If Ω, $\omega << \tau_C^{-1}$, the dispersion of the base fluctuations $\sigma^2 \simeq \sigma_a^2/2$, and the condition $\sigma_a \geq 2.5 _{ca}$ is necessary for satisfaction of Eq. (11). This corresponds to a modulation depth of the base amplitude of ≈2% at $\nu_{ca} = 800$ Hz, $a = 100$ kHz. Note that the noise efficiency is greatest when the maximum in the spectrum of amplitude fluctuations is at the switching frequency of the variable base.

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SPECTRAL LUMINESCENT AND GENERATION PROPERTIES OF NEW ACTIVE MEDIA IN THE BLUE REGION OF THE SPECTRUM

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The range of polyatomic molecules generating emission in the blue region of the spectrum, in vapors and in solutions, is fairly broad. However, the energy parameters of generation of the known active media are not always optimal, and this limits the possibility of using tuned lasers. Thus, the widely known 2,5-diphenyloxazole and its substituted derivatives generating in the 350-400 nm region are insufficiently photochemically stable, and for several active media the threshold levels of the pumping power are high, etc.

The aim of the present work was to seek new active media, effectively generating in the blue region of the spectrum in solutions and in vapors; to study their spectral-luminescent and generation properties; and to establish patterns of their change according to the structure of the molecule.

A promising series appeared to be the distryryl and di(phenylethynyl) derivatives of benzene, diphenyl, diphenylmethane, diphenylene oxide and diphenyl ether, for the following reasons: firstly, it is known that the introduction of styryl and phenylethynyl substituents into different kinds of molecules leads to considerable improvement in their luminescent properties [1, 2], and therefore, on the basis of the above poorly fluorescing nuclei (the fluorescence quantum yield of diphenyl in cyclohexane is 0.18, diphenyl ether 0.12, diphenylmethane 0.20 [3]), effective luminophores can be produced, which find application as activators for liquid or plastic scintillators, as optical bleaching agents of high-molecular weight compounds, etc. Secondly, the study of molecules of this type is undoubtedly of interest from the standpoint of understanding the characteristic features of photophysical processes proceeding in molecules, where photoisomerization may occur during excitation.

Moreover, the new series of luminescing molecules can be used as laser active media in solutions and in vapors.

The compounds studied were obtained by condensation of the corresponding diodoarenes with styrene and phenylacetylene. The method was extended to a wide range of aromatic diiodides and was found to be fairly efficient. The yields of distryrylarenes were 40-80%, and of di(phenylethynyl)arenes 50-90%.

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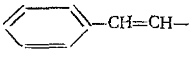
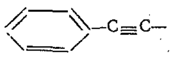
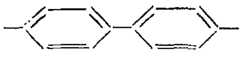
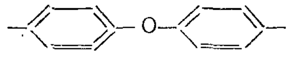
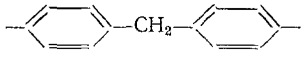
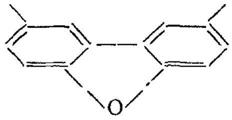
TABLE 1. Spectral Luminescent Characteristics of Distyryl and Di(phenylethynyl)arenes

Nucleus										
	λ_{abs}^{max}, nm	$\varepsilon\cdot10^{-3}$	λ_{fl}^{max}, nm	γ	τ, nsec	λ_{abs}^{max}, nm	$\varepsilon\cdot10^{-3}$	λ_{fl}^{max}, nm	γ	τ, nsec
	342 355 373	58	394 413 437	0.6 (0,78)	1.36	303 321 341	57	353 365 376	0,3	0,84
	349	20	399 420 445	0.3	0.97	326	26	370 389	0.3	0,78
	324	76	358 373 393	0.68	0.40	299	58	350 368 389	0,58	1.04
	303 321 329	41	345 360 379	0.46	0.28	—	—	—	—	—
	308 319 333	45	403 426 450	0.54	1.03	307	44	344 352 388	0,98	4.5

Notes. Solvent – toluene; in brackets, γ taken from [3].

The electronic absorption spectra were run on a Specord UV-VIS two-beam recording spectrophotometer, and the fluorescence spectra on a Fica fluorimeter. The lifetimes of the fluorescent state τ were measured on PRA-300 pulse spectrofluorimeter. The fluorescence quantum yields γ were measured by a method described in [4], using a solution of para-tetraphenyl in toluene with γ = 49% as standard [3].

