HETEROCYCLIC COMPOUNDS AS THE ACTIVE MEDIA OF LASERS (REVIEW)

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The principle of the action of lasers based on crystals and methods for the production of an inverse population are examined. The properties of various classes of heterocyclic compounds used as the active media in lasers based on crystals are discussed. The effect of the triplet states of a dye on generation is examined. The relationship between the generation properties and the structure of the dye molecule and the effect of a solvent on the generation of dyes are discussed.

Lasers differ with respect to the types of substances used as active media. The active centers of gas lasers are atoms, ions, and simple molecules, whereas ions of rare-earth elements in glasses and crystals, as well as the trivalent chromium ion in rubies, are used in solid-state light generators. Up until recently, ions of rare earths incorporated in the compositions of intricate organic complexes (chelates) dissolved in organic solvents were used exclusively in liquid lasers [1]. Solutions of organic compounds, the bulk of which are heterocyclic compounds, have recently come to be widely used as the active media of lasers.

Let us briefly examine the principle of the operation of lasers based on organic compounds. A diagram of the energy levels of a polyatomic molecule is shown in Fig. 1 [2]. The generalized coordinate that characterizes the electron configuration of the molecule is plotted along the axis of abscissas. In the case of an equilibrium thermal distribution at room temperature the molecules are found in the lower vibrational sublevel of the ground electronic state (S_0). When the molecule absorbs light, it is converted to one of the vibrational sublevels of excited state S_i. After the absorption of light, the molecule undergoes vibrational relaxation to the lower vibrational sublevel of excited state S_1. This process takes place in a time span on the order of 10^{-11}-10^{-12} sec, and all of the molecules in S_1 therefore relax before other processes occur. The molecule may revert from the lower level of the S_1 state to the S_0 state via an emissive or nonemissive path. The emissive $S_1 \rightarrow S_0$ transition is called fluorescence. Stimulated emission from the S_1 zero vibrational level to the high-lying sublevels of the S_0 state obtained under conditions of high-power excitation in an optical resonator is generation based on solutions of a dye. If one examines the transitions only between S_0 and S_1, it is apparent from Fig. 1 that absorption and emission take place between four levels of the molecule. Inversion of the populations of the levels is of chief importance for the development of generation, i.e., the number of molecules in the upper level from which emission takes place should exceed the number of molecules in the lower level, to which the molecule falls after light emission.

Under ordinary conditions the number of molecules in the high vibrational sublevels of the lower electronic state (the lower laser level) is very small. In this case an inverse population and, as a consequence of this, the possibility of obtaining stimulated emission arise even in the case of low intensities of the exciting light [3]. This is impossible in a system with two levels in the presence of exciting light [4].

Three different transitions that compete with fluorescence and, consequently, with generation are possible from the S_1 state. First, transitions between S_1 and the higher excited singlet states may lead to absorption of the generation emission and cause losses in the laser. Second, nonemissive transitions (internal and intercombination conversion, respectively) that decrease the fluorescence quantum yields and, consequently, the generation efficiency occur between the S_1 and S_0 and S_1 and T_1 states. Losses due to T_1—T_2 absorption arise during population of the T_1 state. This absorption may have the same frequencies as fluorescence and will thus interfere with the development of generation.

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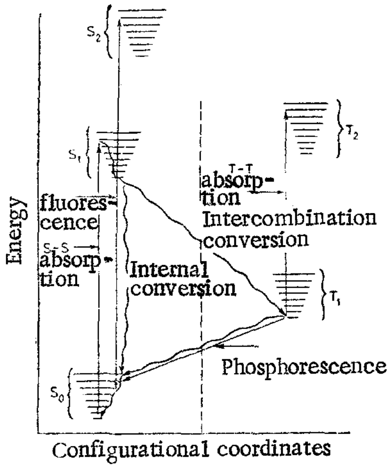


Fig. 1. Diagram of the energy levels of a dye molecule.

Generation based on a solution of an organic compound was first obtained in 1966 [5]. From the very beginning, the development of lasers of this type involved the study of and search for active media from a number of efficiently luminescing organic compounds. However, this painstaking and prolonged search did not always lead to the expected results. Thus far, there are no clear concepts regarding the interrelationship between the molecular structures and physicochemical and laser properties of organic compounds. This hinders the purposeful synthesis and selection of compounds for active media for lasers.

