HETARYLETHYLENE DERIVATIVES OF 2,5-DIARYLOXAZOLES AND 2,5-DIARLOXADIAZOLES AND THEIR LUMINESCENCE AND SCINTILLATION PROPERTIES

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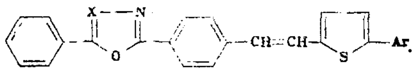
A number of new organic luminophores were synthesized via the Wittig reaction from 2-(4-bromomethylphenyl)-5-phenyloxazole or 2-(4-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole and various heterocyclic aldehydes containing a thiophene ring.

The synthesis of organic luminophores in series of aryl- and hetarylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole (I, II) demonstrated the possibility of obtaining intensely luminescing substances [1-3].

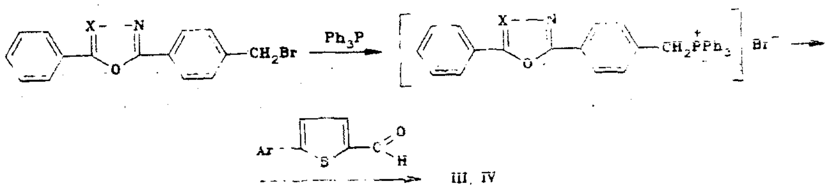
The subjects of the present communication are the synthesis and investigation of the fluorescence and scintillation properties of hetarylethylene derivatives (III, IV) of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole that have more complex structures and contain a thiophene ring.



III, IV

III X=CH, IV X=N: III, IV a Ar= phenyl; b Ar = 4-chlorophenyl; c Ar = 4-bromophenyl IIId Ar=4-tolyl; IIIe, IVd Ar = 4-methoxyphenyl; IIIf, IVe, Ar = 4-nitrophenyl; IIIg Ar = 5-phenyl-2-oxazolyl

The synthesis of III and IV was accomplished via the Wittig reaction. 2-(4-Bromomethylphenyl)-5-phenyloxazole or 2-(4-bromomethylphenyl)-5-phenyl-1,3,4-oxadiazole and 5-aryl-2-formylthiophenes served as the starting compounds.



In conformity with the well-known concepts regarding the mechanism of the Wittig reaction and kinetic studies, electron-donor substituents in aromatic aldehydes decrease the rate of this reaction [4, 5]. Under the most widely used conditions for this synthesis (methanol as the solvent, alkali metal methoxides as the basic agents for conversion of the phosphonium salt to the corresponding phosphorane, and a reaction temperature of 20°C) 2-formyl-5-(4-methoxyphenyl)thiophene does not react with the phosphonium salt, since the thiophene radical evidently displays an electron-donor effect in this reaction. This made it necessary to search for more severe conditions for the synthesis, which we subsequently carried out by heating to 50°C in isopropyl alcohol using sodium isopropoxide as the basic agent for conversion of the phosphonium salt to the corresponding phosphorane.

The Wittig reaction is nonstereospecific and leads to the formation of mixtures of trans and cis isomers [4, 6]. Only the trans isomers have practical value, since they

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	Absorption		Fluorescence		S found, %	Empirical formula	S calc., %	Yield, %
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η				
IIIa	214—215	315 382	2,53 3,03	467	0,18	7,9	$C_{27}H_{19}NOS$	7,9	45
IIIb	217—218	320 394	2,27 3,69	472	0,20	7,1	$C_{27}H_{18}ClNOS$	7,3	73
IIIc	213—214	317 394	2,23 3,99	471	0,20	6,6	$C_{27}H_{18}BrNOS$	6,6	37,5
IIId	198—199	314 383	2,62 2,87	474	0,13	7,8	$C_{28}H_{21}NOS$	7,6	52
IIIe	211—212	315 387	2,91 2,71	482	0,13	7,1	$C_{28}H_{21}NO_2S$	7,3	55
IIIf	234—235	421	4,74	526	0,20	7,0	$C_{27}H_{18}N_2O_3S$	7,1	62
IIIg	202—203	288 414	1,68 5,63	487	0,41	6,6	$C_{30}H_{20}N_2O_2S$	6,8	46
IVa	233—234	297 393	2,70 1,93	465	0,05	7,7	$C_{26}H_{18}N_2OS$	7,9	51
IVb	229—230	298 381	2,33 2,10	468	0,12	7,4	$C_{26}H_{17}ClN_2OS$	7,3	62
IVc	250—251	299 377	2,73 2,39	466	0,07	6,3	$C_{26}H_{17}BrN_2OS$	6,6	64
IVd	199—201	301 383	3,03 2,13	484	0,06	7,4	$C_{27}H_{20}N_2O_2S$	7,35	48
IVe	266—267	415	3,50	509	0,14	8,3	$C_{26}H_{17}N_3O_3S$	8,6	58