The generation properties of the solutions were studied on an apparatus described in [5]. In the study of vapors, a high pressure cuvette [6] was used. An excimeric XeCl* laser with a power of up to 2 MW served as the pumping source, the pulse duration at the half-height was 20 nsec, repetition frequency of pulses 1 Hz [7]. The spectrum and the generation pulse were recorded photoelectrically, and the value of the threshold level of the pumping power was also measured.

The results of our study are summarized in Tables 1 and 2. In discussing the results obtained, it is necessary to determine the features of the spectral image of styryl and phenylethynyl substituents in the series of molecules studied and to examine the spectral–luminescent and generation properties in the series of distyryl- and di(phenylethynyl)arenes in dependence on the "nucleus" of the molecules.

The introduction of a phenylethynyl fragment into the series of molecules studied is characterized by a short-wave shift of the absorption and fluorescence bands. This fact has already been noted in substituted derivatives of benzoxazole derivatives [2]. However, the value of this shift depends substantially on the nucleus of the molecule (see Table 1).

The greatest short-wave shift of the absorption band (for all the compounds studied, the $\pi\pi^*$-type bands, most of them having a sharply expressed vibrational structure) is observed for benzene derivatives ($\Delta\lambda_{abs}$ = 34 nm), while the smallest short-wave shift of the absorption is observed in the case of diphenyl oxide ($\Delta\lambda_{abs}$ = 12 nm). The fluorescence band is also shifted to the short-wave region, but for the two above compounds, the shift is approximately the same: 48 and 51 nm.

On transition from styryl to phenylethynyl fragment, the short-wave shift of absorption and fluorescence is probably due to the fact that the triple bond is more "rigid" than the double bond and more poorly transmits the conjugation between the benzene rings. The degree of this effect depends on the nucleus of the molecules into which these fragments are introduced. It can thus be seen that for benzene derivatives the conjugation disruption effect is quite high, and the short wave shift of absorption is maximal, while in the diphenyl ether derivatives, this effect is smaller, since conjugation is poorly transmitted through the oxygen bridge. The short-wave shift of the absorption and fluorescence spectra is also smaller for diphenyl derivatives, which is probably due to a smaller conjugation transmission through the diphenyl nucleus because of the absence of coplanarity.

The Stokes' shift is different for compounds with styryl and phenylethynyl fragments. For styryl-substituted derivatives it is somewhat higher, which may be due to greater possibilities of formation of photoisomers.

With regard to the fluorescence efficiency of the compounds studied, it can be noted that a definite trend in the change of γ was not observed on transition from distyrylarenes to diphenylethynylarenes. Thus, while for the benzene derivatives, γ decreases from 0.6 to 0.3 on transition to the phenylethynyl substituted derivative, for diphenylene oxide derivatives it increases from 0.54 to 0.98, and for diphenyl and diphenyl ether derivatives it practically does not change.

For most of the compounds studied $\tau \sim 1$ nsec. It should be noted that for 4,4'-distyrylphenylmethane two exponents were observed in measuring τ: of a long-lived fluorescing center ($\tau = 3.28$ nsec; 5.5%) and a short-lived one ($\tau = 0.3$ nsec; 94.5%), which may indicate the possibility of formation of a cis-isomer during photo-excitation or the possible admixture of the cis-isomer in the initial compound. For the remaining compounds studied, one exponent was observed with a short duration τ (Table 1).

We shall now examine the changes in the spectral-luminescent properties in the distryryl- and di(phenylethynyl)arene series, in dependence on the nucleus of the molecule.

In the series of nuclei (benzene, diphenyl, diphenyl ether, diphenylmethane, diphenylene oxide), as expected, benzene and diphenyl derivatives have the greatest long-wave absorption. In the remaining molecules, the presence of bridges in the form of oxygen or CH_2 group, leads to a decrease in the length of the conjugation chain, as a result of which the absorption of these molecules is to a certain degree short-wave. However, for the molecule of 4,4'-distyryldiphenylmethane, the long-wave shift of the spectrum, compared with stilbene ($\lambda_{abs.}^{max} = 290$ nm) is nevertheless observed, while, in particular, the absence of conjugation transfer through the CH_2 group should have determined the absorption of 4,4'-distyryldiphenylmethane. This may indicate the possibility of conjugation transfer through the CH_2 group.