Lasers based on organic compounds still cannot compete with solid-state lasers with respect to energy and emissive power. However, since the width of the luminescence band of solutions of organic compounds is quite large (up to 200 nm), one can tune the generation frequency within the limits of this band. This important property of organic compounds is due to the recent markedly increased interest in the study of their spectroscopic and generation properties. The great and important task of the creation of new active media with improved characteristics can be solved only by the joint efforts of physical chemists, spectroscopists, and organic chemists. The aim of the present review is to acquaint organic chemists, particularly those engaged in research on heterocyclic compounds, with the modern state of the problem of the active media of lasers based on organic compounds. For this, in the present review we examine the principles of the operation of such lasers, the principal criteria of the capacity of organic compounds for generation, the principal classes of compounds that are used in active media, and methods for increasing the efficiency of the generation of lasers based on organic compounds.

1. Characteristics of the Principal Classes of Generating Compounds

The following principal criteria for substances that are capable of generation can be formulated.

1. The compound should have strong absorption at the excitation wavelengths ($\varepsilon \geqslant 10^4$ liters/mole cm) and, at the same time, should have minimal absorption at the generation wavelength, for which the absorption spectrum of the organic compound should overlap with its fluorescence spectrum as little as possible.

2. The fluorescence quantum yield should be quite high (0.5-1.0).

3. The optimum fluorescence lifetime should be on the order of 5-10 nsec.

4. An efficient laser compound should have minimal absorption in the first excited state at the excitation and generation wavelength.

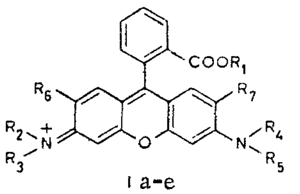
5. The compound should have a low probability of intercombination conversion ($S_1 \rightarrow T_1$), and the spectrum of triplet—triplet absorption should not overlap with the generation spectrum.

6. The substance should be sufficiently photochemically stable.

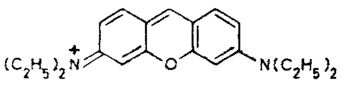
7. An ideal laser substance should dissolve in water and should retain its properties in the dissolved state; in particular, it should not form dimers at the concentrations used in the laser (10^{-2}-10^{-4} mole/liter) and should not react with substances that hinder aggregation. Since the refractive index of water changes only slightly with the temperature, it

is the best solvent for laser substances, since a certain amount of thermal energy is released in the generation process, and this leads to temperature gradients and optical nonuniformity of the solution.

Xanthene dyes are most widely used as active media in lasers [6-16]. They generate over a broad spectral range (500-700 nm) and are very efficient. The following xanthene dyes are widely used in lasers: unsubstituted rhodamine (Ia) [17], rhodamine Zh (Ib), rhodamine 6Zh (Ic) [18-23], rhodamine C (Id) [24], rhodamine 3C (Ie) [17, 25], and pyronine C (II) [26].



I a-e



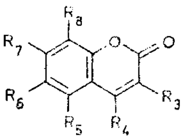
II

a $R_1, R_2, R_3, R_4, R_5, R_6, R_7 = H$; b $R_1, R_3, R_5 = C_2H_5$; $R_2, R_4, R_6, R_7 = H$;
c $R_1, R_3, R_5 = C_2H_5$; $R_2, R_4 = H$; $R_6, R_7 = CH_3$; d $R_1, R_6, R_7 = H$; $R_2, R_3, R_4, R_5 = C_2H_5$
e $R_6, R_7 = H$; $R_1, R_2, R_3, R_4, R_5 = C_2H_5$

The dipole moment of the transition of the principal absorption band of xanthene dyes, which is situated between 450 and 600 nm, is parallel to the long axis of the molecule. The transitions to the shortwave region have a moment that is perpendicular to the long axis of the molecule. The position of the longwave band depends substantially on the substituents in the 3 and 7 positions of the molecule. The carboxyphenyl group has virtually no effect on the absorption spectrum, and pyronines therefore absorb light in the same region as rhodamines. Esters of rhodamines have absorption spectra that are the same as the spectra of the free acids. Methyl groups in the 3 and 7 positions in rhodamine do not affect either the absorption spectra or the fluorescence spectra. The position of the maxima of the absorption spectra of rhodamines depend substantially on the solvent, particularly for dyes in which the amino groups are not completely methylated [27].

