SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2-ARYLOXAZOL-5-ONES

B. M. Krasovitskii, I. V. Lysova,
and L. Sh. Afanasiadi

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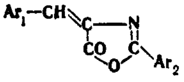
A number of aryloxazol-5-ones were synthesized by condensation of aromatic aldehydes with hippuric acid and substituted hippuric acids. Most of the products have intense luminescence in the solid state; all of them have luminescence in toluene at 77°K. Lengthening of the conjugation chain in the oxazolone molecules leads to a shift in their luminescence to the long-wave region. The compound that contains a conjugated system including two oxazolone rings also luminesces intensely in toluene at room temperature.

We have obtained a number of oxazol-5-one derivatives by the Plöchl—Erlenmeyer reaction [1, 2] by condensation of aromatic aldehydes with hippuric acid and substituted hippuric acids.



I

The literature contains indications of the application of 2-phenyl-4-(p-dimethylaminobenzylidene)oxazol-5-one in luminescence defectoscopy [3], but we have not encountered a detailed study of the luminescence properties of compounds of this series.

The absorption spectra of the products have a vibrational structure, and the character of the spectra changes only slightly as a function of the structure of Ar_1 and Ar_2. They all have an intense long-wave band with a maximum at 340-500 nm and a less intense short-wave band (λ_{max} 255-330 nm) that is relatively slightly sensitive to changes in the structure of the aromatic groups. We will subsequently examine only the long-wave K band responsible for the luminescence.

Lengthening of the conjugation chain in the arylidene grouping by replacement of the phenyl group of 2-phenyl-4-benzylideneoxazol-5-one (Ia) by 4-diphenylyl, 2-naphthyl, or 9-anthryl group (Ib-d) is accompanied by a considerable bathochromic effect. However, one should note the decrease in intensity of the absorption in the spectra of compounds with a 9-anthryl group, which creates steric hindrance (Table 1).

The introduction of nitro and dimethylamino groups in the para position of the phenyl group of the benzylidene grouping also gives rise to a bathochromic effect, which is not, however, accompanied by a change in the character of the spectrum. In the case of the dimethylamino derivative this effect is considerably greater because of the donor—acceptor interaction of the p-dimethylamino group with the carbonyl group of the oxazolone ring. Lengthening of the conjugation chain by the introduction of a second vinylene group (If and Ih) in the molecules of these compounds leads to a further long-wave shift of ∿30 nm in the absorption maxima.

In the case of Ij, as compared with the compound that does not contain a nitro group (Ig), the absorption maximum is shifted sharply to the short-wave side, and the intensity of the absorption decreases markedly. These effects are evidently the result of the superimposition of two competitive effects. On the one hand, as in the case of the compound that does not contain a nitro group, the interaction between the dimethylamino and carbonyl groups is retained. On the other hand, this interaction is weakened markedly by the strong conjugation of the dimethylamino group with the nitro group. The result of these interactions is a

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Ar_1	Ar_2	mp, °C	Empirical formula	N, %		Absorption, λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)	Fluorescence		Yield, %
					found	calc.		λ_{max} 77°K, nm	λ_{max} in powders, nm	
Ia	Phenyl	Phenyl	166	—	—	—	360 (3,9)[4].	425, 455	Does not fluoresce	—
Ib	p-Diphenylyl	„	184	$C_{22}H_{15}NO_2$	4,3	4,3	390 (4,5)	460, 490	505	54
Ic	2-Naphthyl	„	156	$C_{20}H_{13}NO_2$	4,6	4,7	405 (2,7)	450, 485	515	37
Id	9-Anthryl	„	246	$C_{24}H_{15}NO_2$	4,2	4,0	460 (1,2)	540	Does not fluoresce	41
Ie	p-Nitrophenyl	„	—	—	—	—	380 (3,3)[4]	—	—	—
If	p-Nitrocinnamoyl	„	206	$C_{18}H_{12}N_2O_4$	8,5	8,7	410 (5,4).	500, 530	575	73
Ig	p-Dimethylaminophenyl	„	213[5]	—	—	—	470 (5,5).	560	Orange-red fluorescence	
Ih	p-Dimethylaminocinnamoyl	„	205	$C_{20}H_{18}N_2O_2$	9,0	8,8	500 (5,2)	620	Red luminescence	30
Ii	p-Nitrophenylfuryl	„	233	$C_{20}H_{12}N_2O_5$	7,5	7,7	445 (2,6)	535, 575	710	50
Ij	p-Dimethylaminophenyl	p-Nitrophenyl	231	$C_{18}H_{15}N_3O_4$	12,2	12,4	340 (1,2)	Fluoresces weakly	Does not fluoresce	61
Ik	p-Nitrophenyl	p-Dimethylaminophenyl	205	$C_{18}H_{15}N_3O_4$	12,5	12,4	345 (1,6)	635	Does not fluoresce	57
II			273	$C_{26}H_{16}N_2O_4$	6,9	6,7	435 (7,0)	525, 570	595	15