The change in the spectral—luminescent properties in diphenylene oxide derivatives is interesting. The absorption band of 3,6-distyryldiphenylene oxide is shifted to a short-wave region of the spectrum, compared with the band of 4,4'-distyryldiphenyl, which indicates a lower efficiency of conjugation transmission in this compound. The fluorescence, however, lies in the same region as in the case of 4,4'-distyryldiphenyl, which indicates a possible change in the geometry of the molecule during excitation.

Similar changes in the absorption and fluorescence for the series of nuclei studied are observed also in the case of di(phenylethynyl)-arenes, but all these spectra are shifted to the short-wave region.

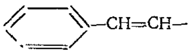
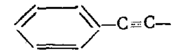
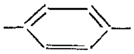
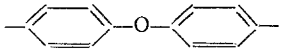
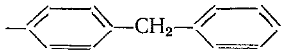
In the study of the generation properties of the molecules, toluene was used as the solvent. A lateral variant of pumping was used, the cuvette was 10 × 10 × 20 mm, and the solution was stationary.

The results obtained are listed in Table 2. Note that the generation was obtained on molecules, whose structure was previously not considered favorable for obtaining generation (4,4'-distyryldiphenyl ether, 4,4'-distyryldiphenylmethane).

The new active media have fairly good energy parameters. Thus, the threshold level of pumping power W_{thr} of 4,4'-di(phenylethynyl)diphenyl is comparable with W_{thr} of the well known 1,4-distyrylbenzene, but the generation is realized in a shorter-wave region of the spectrum and the duration of the generation pulse is much longer than in the case of 1,4-distyrylbenzene and 1,4-di(phenylethynyl)benzene. This indicates a smaller influence of harmful losses for this molecule. The photostability of this solution is high, after 10^4 pulses the radiation intensity practically did not change. The threshold levels of pumping power in 4,4'-distyryldiphenyl ether and 4,4'-distyryldiphenylmethane are higher. This is due to the influence on the generation process of different possible structure distortions in the second case, or due to the influence of induced absorption from the excited states, as the duration of the pulse generation of the first compound (8 nsec) is much shorter than that of the pumping pulse.

Despite the favorable spectral-luminescent characteristics of 4,4'-di(phenylethynyl) ether (Table 1), its generation in a toluene solution could not be obtained. The harmful influence

TABLE 2. Generation Properties of Distyryl- and Di(phenylethynyl)arenes in Toluene

Nucleus						
	λ_{gen}^{max}, nm	W_{thr}, MW/cm²	t_{puls}, nsec	λ_{gen}^{max}, nm	W_{thr}, MW/cm²	t_{puls}, nsec
	416	0.25	14	370	0.35	14
	423	0.70	10	392*	0.25	28
	376*	5	8	—	—	—
	395*	2.3	—	—	—	—

Note. $t_{pump.pulse}$ = 30 nsec; for para-tetraphenyl W_{thr} = 0.35 MW/cm².

*Generation was obtained for the first time.

of impurity should probably be excluded, since three samples were studied, which were purified to different degrees. For reasons not established, generation was not obtained for solutions of 3,6-distyryl-, 3,6-di(phenylethynyl)-diphenylene oxide and 4,4'-di(phenylethynyl)-diphenyl ether. The pumping power exceeded by one order of magnitude the threshold levels of pumping power for other derivatives studied (Table 2).

Thus, the most effective new method is a solution of 4,4'-di(phenylethynyl)diphenyl in toluene. It can find application in tuned lasers in this range of the spectrum.

Certain new active media, generated in a nonpolar solvent, toluene, were found to be capable of also generating in a gaseous phase: 4,4'-di(phenylethynyl)- and 4,4'-distryryldiphenyls generate in the 370 and 400 nm regions at a high pentane concentration ($\geq 6.9 \cdot 10^{20}$ cm³). Of the analogous benzene derivatives, only 1,4-di(phenylethynyl)benzene generated in the gaseous phase [8]. This may be due to the fact that the introduction of the phenylethynyl substituent makes the molecules more rigid, and decreases the possibility of rotation of fragments in the gaseous phase. However, the fact that the generation of 1,4-distyrylbenzene in the gaseous phase was not obtained, indicates the higher possibilities of this molecule to undergo photoisomerization in the vapor state, than in the case of 4,4'-distyryldiphenyl. The threshold levels of the pumping power of the new active media in vapors are relatively low, and change depending on temperature and pressure of pentane. In generation efficiency, some of them, as for example, 4,4'-di(phenylethynyl)diphenyl, are close to the known active medium in the gaseous phase, para-tetraphenyl. Their high photosensitivity, and generation characteristics in toluene did not change after the experiment in the gaseous phase.