The fluorescence spectra of xanthene dyes are close to mirror reflections of the longwave bands of the absorption spectra. The maximum of the fluorescence spectrum is shifted as compared with the maxima of the absorption spectra (the so-called Stokesian shift) to the extent of 10 nm for pyronines and 20 nm for rhodamines. The fluorescence quantum yields (φ) of xanthene dyes are independent of the excitation wavelength [28, 29], but in some cases do depend on the acidity of the solution [27]. Fluorination of the dyes or the solvent increases φ. Rhodamine dyes have φ values ranging from 0.6 to 0.9, high generation efficiency, and high solubility in various solvents, particularly in water. This makes it possible to obtain generation in aqueous solutions in the presence of substances that hinder the formation of dimers [30].

Dyes that have structural formula III are classified as coumarin dyes [31-36].



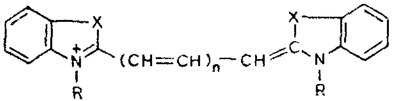
III

d,e,f $R_3, R_4, R_5, R_6, R_8 = H, Alk$
$R_7 = OH, N(C_2H_5)_2$

For efficient coumarin dyes the φ values range from 0.5 to 0.8 [37-43]. The spectral range of generation of coumarin dyes is 400 to 560 nm [44-48]. Coumarin dyes with substituents in the 4, 6, and 7 positions have the most efficient generation [27]. Benzocoumarins are promising from the point of view of generation [49]. The recently synthesized water-soluble coumarins [50], which generate with high efficiency at 450 to 520 nm, are of great interest.

Oxazine dyes (phenoxazine derivatives) have maxima in their absorption spectra ranging from 578 nm for resorcinol to 635 nm for Nile blue. The Stokesian shift of the fluorescence spectra of oxazine dyes in ethanol is ~ 30 nm. The range of generation of this class of dyes is 650 to 750 nm. The efficiency of generation and the photostability of these dyes make them the best active media in the red and near-IR regions [27]. Because of the small difference in the energies of the ground and excited states, the effect of the vibrations of the C–H bonds of the terminal groups is stronger than in the case of xanthene dyes. The use of deuterated alcohol as the solvent therefore increases the fluorescence efficiency of these dyes [17]. Like the xanthene derivatives, the oxazine dyes have reduced φ values in ethanol. However, the fluorescence efficiency of oxazine perchlorate is quite high in dichloroethane, 1,2-dichlorobenzene, and trifluorotoluene [17]. Fluorinated alcohols cannot be used, since they react with the central nitrogen atom and reduce the φ values of oxazines.

Polymethine dyes constitute the most highly populated class of laser organic compounds [51-53]. They generate in the red and IR spectral ranges up to 1175 nm [27]; however, they are less efficient than oxazine compounds at wavelengths shorter than 750 nm. Of the variety of polymethine dyes, polycarbocyanine dyes with structural formula IV have the best generation characteristics.



IV

d,e,f $R = CH_3, C_2H_5$; $X = O, S, -CH(CH_3)_2$

$n = 1, 2, 3$

Dyes IV with n = 2 have the highest generation efficiency [54, 55]. Polymethine dyes have φ values ranging from 0.3 to 0.6 and are quite soluble in organic solvents. The advantages in the use of solutions of polymethine dyes in dimethyl sulfoxide (DMSO) have been noted [55]. The photostability of this class of compounds is determined not only by their nature but also by the temperature, the nature of the solvent, and the intensity of the exciting light [56]. In contrast to other classes of dyes, isomerization reactions proceed at a high rate in the case of polymethine dyes in the excited singlet state [57-61].

The examined classes of dyes, as well as acridine [62] and phthalimide [63-65] derivatives and some hydroxy and amino derivatives of aromatic hydrocarbons [66-78], ensure generation in the visible and IR spectral regions. Organic scintillators generate in the near-UV and violet regions of the spectra [79-95]. The structures of scintillators that generate in the UV and violet regions can be represented by formulas V and VI, respectively.

$R_1—X—R_2$ V

$R_1—X—R_2—X—R_1$ VI

Note. R_1 and R_2 are phenyl groups, and X is a five-membered ring (oxazoles and oxadiazoles) or a p-polyphenyl grouping.

