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SYNTHESIS, SPECTRAL LUMINESCENT AND SCINTILLATION PROPERTIES OF ORGANIC LUMINOPHORES BASED ON CARBONYL-CONTAINING DERIVATIVES OF 2-(FUR-2-YL)-5-PHENYLOXAZOLE

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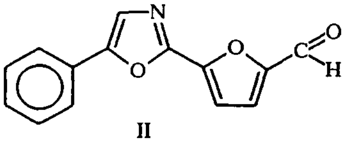
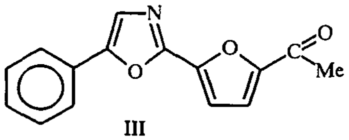
A series of derivatives of 2-(fur-2-yl)-5-phenyloxazole with various substituents in the 5-position of the furan ring and furan-containing analogs of 1,4-bis(5-phenyloxazol-2-yl)benzene are synthesized. Their spectral-luminescent properties are investigated.

Previously we have investigated acylation of 2-(fur-2-yl)-5-phenyloxazole (I) and synthesized derivatives II-IV with carbonyl-containing substituents in the 5-position of the furan ring. These groups are conveniently located for further modification of the molecular structure in order to prepare new effective luminophores. In the present work, the series of functionally substituted 2-(fur-2-yl)-5-phenyloxazole is expanded and certain furan-containing analogs of 1,4-bis(5-phenyloxazol-2-yl)benzene, which is widely used as displacer of spectra for liquid and plastic scintillators [2] and as dye for liquid lasers [3], are synthesized. Their spectral-luminescent properties are investigated.



II



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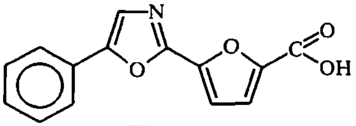
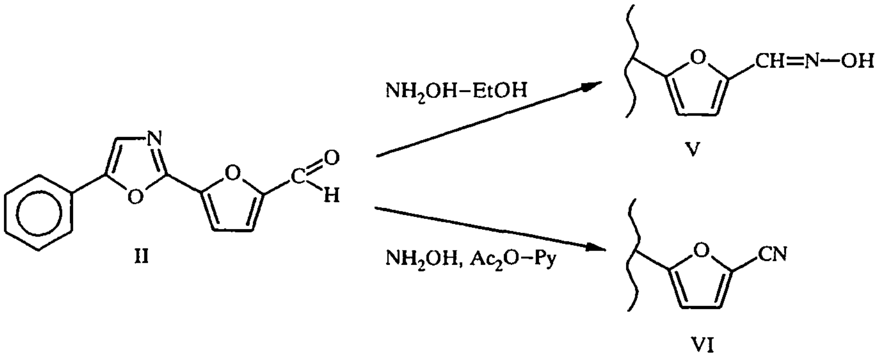


IV

The reaction of 2-(5-phenyloxazol-2-yl)furan-5-carboxaldehyde (II) with hydroxylamine in ethanol yields oxime V. On heating of II in pyridine in the presence of acetic anhydride, nitrile VI is obtained:



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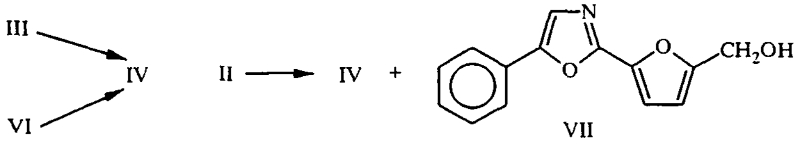
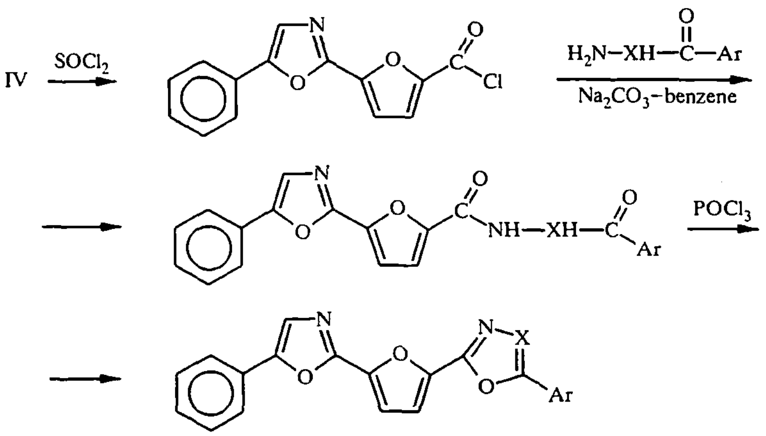
We previously have prepared carboxylic acid IV by oxidation of ketone III with sodium hypobromite and also by the action of alkali alcohol solution on aldehyde II [1]. In the latter case, the hydroxymethyl derivative VII is isolated as a secondary product of disproportionation. The yields of the desired product IV by both methods are low (50 and 40%, respectively). Therefore, in this work carboxylic acid was synthesized by hydrolysis of nitrile VI with an aqueous-alcoholic solution of NaOH. The yield of acid IV by this method is higher (80% calculated on the basis of initial aldehyde II). The product is easier to purify.



Carboxylic acid IV was used to synthesize the furan-containing analogs of 1,4-bis(5-phenyloxazol-2-yl)-benzene VIII-XI. Acid chloride prepared by boiling acid IV in excess of thionyl chloride, was reacted with α-aminoacetophenone or with hydrazides of carboxylic acids. The condensation products formed were subjected to cyclodehydration by phosphonyl chloride.



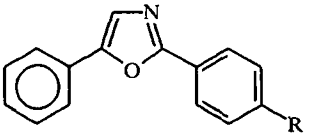
VIII–XI

VIII X = CH, Ar = Ph; IX X = N, Ar = Ph;
X X = N, Ar = 2-furyl; XI X = N, Ar = 4-pyridyl

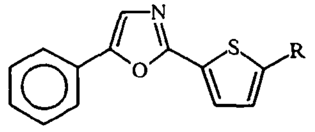
The IR spectra of all products obtained are consistent with the proposed structures.

We have investigated the spectral-luminescent properties of the synthesized compounds. Characteristics of the absorption and fluorescence spectra of compounds I-VII and those of certain previously studied compounds containing benzene XII-XV or thiophene XVI-XIX ring instead of furan ring are presented in Table 1.

Table 1 shows that compounds containing furan ring, as a rule, absorb and emit light at longer wavelengths than substituted 2,5-diphenyloxazoles of similar structure [4, 5] but at shorter wavelengths than thiophene analogs [6]. The 2-furyl group is a stronger electron donor than 2-thienyl group [7]. Therefore, the observed trend is most likely related to the greater polarizability of the thiophene ring.



XII–XV



XVI–XIX

XII, XVI R = H; XIII, XVII R = CHO; XVIII R = COMe;
XIV, XIX R = COOH; XV R = CN

TABLE 1. Spectral Luminescent Properties of Compounds I-VII and XII-XIX

Compound	In toluene				In ethanol			
	absorption		fluorescence		absorption		fluorescence	
	λ_{max}, nm	$\varepsilon \times 10^{-3}$	λ_{max}, nm	η	λ_{max}, nm	$\varepsilon \times 10^{-3}$	λ_{max}, nm	η
I	314	30,0	368	0,40	312	30,0		
II	355	36,5	No fluoresc.		345	26,9	465	0,31
III	348	31,6	No fluoresc.		345	38,0	455	0,44
IV	335	28,9	400	0,52	323	37,0	380	0,73
V	345	47,7	395	0,62	343	36,9	400	0,70
VI	335	24,4	390	0,53	330	30,2	395	0,60
VII	323	30,3	370	0,38	310	35,2	370	0,58
XII	307	28,0	365	0,51	300	27,2	363	0,62
XIII	346	25,0	No fluoresc.		337	25,7	480	0,40
XIV	335	47,5	400	0,58				
XV	337	35,0	395	0,62				
XVI	324	24,0	389	0,31	319	32,4	385	0,33
XVII	370	25,0	Weak fluoresc.		365	21,3	485	0,53
XVIII	365	22,8	Weak fluoresc.		363	24,2	470	0,53
XIX	355	21,5	425	0,19	335	33,9	427	0,20

