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## SYNTHESIS AND SPECTRAL-LUMINESCENCE

PROPERTIES OF 2-ARYL-4-BENZYLIDENE-

#### 5-OXAZOLONES

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A number of 2-aryl-4-benzylidene-5-oxazolones was obtained by condensation of benzaldehyde with N-acylglycines. The absorption and fluorescence spectra in chloroform at 77°K were measured. The spectral characteristics of the investigated and previously synthesized 2-phenyl-4-arylidene-5-oxazolones are compared.

In connection with the search for organic luminophores among 5-oxazolone derivatives we synthesized 2-aryl-4-benzylidene-5-oxazolones (I), traced the dependence of the change in their spectral-luminescence properties on the structure of the 2-aryl group, and compared these properties with the properties of 2-phenyl-4-arylidene-5-oxazolones (II) [1].



All of the investigated compounds were obtained in the form of trans isomers [2] by condensation of aromatic aldehydes with substituted hippuric acids (III - in acetic anhydride in the presence of anhydrous sodium acetate.

Compounds III were synthesized by acylation of hippuric acid with the chlorides of the corresponding aromatic acids. In those cases in which the acid chlorides were liquid substances, the acylation was carried out in an aqueous alkali medium at room temperature by the method in [3]. In the case of solid acid chlorides substituted hippuric acids were synthesized by two methods, viz., in glacial acetic acid at 50-60°C (method A)

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TABLE 1. Hippuric Acids II

Com <del>-</del> pound	mp, °C	λ <sub>max</sub> , nm (ε·10 <sup>-4</sup> )(in water)	N found, %	Empirical formula	N calc., %	Yield, %
IIIa IIIb IIIc IIId IIIe IIIf	159—160 238—239 205—206 217—218 148—149 134—135	$\begin{array}{c} 250 \ (1,88) \\ 260 \ (1,90) \\ 230 \ (1,48) \\ 240 \ (2,00) \\ 250 \ (1,29) \\ 245 \ (1,80) \end{array}$	$\begin{array}{c} 6.8 \\ 12.4 \\ 4.9 \\ 5.4 \\ 6.1 \\ 6.7 \end{array}$	$\begin{array}{c} C_{10}H_{11}NO_4\\ C_{11}H_{14}N_2O_3\\ C_{10}H_3F_2NO_5S\\ C_{15}H_{13}NO_3\\ C_{13}H_{11}NO_3\\ C_{13}H_{11}NO_3\\ C_{11}H_{11}NO_3\\ \end{array}$	$ \begin{array}{c} 6,7\\12,6\\4,8\\5.5\\6,1\\6,8\\\end{array} $	65 60 70 80 85 78

and by the method in [3] with benzene as the solvent (method B). Identical N-acylglycines were obtained in both cases, and method B makes it possible to obtain these compounds in up to 85% yields.

In a previous investigation of the absorption spectra of II and on the basis of quantum-mechanical calculation made for 4-hetarylidene-2-aryloxazolones [1, 2] it was concluded that the nature of the long-wave absorption band of oxazolones II can be interpreted on the basis of concepts regarding the localization of the electronic excitation in the arylideneoxazolone fragment. An analysis of the spectral features of I confirms the possibility of the same approach to the interpretation of the absorption and fluorescence spectra of I also, which contain various aromatic groupings (Ar).

The  $S_0 \rightarrow S_1^*$  transition in the case of IIc-g is associated with redistribution of the electron density primarily in the arylideneoxazolone fragment, and the electron density is shifted toward the arylidene grouping. Electron-donor substituents in the arylidene grouping hinder this shift. Interaction of the arylidene grouping with the electron-acceptor carbonyl group is intensified under their influence, and, correspondingly, the interaction of the carbonyl group with the arylazomethine fragment decreases. The donor-acceptor interaction of the substituents with the carbonyl group of the oxazole ring is evidently also the reason for the significant bathochromic and hyperchromic effects observed for IIa and IIb.

In the comparison of I with the corresponding II, one's attention is drawn to the dimethylamino-substituted compounds (Ic and IIb), the positions of the absorption maxima of which differ by 90 nm. The difference between 2- and 4-substituted 5-oxazolones is considerably smaller (15 nm; compare Ib and IIa) when an electron-donor substituent (a methoxy group) that is weaker than the dimethylamino group is present in the 2aryl grouping.

The role of the arylazomethine grouping in the  $S_0 \rightarrow S_1^*$  transition increases when the conjugation chain in the 2-aryl grouping directly bonded to the azomethine group is lengthened (If-h), and the effect of the carbonyl group decreases; a shortwave shift of the absorption maxima as compared with the corresponding IIe-g is observed in this case.