Organic scintillators have high φ values (≈ 0.8) and rather short lifetimes of the molecules in the excited state (τ = 1-5 nsec). Lamp excitation of organic scintillators makes it possible to obtain generation in the UV region up to 330 nm [96]. The efficiency of the generation of organic scintillators in the case of lamp excitation is one to two orders of magnitude lower than in the case of the dyes of the visible range; this is probably associated with the stronger triplet–triplet absorption [97].

2. Utilization of Rapid Reactions in the Excited State to Obtain an Inverse Population in Lasers

An inverse population of the electron levels of a generating form can be easily obtained if this form is obtained due to a rapid reaction in an excited electronic state. Reactions of this sort may include reactions involving electron and proton transfer, isomerization reactions, and various intramolecular rearrangements [98, 99]. The generating particle virtually does not exist in the ground electronic state because of a rapid reverse reaction. The principal requirements for systems for the production of generation of the forced emission by this method are a large value of the reaction rate constant in the excited state, a large difference in the equilibrium constants in the ground and excited states, a large value of the coefficient of absorption of the starting compound, a small degree of absorption by the excited molecules over the emission range, a high luminescence quantum yield of the generating particle, and the absence of photochemical side reactions.

It is known that the ability of hydroxy derivatives of aromatic hydrocarbons to split out a proton from the hydroxy group increases and that the pK value of the acid—base equilibrium decreases as compared with the ground state when these compounds are excited [100]. The first dye-based laser, in which a protolytic reaction in the excited state was used was created in a solution of sodium acetamidepyrenetrisulfonate, which in the excited state loses a proton from the amino group and forms a quadruply ionized anion [27]. Solutions of 4-methylumbelliferone in water and alcohol, in which the generating forms are obtained as a result of a protolytic reaction in the excited state, have been studied in detail. Various forms of 4-methylumbelliferone exist in the excited state, depending on the acidity of the solution [101]. By changing the percentage of water or acid in alcohol solution, one can obtain a mixture of various forms that generate over a broad spectral range (375-600 nm). During a study of the spontaneous and stimulated emission of various solutions of 4-methylumbelliferone it was found that when water, HCl, or $HClO_4$ is added to an alcohol solution of the dye, the absorption spectra of the solutions do not change, whereas new bands, which evidently belong to forms that exist only in the excited state, appear in the fluorescence spectra [102]. These are forms of two types, viz., those that are protonated at the carbonyl group, and those that are protonated at the ring oxygen atom. It was shown that the two forms are produced successively in the case of umbelliferone: the carbonyl group is protonated initially, after which a form that is protonated at the ring oxygen atom is produced from this form [103]. The form that has an emission maximum at 485 nm is the phototautomer of the starting 4-methylumbelliferone molecule, which is formed in the excited state via a two-step proton transfer reaction [104]. Protolytic reactions in the excited state have been used to expand the spectra of generation of solutions of esculin, 4-methylumbelliferone, and 3-methoxybenzanthrone [105]. Generation of the deprotonated form of sodium 8-hydroxypyrene-1,3,6-trisulfonate, which is formed due to a proton-transfer reaction in the excited state, in water has been produced [106]. The generation of complexes with a hydrogen bond that are formed by excited 4-aminomethylphthalimide molecules with alcohol or water molecules in dioxane solution has been demonstrated [107].

Fast electron-transfer reactions can also be used to obtain an inverse population of the levels and laser generation. Thus, the addition of small amounts of N,N-dimethylaniline to a pyrylium salt gives rise to a 10-nm shift of the spectrum of laser emission due to the formation of a charge transfer complex in the excited state [108]. A similar laser effect was found for exiplexes formed by intramolecular electron transfer [109]. The stimulated emission of the intramolecular exiplex of p-(9-anthryl)dimethylaniline is found only in nonpolar and weakly polar solvents.

