the compounds having the dimethylamino group (Id, IId) up to 6700 cm^{-1} is, presumably, due to the flattening of their molecules during the transition to the excited state.

The chlorosubstituted compounds (Ie, IIe, IVe) are not different from the unsubstituted compounds with respect to the position of the absorption and luminescence maxima; however, their absorption spectra have the structured character. An analogous phenomenon has also been observed in the case of the corresponding formyl-substituted 2,5-diaryloxazoles [3].

The complication of the structure of the 5-aryl fragment of compounds I, II, and IV during replacement of the phenyl radical by the 4-biphenyl (If, IIf, IVf) or by the 1-naphthyl radical is accompanied by a shift of the absorption and luminescence spectra toward longer wave lengths. It is interesting to note that the absorption maxima of compounds with the 1-naphthyl radical are shifted hypsochromically as compared with the compounds containing the 4-biphenylyl moiety, while in the luminescence spectra the opposite relationship takes place. We have observed analogous effects during investigation of other substituted 2,5-diaryloxazoles with the 1-naphthyl radical, and these effects have been explained by the nonplanar structure of molecules of these compounds in the ground state and their planarization during the transition to the excited state.

Taking into consideration the photostabilizing influence of electron-withdrawing substituents in the series of 2,5-diaryloxazoles, we investigated the stability of solutions of compounds Ia (J* 66%), IIa (J* 52%), IVa (J* 28%), and for comparison of 2,5-diphenyloxazole (J* 25%), in dioxane toward the unfiltrated UV irradiation. The photostability was characterized by the change in the luminescence intensity of the samples at the maximum of radiation (J*) with respect to the luminescence intensity of unradiated samples at the maximum of radiation, which was assumed to be 100%.

The effect of the carboxyl, carbomethoxy, and carbamide groups on the stability of 2,5-diaryloxazoles toward UV irradiation is the more pronounced, the stronger electron-withdrawing properties of the introduced substituent.

EXPERIMENTAL

The absorption spectra of the toluene solutions were measured on a Hitachi-330 spectrometer ($c\ 1 \cdot 10^{-4}$ M); the luminescence spectra were taken on a system consisting of a ZMR-3 monochromator, FÉU-18, and an M-95 microammeter. The photoluminescence was induced by a SVDSh-500 lamp, from the spectrum of which light with the wavelength of 365 nm was isolated using a DMR-4 monochromator. The absolute luminescence quantum yields were determined by the equal absorption method [5]. The photostability was characterized by the change in the fluorescence intensity of dioxane solutions of luminophores ($c\ 1 \cdot 10^{-3}$ M, layer thickness 2 cm) at the radiation maximum with respect to the fluorescence intensity of unradiated samples during radiating them with unfiltered light of mercury—quartz PRK-2 lamp. The power of the lamp was 375 watt, the distance between the lamp and the sample was equal to 12 cm, the temperature of the radiated field was 26°C, the radiation time — 6h, and the illumination of the field was 25,000 lx.

2-(4-Carbomethoxyphenyl)-5-aryloxazoles (IIa-g). To a mixture of solutions of equimolar quantities of 1 mmole of acid chloride of monomethyl terephthalate [4] in 150 ml of benzene and ω-aminomethylarylketone hydrochloride in 400 ml of water was added with intensive stirring at 25°C a 10% solution of sodium carbonate until litmus paper showed the basic reaction. The mixture was stirred for 1 h, the precipitated amide was filtered off, washed with water, and dried. The cyclization of the amide during preparation of compounds IIa, b, e was carried out in a 10-fold (by weight) amount of concentrated H_2SO_4. A dark-brown solution was kept at 25°C for 2 h and poured on 1 kg of ice. The precipitate was filtered off, washed with 500 ml of water, and dried. During synthesis of compounds IIc, d, f, g the amide was boiled for 2 h in a four-fold (by weight) amount of $POCl_3$. The obtained solution was poured in small portions on 1 kg of ice. The precipitate was filtered, washed with 500 ml of water, and dried. The purification was carried out by chromatography of their heptane solution on Silochrome S-120 in a continuous action column.

2-(4-Carboxyphenyl)-5-aryloxazoles (Ia-g). To a refluxed suspension of a 1 mmole of 2-(4-carbomethoxyphenyl)-5-aryloxazole in a 15-fold (by weight) amount of ethanol (during preparation of Ia, c, d) or acetone (during synthesis of Ib, e-g) was added in 15 min 2 mmole of sodium hydroxide in 50 ml of water. The mixture was refluxed for additional 3 h and poured in 2 liters of water (for compound If — in 4 liters), then it was heated to boiling and filtered when still hot. After cooling to 20°C, the solution was acidified with hydrochloric acid (for compound Id — with acetic acid) to pH 6. The precipitate was filtered off, washed with 500 ml of water and dried. Purification of compounds was carried out by chromatography of their benzene solutions on Silochrome S-120 in a continuous action column.

Acid Chloride of 2-(4-Carboxyphenyl)-5-phenyloxazole (IIIa). A sample of 1 mmole of 2-(4-carboxyphenyl)-5-phenyloxazole in 100 ml of thionyl chloride was boiled for 2 h. Excess of the thionyl chloride was evaporated under vacuum of a water aspirator. The compound was purified by recrystallization from benzene with addition of charcoal. Acid chlorides IIb, c, e-g were obtaine analogously.

2-(4-Carbamidophenyl)-5-aryloxazoles (IVa-c, e-g). To a solution of 1 mmole of acid chloride of 2-(4-carboxyphenyl)-5-aryloxazole in 200 ml of benzene was added at 20°C 150 ml of 10% aqueous solution of ammonia with vigorous stirring. The precipitate was filtered off, washed with water, and dried. The compounds were purified by chromatography of their benzene solutions on Silochrome S-120 in a continuous action column.

LITERATURE CITED

1. B. M. Krasovitskii and V. M. Shershukov, Khim. Geterotsikl. Soedin., No. 1, 35 (1979).
2. B. M. Krasovitskii, V. M. Shershukov, and L. M. Yagupol'skii, Khim. Geterotsikl. Soedin., No. 8, 1042 (1982).
3. V. L. Volkov, B. M. Krasovitskii, and V. M. Shershukov, Physics and Chemistry of Optical and Scintillation Materials [in Russian], Vol. 14, Scientific-Research Institute of Monocrystals, Kharkov (1985), p. 131.
4. B. M. Krasovitskii, V. L. Volkov, V. M. Shershukov, and S. A. Berezubova, Physics and Chemistry of Monocrystals and Scintillators [in Russian], Vol. 7, Scientific-Research Institute of Monocrystals, Kharkov (1981), p. 184.
5. A. S. Cherkasov, Zh. Fiz. Khim., 29, 2209 (1955).