Introduction of carbonyl-containing groups (compounds II-IV) into 2-(fur-2-yl)-5-phenyloxazole (I) molecule leads to approximately the same shift to long wavelengths in the absorption spectra as for the 2,5-diphenyloxazole and 5-phenyl-2-(thien-2-yl)oxazole analogs. Judging from the magnitude of the bathochromic shift (~20-40 nm), it is due not only to the elongated conjugation chain but also to electron-acceptor influence of the substituent: the greatest shift is observed for the formyl substituent and the least, for the carboxyl.

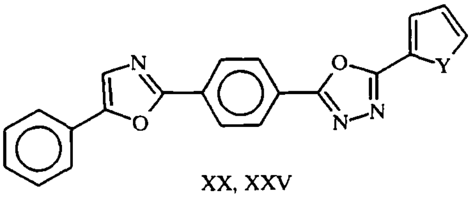
Aldehyde II and ketone III, like the aldehyde XIII, do not fluoresce in toluene. Such quenching was assigned [6] to effective population of the triplet $n\pi^*$-levels of the carbonyl group. The occurence of weak fluorescence for the thiophene-containing compounds XVII and XVIII (regardless of the quenching effect of the heavy sulfur atom) is explained by significant decrease of energy of the S^1 $\pi\pi^*$-state, which becomes lower than T $n\pi^*$. For compounds II and III, the electron-donor influence of the 2-furyl is evidently insufficient to invert the S^1 $\pi\pi^*$- and $T\,n\pi^*$-levels and consequently these compounds do not fluoresce.

Changing from toluene to polar ethanol produces a slight shift of the absorption bands of the carbonyl-containing compounds to shorter wavelengths. This indicates that the molecules are weakly polar in the ground state and are better solvated in toluene. Upon excitation the molecules are significantly polarized due to the shift of electron density onto the carbonyl group. As a result, the excited state is better solvated in polar medium. The relaxation of solvent molecules caused by the charge redistribution increases the Stokes shift in ethanol (7480 cm^{-1} for II and 7010 cm^{-1} for III). Formation of hydrogen bonds *via* the oxygen atom of the carbonyl group reduces the energy of the S^1 $\pi\pi^*$-state, which becomes lower than T $n\pi^*$ and as the result an intense fluorescence occurs. A deciding role of specific interaction in particular, in stimulating fluorescence is confirmed by the fact that any noticeable luminiscence is not observed in such polar aprotic solvents as acetone, dioxane and DMF; at the same time in acetic acid intense azure fluorescence is observed. Fluorescence is also stimulated if small (equimolar) quantities of proton-donor solvents are added to non-fluorescent solutions of carbonyl-containing compounds in aprotic media.

With respect to carboxylic acid IV, the T $n\pi^*$ level of the carboxyl group lies higher than that of the aldehyde and acetyl group [8, 9] and, apparently, higher than the S^1 $\pi\pi^*$-state. This is consistent with occurence of the fluorescence in toluene solutions. The weak electronacceptor ability of the carboxyl group causes the weaker solvation effects than for compounds II and III. Thus, the Stokes shifts for acid IV are only 4210 cm^{-1} in toluene and 3930 cm^{-1} in ethanol.