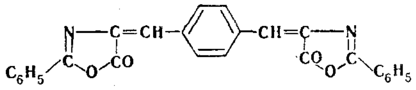
considerable hypsochromic effect. With respect to its spectral characteristics Ij differs very little from the isomeric Ik, in which the dimethylamino group is in the Ar_2 group and the nitro group is in the Ar_1 group, and conjugation of the former with the carbonyl group of the oxazolone ring is thus excluded. The effect of the donor—acceptor interaction of the dimethylamino and nitro groups consequently is of decisive value for the determination of the character of the K band in the spectra of both of these compounds.

It is interesting to compare the absorption spectra of Ie and If with the spectrum of Ii, which contains, between the p-nitrophenyl group and the vinylene group, a furan ring that is included in the conjugation chain. Whereas the inclusion of another vinylene group between the structural groupings (If) gives rise to a bathochromic effect of ∿30 nm, the furan ring shifts the absorption maximum 65 nm to the long-wave region. We associate this with the further increase in the conjugation chain and to a lesser degree with the aromatic character of the incorporated heteroring.

Most of the oxazolones luminesce intensely under the influence of UV rays in the solid state, all of them luminesce at 77°K, and some of them also luminesce in solution at room temperature.

The luminescence spectra of frozen solutions are shifted bathochromically relative to the luminescence spectra of solutions at room temperature, and in the case of most of the compounds have two distinctly expressed maxima. The compound with a p-dimethylaminocinnamoyl group (Ih) has the longest-wave luminescence (λ_{max} 620 nm). Even longer-wave luminescence is observed for oxazolones in the solid state; a luminophore with red luminescence and a luminescence maximum at 710 nm (Ii) are observed.

Compound II with two conjugated oxazolone rings is of interest as a luminophore.



II

In contrast to Ia, which does not luminesce either in the solid state or in solution, II under these conditions displays intense yellow-green luminescence in toluene (λ_{max} 515 nm) and orange-red luminescence in the crystalline state (595 nm). Thus by lengthening the conjugation chain in the oxazolone molecules one cannot only shift their luminescence to the long-wave region but can also obtain compounds that luminesce in solution at room temperature.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds (c $3 \cdot 10^{-3}$ mole/liter) were measured with an SF-4 spectrophotometer. The fluorescence spectra were measured with an apparatus consisting of a ZMR-3 monochromator, an FÉU-18 photoelectric amplifier, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a DMR-4 monochromator.

Aryloxazol-5-ones. A mixture consisting of 0.022 mole of hippuric acid or p-substituted hippuric acid, 0.02 mole of the corresponding aldehyde (0.04 mole in the preparation of II), 0.01 mole of sodium acetate, and 15 ml of acetic anhydride was heated at 100°C for 15 min. The resulting precipitate was cooled, removed by filtration, washed with 15 ml of alcohol, and purified by recrystallization from suitable solvents: Ib-d, Ig, and Ii from acetic acid, If, Ih, Ij, and Ik from xylene, and II from dimethylformamide (Table 1).

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PHOTOCHROMIC AND THERMOCHROMIC SPIRANS

VII.* SPIRO(4-OXO-3,4-DIHYDRO-2H-1,3-BENZOXAZIN-2,2'-[2H]BENZOPHYRANS)

B. S. Luk'yanov, Yu. I. Ryabukhin,
G. N. Dorofeenko, L. E. Nivorozhkin,
and V. I. Minkin

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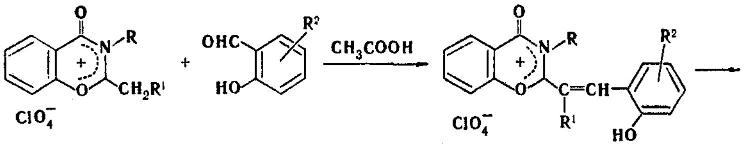
New spiropyrans of the 4-oxo-3,4-dihydro-2H-1,3-benzoxazine series, individual representatives of which have photochromic properties, were obtained by condensation of 2-alkyl-4-oxo-1,3-benzoxazinium perchlorates with aromatic o-hydroxy aldehydes in acetic acid and subsequent treatment of the 2-(o-hydroxystyryl) derivatives with pyridine or triethylamine. The structures of the synthesized compounds were confirmed by the PMR, IR, and UV spectroscopic data.

New spiropyran systems of the 4-oxo-3,4-dihydro-2H-1,3-benzoxazine series were obtained from 2-alkyl-4-oxo-1,3-benzoxazinium salts [2] via the scheme



Ia-d, g IIa-h

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*See [1] for communication VI.

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