The interpretation of the absorption spectra of Id,e is more difficult. One would think that the introduction of strong electron-acceptor groups in the 2-phenyl group of 5-oxazolones should to a certain extent hinder the above-noted shift of the electron density toward the arylidene fragment and entail a hypsochromic shift of the absorption band as compared with IIc,d. The difference in the position of the absorption maxima of these compounds is either experimentally absent, or a slight red shift of the long-wave absorption band is observed. The contribution of quinoid from IV [4], in which the  $S_0 \rightarrow S_1^*$  transition is determined by the length of the conjugation chain, evidently increases when electron-acceptor substituents are introduced in the 2-aryl grouping. A consequence of this is a bathochromic effect as compared with oxazolones II. In the opinion of Bassi and co-workers [4], the difference in the energies of the ground and first excited states of IIc is higher than in the case of Id, and this also leads to shorter-wave absorption for the former.



Compounds I fluoresce when they are irradiated with UV light in the crystalline state and in frozen solutions in chloroform. The fluorescence spectra of solutions at 77°K have a distinctly expressed vibrational structure and, except for Id, e, are shifted to the short-wave region as compared with the spectra of 4-aryli-dene-substituted 5-oxazolones.

TABLE 2.	2-Aryl-4-ar	ylideneoxazolon	es I a	ind II
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Com- pound	mp, °C	λ <sub>max</sub> , (abs.), nm (ε·10 <sup>-4</sup>	λ <sub>max</sub> (f <b>l.)</b> , nm, at 77°K	N found, %	Empirical formula	N calc., %	Yield, %
Ia Ib Ic Id If If If Ilb Ilc Ilc Ilf Ilg	$\begin{array}{c}\\ 217218\\ 241243\\ 237\\ 230231\\ 201203\\ 126127\\ 136137\\ 159161\\\\\\ 193\\\\ 169170\\ 152154\\ \end{array}$	$\begin{array}{c} 360^3 \ (3.90) \\ 375 \ (8,15) \\ 380 \ (4.98) \\ 380^a \ (3.30) \\ 380 \ (5.60) \\ 380 \ (5.60) \\ 380 \ (4.92) \\ 380 \ (4.92) \\ 380 \ (4.92) \\ 375^a \ (3.66) \\ 375^a \ (3.66) \\ 370 \ (5.55) \\ 390 \ (4.50) \\ 390 \ (4.80) \end{array}$	$\begin{array}{r} 425, 455\\ 440, 470\\ 450, 480\\ 510\\ 440, 475\\ 445, 470\\ 450, 480\\ 465, 495\\ 455, 480\\ 560\\ 485\\ 440, 465\\ 460, 490\\ 475, 505\\ 480, 510\\ \end{array}$	4,9 9,4 9,6 8,9b 4,0 4,5 5,3 5,2  8,6 <b>b</b> 	$\begin{array}{c} \hline & & \hline \\ C_{17}H_{13}NO_3\\ C_{18}H_{16}N_2O_2\\ C_{16}H_{10}N_2O_4\\ C_{17}H_{11}F_2NO_4S\\ C_{22}H_{15}NO_2\\ C_{20}H_{13}NO_2\\ C_{17}H_{13}NO_3\\ \hline \\ \hline \\ C_{17}H_{11}F_2NO_4S\\ \hline \\ C_{20}H_{13}NO_2\\ C_{17}H_{13}NO_2\\ \hline \\ C_{17}H_{11}F_2NO_4S\\ \hline \\ C_{20}H_{13}NO_2\\ C_{18}H_{13}NO_2\\ \hline \end{array}$	5.0 9,6 9,5 8,8 4,3 4,7 5,1 5,1 8,8 b 4,7 5,1	$     \begin{array}{r}             46 \\             37 \\             42 \\             28 \\             36 \\             41 \\             30 \\             54 \\             - \\             38 \\             - \\             38 \\             46 \\             58 \\             46         $

<sup>a</sup> Data from [4]. <sup>b</sup> Analysis for the S content.

# EXPERIMENTAL

The absorption spectra of solutions of the oxazolones in chloroform (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 adapter, and an M-95 micrommeter. Photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 mm was isolated with a DMR-4 monochromator.

<u>N-Substituted Hippuric Acids (Table 1).</u> A) A 0.011-mole sample of an aromatic acid chloride and 0.8 g of freshly calcined sodium acetate were added in portions with stirring to a solution of 0.01 mole of glycine in 20 ml of glacial acetic acid, and the mixture was heated at 50-60°C for 2 h. It was then cooled, and the precipitate was removed by filtration, dried, and recrystallized from water in the presence of activated charcoal.

B) A solution of sodium hydroxide (0.02 mole) and 0.011 mole of the chloride of the corresponding acid in 50 ml of benzene was added with vigorous stirring in the course of 1.5 h to 0.01 mole of an aqueous solution of glycine in such a way that the pH of the solution was constant at eight to nine. The mixture was then poured into hydrochloric acid, and the precipitate was recrystallized from water.

2-Aryl-4-benzylidene-5-oxazolones (Table 2). These compounds were obtained by the method in [1].

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