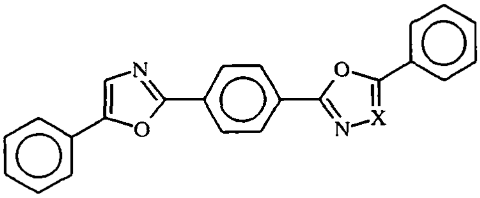
The nitrile group (compound VI) causes the same shift of the absorption band as carboxyl group (compound IV). A slightly greater effect is seen for oxime V. A weak electrondonor, the hydroxymethyl group (compound VII), produces a slight shift of absorption maxima to longer wavelengths.

The spectral luminescent characteristics of the furan-containing analogs of the 1,4-bis(5-phenylazol-2-yl)-benzenes are given in Table 2. The literature data for compound XX and related compounds that contain benzene or thiophene rings instead of furan rings [10] are presented for comparison. Replacing the benzene rings in compounds XXI and XXII with furan rings (compounds VIII-XI and XX) produces a shift to longer wavelengths for the absorption and emission maxima. However, this shift is less than in the series of thiophene-containing analogs XXIII-XXVI. Furthermore, replacing the central ring produces stronger effect than replacing a terminal ring. Such an effect was connected with the fact that the $S_0 \rightarrow S_1$ electronic transition, which is responsible for the long-wavelength absorption band and fluorescence of the polycyclic compounds possessing "chain" structure, is almost completely (~95%) localized on the three central rings [10]. The fluorescence quantum yields of compounds that incorporate furan ring have about the same values as compounds XXI and XXII. These values increase noticeably only for XX.



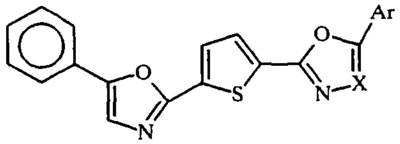
XX, XXV

XX Y = O; XXV Y = S



XXI, XXII

XXI X = CH; XXII X = N



XXIII, XXIV, XXVI

XXIII X = CH, Ar = Ph; XXIV X = N, Ar = Ph;
XXVI X = N, Ar = thien-2-yl

TABLE 2. Spectral Luminescent Properties of Compounds VIII-XI and XX-XXVI in Toluene

Compound	Absorption		Fluorescence	
	λ_{max}, nm	$\varepsilon \times 10^{-3}$	λ_{max}, nm	η
VIII	375	43,9	430	0,55
IX	360	34,8	415	0,50
X	355	50,0	420	0,50
XI	360	45,3	425	0,52
XX	354	45,1	410	0,71
XXI	365	52,0	415	0,41
XXII	350	44,5	405	0,57
XXIII	390	44,5	457	0,29
XXIV	375	34,4	443	0,26
XXV	380	39,9	445	0,29
XXVI	356	46,4	412	0,63

TABLE 3. Properties of Scintillators Based on Polystyrene with *p*-Terphenyl (2%) as Primary Additive

Spectral shifter (0.02%)	I_{sc}, %	$\lambda_{max\ sc}$, nm
VIII	42,4	435
IX	45,2	415
X	28,0	420
XI	43,8	425
XXI	53,6	420

TABLE 4. Characteristics of Synthesized Compounds

Compound	Empirical formula	Found, %	Calc., %	mp, °C	Yield, %
		N	N		
IV	$C_{14}H_9NO_4$	*		220,5...222,5	93
V	$C_{14}H_{10}N_2O_3$	11,14	11,02	235,5...236,5	95
VI	$C_{14}H_8N_2O_2$	12,04	11,86	148,5...150,5	86
VIII	$C_{22}H_{14}N_2O_3$	*2		172...174	56
IX	$C_{21}H_{13}N_3O_3$	12,12	11,83	220...220,5	61
X	$C_{19}H_{11}N_3O_4$	12,18	12,17	217...218	62
XI	$C_{20}H_{12}N_4O_3$	15,98	15,73	244,5...245,5	26

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* Compound IV is described in [1].

*2 Compound VIII is described in [12].