luminesce more intensely. For conversion of the cis isomer to the trans form the reaction product was therefore heated in xylene with crystalline iodine for 4 h.

The structures of III and IV were confirmed by IR spectral data. Out-of-plane deformation vibrations of the hydrogen atoms of the trans-vinylene group at 945-960 cm^{-1} and characteristic frequencies of thiophene (710-730, 1410-1420, 1510-1550 cm^{-1}), oxazole and oxadiazole (1560-1590 cm^{-1}), phenyl (620-740, 1000, 1445, 1500 cm^{-1}), and 1,4-phenylene (485, 640, 1110, 1250 cm^{-1}) rings appear in the spectra. It should be noted that the stretching vibrations of the C=C bond are masked to a significant extent by the absorption of the aryl fragments.

As a rule, two bands are observed in the absorption spectra (Table 1). The interpretation of the short-wave band with a maximum at 315-320 nm (ε = 22,000-29,000 liter•mole^{-1}•cm^{-1}) for III and at 297-301 nm (ε = 23,000-30,000 liter•mole^{-1}•cm^{-1}) for IV is difficult because of the possibility of superimposition of several electron transitions localized in the arylazole and thienylethylene fragments. In the case of III and IV this band is only slightly sensitive to the introduction of CH_3 and OCH_3 groups and halogen atoms into the phenyl ring but changes substantially when a nitro group is present (IIIf and IVe).

The long-wave band that is responsible for fluorescence and is more sensitive to the effect of substituents in the arylthiophene fragment is of considerably greater interest for consideration.

A comparison of the spectral characteristics of IIIa and its aromatic analog I (Ar = $C_6H_5-C_6H_4$) shows that replacement of the benzene ring by a thiophene ring changes the character of the absorption spectra significantly and is accompanied by a bathochromic shift of the long-wave band. This effect is evidently a consequence of not only an increase in the extent of the π system but is also associated with the electron-donor character of the thiophene ring.

The absorption intensity of IIIa is substantially lower than that of its aromatic analog. From the point of view of their electronic structures these two systems are formally similar. However, if one ascribes the decrease in the extinction coefficient only to the presence of the heteroatom, the same regularity should also have occurred in series of, for example, furylethylene derivatives of 2,5-diphenyloxazole, but, in fact, this was not observed [2, 7]. The explanation of this fact requires further theoretical examination.

When substituents with a relatively weakly expressed electronic effect (Cl, CH_3, OCH_3) are introduced into the phenyl ring bonded to the thiophene ring, the position of the absorption maximum of the long-wave band remains virtually unchanged.

TABLE 2. Scintillation Characteristics of III

Compound	Scientillation efficiency, %		
	α-methylnaphthalene (c 5 g/liter)	ditolylmethane (c 5 g/liter	α-methylnaphthalene (c 0.1 g/liter)
IIIa	48	52	60
IIIb	50	54	62
IIIc	50	54	66
IIId	—	—	56
IIIe	42	50	48
IIIf	46	56	—

The long-wave absorption band in the spectrum of the simplest I (Ar = C_6H_5) corresponds to primary localization of the electronic excitation in the $S_0 \rightarrow S_1$ transition in the arylazolylethylene fragment and is the result of the superimposition of electron shifts that take place in two directions: from the phenylazole grouping and from the phenyl ring containing the substituent to the ethylene bridge [8]. As in the I series, the introduction of a nitro group into the phenylthienyl fragment leads to a significant change in the nature of the long-wave absorption band, which becomes a band of charge transfer from the phenyl grouping to the nitrophenylthienyl grouping.