Thus, a series of organic luminophores based on benzene, diphenyl, diphenyl ether, diphenylmethane and diphenylene oxide (4,4'-distyryldiphenyl ether and 3,6-distyryldiphenylene oxide were obtained for the first time) were synthesized by a new method, and new patterns of change in their spectral-luminescent properties, depending on the structure of the molecules, were found. The generation of emission obtained for the new compounds in vapors and in solutions is fairly efficient, especially in the case of 4,4'-di(phenylethynyl)diphenyl.

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X-RAY AND THERMALLY STIMULATED LUMINESCENCE IN YAG

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UDC 535.37

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) crystals with rare earth ion (REI) impurities are widely used in laser technology and also in the capacity of cathode luminophors [2]. Recently they have attracted the attention of researchers for their possible use as x-ray luminophors [3], scintillators, and thermoluminescent detectors [4]. However, research in these areas is not very comprehensive.

This work compares the intensity of x-ray luminescence (XRL) and the inertial characteristics of YAG monocrystals that are activated by REI (Ce^{3+}, Sm^{3+}, Dy^{3+}, Tm^{3+}, and Er^{3+}), with the x-ray luminophore CsI-Tl. Since the existence of deep capture levels exerts a significant influence on the useful properties of x-ray luminophores, YAG thermoluminescence was also studied. Monitoring the REI concentration was done by observing the absorption spectra using an MPS-50L spectrophotometer. The XRL spectra for the visible portion of the spectrum were analyzed using a DMP-4 monochromator and a FEU-106 photomultiplier and the XRL and TSL intensities were recorded directly by a photomultiplier in conjunction with a KSP-4 and H-306 recording potentiometer. The samples were excited with x-rays (W-anticathode, 50 kV, 10 mA). To study the afterglow extinction kinetics, the samples were excited by pulsed x-radiation $4 \cdot 10^{-4}$ sec in duration from a tube operating in the pulsed regime, and the signal from the photomultiplier was fed to a S1-70 oscillograph.

YAG X-Ray Luminescence

All studied samples have clear XRL in the visible portion of the spectrum, the spectral composition of which is characteristic for the rare earth ion introduced in the YAG. The luminescence light is visibly close to white for Dy^{3+}-YAG and Tm^{3+}-YAG, it is yellow-green for crystals activated by cerium, blue for erbium, and orange for samarium.

The XRL intensity of garnets was compared with the XRL intensity of the CsI-Tl x-ray luminophore, taken as 100 units by convention. These data are generalized in Table 1, from which it is clear that samarium activated YAG has the brightest XRL in comparison with CsI-Tl. For Ce^{3+}-YAG, the relative XRL intensity value obtained coincides with the data in Ref. [3] and apparently, for the given samples having a high cerium content, the value is close to maximum (the integrated absorption coefficients of the most intense REI absorption bands, situated in the visible part of the spectrum, are cited in Table 1). For other REI, the YAG XRL intensity is significantly less.

One of the fundamental requirements imposed on x-ray luminescence is a small amount of afterglow intensity I_a. The relative afterglow $A = (I_a/I) \cdot 100\%$, where I is the XRL intensity, is usually used in place of I_a. For the x-ray luminophor CsI–Tl, useful in defectoscopy, the authors of Ref. [5] proposed measuring the relative afterglow value 5 seconds after cessation of the excitation and indicated its criteria (not more than 1.5%). In using the x-ray luminophore in devices for recording rapid processes, for example, in x-ray electrooptical transducers, the value of A can be estimated $1 \cdot 10^{-3}$ sec after cessation of the excitation [6]. Cited in Table 1 are the comparative data that we obtained for the studied YAGs and for the CsI-Tl x-ray luminophore.

For an estimate of the persistent afterglow, the extinction of luminescence was analyzed after cessation of stationary x-ray excitation. In this case the value of A 5 sec after cessation of the excitation is the smallest in cerium activated garnet and is comparable to CsI-Ti in the remaining crystals.

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