It seemed interesting to investigate the ability of furan analogs of 1,4-bis(5-phenyloxazol-2-yl)benzene to shift spectra of plastic scintillators based on polystyrene. The primary additive was *p*-terphenyl (2%). The shifter content was 0.02%. In table 3 the scintillation properties are listed: ISC is the light output relative to anthracene single crystals (100%) and $\lambda_{max,\ sc}$ is the position of the emission band of the scintillator. The use of mentioned additives as spectral shifters did not increase the light output of scintillation. However, the use of shifter VIII shifts the emission band to longer wavelengths so increasing the transparency of scintillator to its own emission, which is exceedingly important for large-scale scintillators.

EXPERIMENTAL

Electronic absorption spectra were recorded on an SF-26 instrument. Fluorescence spectra were recorded on an apparatus consisting of a ZMR-3 reflecting monochromator, and FEU-18 optical emission tube, and a M-95 microammeter. Photoluminescence was stimulated with an SVDSh-500 lamp. A DMR-4 quartz monochromator was used to isolate light of wavelength 365 nm. Spectra were corrected for the calculated spectral sensitivity coefficients of the apparatus. Fluorescence quantum yields were determined by equal absorption method [11]. IR spectra were obtained on a Specord IR-75 spectrometer in KBr pellets.

2-[5-Cyano(fur-2-yl)]-5-phenyloxazole (VI). To solution of aldehyde II (23.9 g, 0.1 mol) and hydroxylamine hydrochloride (13.1 g, 0.19 mol) in dry pyridine (145 ml) with mixing and cooling acetic anhydride (42 ml, 0.39 mol) was added. The mixture was stirred for 3 h at 100°C and poured into water (3 l). The product was purified on a continuous chromatographic column (adsorbent was silochrom, S-120 grade, eluent – hexane). IR spectrum (KBr): 2225 cm^{-1} (C≡N).

2-[5-Carboxy(fur-2-yl)]-5-phenyloxazole (IV). Mixture of nitrile VI (11.8 g, 0.05 mol) and NaOH (16.5 g) was boiled in water (50 ml) and EtOH (18 ml) for 1.5 h. Alcohol was distilled off and water (450 ml) was added to the residue. The mixture was boiled with a small quantity of activated carbon for 30 min and filtered. The filtrate was acidified with HCl to pH 2-3. The product was filtered off and purified as described in [1]. IR spectrum (KBr): 1625, 1675 cm^{-1} (C=O).

2-(5-Phenyloxazol-2-yl)furan-5-carboxaldehyde Oxime (V). To solution of aldehyde II (1.2 g, 5 mmol) in EtOH (40 ml) at room temperature solution of hydroxylamine hydrochloride (0.36 g, 5 mmol) and Na_2CO_3 (8.3 g, 7.8 mmol) in water (20 ml) was added. The mixture was stirred for 10 min, the formed precipitate was filtered off and recrystallized from chlorobenzene. IR spectrum (KBr): 3135 cm^{-1} (OH_{bound}), 3240 cm^{-1} (OH_{free}).

5-(5-Arylazol-2-yl)-2-(5-phenyloxazol-2-yl)furans (VIII-XI). The acid chloride obtained by boiling of carboxylic acid IV (2.55 g, 0.01 mol) and thionyl chloride (25 ml) in dry benzene (70 ml), was added to solution of α-aminoacetophenone hydrochloride or aroylhydrazine (0.01 mol) in 25 ml of 3% HCl; saturated solution of Na_2CO_3 was added under vigorous stirring until the solution was slightly basic. The condensation product was boiled for 5 h with 10 times the mass of $POCl_3$ and then poured into ice under stirring. The precipitate was filtered off and dried. The products were purified by chromatography on Al_2O_3 column (eluent benzene) and crystallized from ethanol.

The properties of the synthesized compounds are listed in Table 4. The progress of the reactions and the purity of the products were followed by TLC.

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