One's attention is directed to the large extinction coefficient of IIIg. This increase in the probability of an electron transition is evidently not only a consequence of an increase in the overall extent of the π-electron system of the molecule, owing to which the probability of its interaction with the field of the light wave increases, but is also the result of the perturbing effect of the phenyloxazole residue introduced into the 5 position of the thiophene ring.

Upon irradiation with UV light all of the III and IV obtained fluoresce in the crystalline state and in toluene solutions at 20°C. Their quantum yields range from 0.01 to 0.41 and are substantially lower than in the case of the similarly constructed furylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole [2]. The decrease in the photoluminescence quantum yield may be due to intercombination conversion reinforced by the presence of a heavy sulfur atom.

The fluorescence spectra of the investigated compounds are characterized by a weakly expressed vibrational structure. There is almost no difference in their spectra. However, the oxadiazole analogs have considerably lower fluorescence quantum yields than their oxazole derivatives. It should be noted that the nitro group does not exert its characteristic quenching effect [9], and IIIf and IVe fluoresce just like the unsubstituted compound.

Substituents in the phenyl ring bonded to the thiophene ring have a relatively small effect on the positions of the fluorescence bands, although one can note a tendency for an increasing bathochromic shift of these band when substituents with a weakly expressed electronic effect are introduced: $Cl < CH_3 < OCH_3$. As in the absorption spectra, a substantial shift of the fluorescence bands to the longer-wave region is observed for the nitro derivatives (IIIf, IVe).

We investigated III as spectral activators (concentration 5 g/liter) and shifters (concentration 0.1 g/liter) in liquid scintillators (LS). The efficiencies of the LS were measured from the change in the photocurrent of an FÉU-13 photomultiplier; ^{137}Cs served as the source of γ excitation. A solution of a mixture of p-terphenyl (4 g/liter) with 1,4-bis(5-phenyl-2-oxazolyl)benzene (0.1 g/liter) in toluene, which is usually utilized for this purpose, was used as the standard scintillator. In the investigation of III as spectral shifters in α-methylnaphthalene, 2-(1-naphthyl)-5-phenyloxazole (α-NPO) was used as the activator. It is apparent from the data in Table 2 that III cannot be used as spectral activators and shifters in LS. The effect of the heavy sulfur atom evidently has a negative influence on the efficiency of the LS.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds (c $5 \cdot 10^{-5}$ M) were measured with a Specord spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter; photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator. The IR spectra were obtained with a UR-20 spectrometer.

The hetarylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole were obtained by the method in [7] and were purified by chromatography on aluminum oxide in benzene with subsequent recrystallization from a suitable solvent.

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POLYNUCLEAR HETEROCYCLIC COMPOUNDS BASED ON THE ADDUCT OF o-CINNAMOYLBENZOIC ACID AND CYCLOHEXANONE

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The product of addition of cyclohexanone to o-cinnamoylbenzoic acid, which has the 4-phenyl-8a-hydroxyperhydrochroman-2-spiro-3'-phthalide structure, reacts with nitrogen-containing nucleophiles to give hydrogenated derivatives of oxa-(aza, thia)indolizinespirophthalide and pyrido[1',2':1,2]imidazo[2,3-a]-isoindole, as well as 4-R-1-phthalazones. An isoindolo[1,2-a]quinoline derivative and a compound with a 7,8-diaza-D-homosteroid skeleton were obtained from the latter.

Semicyclic 1,5-diketones that contain reactive substituents in the ortho position relative to the aroyl carbonyl group are convenient starting compounds for the synthesis of polynuclear (including new) heterocyclic systems; in particular, the synthesis of compounds with a heterosteroid skeleton is possible. We have previously described the synthesis and properties of o-hydroxy- and o-amino-substituted semicyclic 1,5-diketones [1, 2]. In order to synthesize an o-carboxy-substituted diketone we realized the addition of cyclohexanone to o-cinnamoylbenzoic acid; we have previously briefly reported the synthesis and some properties of adduct I [3] (see scheme on following page).

The addition proceeds readily in the presence of KOH; adduct I has the 4-phenyl-8a-hydroxyperhydrochroman-2-spiro-3'-phthalide (IA) structure [3]. In the reaction of I with nitrogen nucleophiles we isolated products, the formation of which can be explained by prior opening of the hydropyran and phthalide fragments and conversion of I to the o-carboxy-sub-

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