Singlet—singlet energy transfer is an interesting method for the production of a laser effect for compounds with low absorption efficiency. In essence, this method consists in the fact that the exciting light is absorbed by one substance (the energy donor), after which nonemissive transfer of energy to the excited level of another compound (the energy acceptor) occurs, and generation of this second substance is observed. The donor in this case should have a large coefficient of absorption, while the acceptor should have a high fluorescence quantum yield. The problem here consequently consists in selection of the optimal donor-acceptor pairs of compounds. In doing this, one must take into account the facts that a) both compounds should generate independently, b) the absorption spectra of the donor and acceptor should not overlap, c) the donor should not have T—T absorption in the fluorescence band of the acceptor, and d) the substances should be chemically compatible and resistant to the action of intense light exposure. A compound that has a large coefficient of absorption and good overlapping of the emission spectrum with the absorption spectrum of the acceptor can be a good donor for generation if its fluorescence quantum yield is low. A mixture of 7-diethylamino-4-methylcoumarin, acriflavine, and rhodamine C is an example of the use of energy transfer from a donor to an acceptor [110]. In the case of laser excitation of 7-diethylamino-4-methylcoumarin, generation of two other substances is observed along with its generation. Energy transfer is the principal pathway for populating the excited levels of acriflavine and rhodamine C. The use of donor-acceptor pairs in tunable lasers makes it possible to increase their efficiency and range of tuning of the generation frequency and also makes it possible to shift it within certain limits by changing the relative concentrations of the compounds [111].

3. Effect of Triplet—Triplet Absorption on the Generation of Organic Compounds

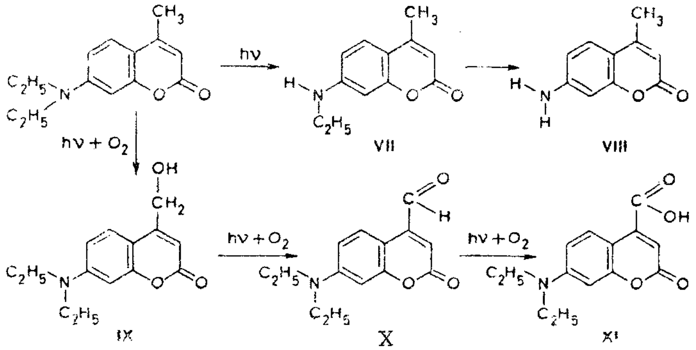
As discussed above, triplet—triplet absorption may interfere with generation. The detrimental effect of this absorption will be greater in the case of lamp excitation than in the case of laser excitation because of the greater duration of the exciting pulse. The effect of the population of the lower triplet level on the generation of organic compounds in the case of lamp excitation has been examined repeatedly [112-115]. To obtain the dependence of the characteristics of generation on the properties of a triplet system of levels one must know the rate of the intercombination conversion, the coefficients of T—T absorption, and the lifetime of the lower triplet state.

To decrease the losses caused by T—T absorption, it has been proposed that a substance that effectively increases the rate of triplet—singlet conversion [116] and consequently decreases the population of the T level be added to a solution of the dye. The fundamental possibility of increasing the efficiency and duration of generation by means of substances that extinguish the triplet state has been demonstrated theoretically and experimentally [117]. Oxygen is an efficient extinguisher of the triplet state. The positive effect of oxygen, cyclooctatetraene, and dicyclopentadiene was observed during a study of the effect of oxygen, cyclooctatetraene, dicyclopentadiene, cyclohexadiene, p-cymeme, m-dinitrobenzene, and phenanthrene on the efficiency of generation of rhodamine dyes [118]. The dependence of the generation energy on the concentration of the extinguishing agent has an optimum value for all of these extinguishing agents. The existence of an optimal concentration is due to the fact that the extinguishing agents not only decrease the lifetime of the triplet level (positive effect) but also increase the probability of an intercombination transition (negative effect). In addition, the negative effect of the extinguishing agents is associated with their photodecomposition under the influence of the UV component of the excitation; the products may either absorb the emission in the range of the generation spectrum or promote photoconversion of the dye molecules. During a study of the generation characteristics of a solution of fluorescein sodium in ethanol, it was shown that the solution does not generate with the excitation parameters used in the experiment [118]. Generation was observed when anthracene, which is an efficient extinguisher of the triplet state, was added to the solution. The addition of anthracene led to lowering of the generation threshold and to a decrease in the photodecomposition of the fluorescein sodium. It was demonstrated theoretically that the same extinguishing agent may both increase and decrease the energy of the generated emission, depending on its concentration and the duration of the exciting pulse [119]. A large collection of extinguishers of the triplet state, viz., 1,3-cyclooctadiene, bicyclo[2.2.1]hepta-2,5-diene, cycloheptatriene, N-aminohomopiperidine, sodium nitrite, pyrazine, carbon disulfide, S-triazine, sulfur dioxide, cyclooctatetraene, and oxygen, has been proposed for improvement of the generation properties of a number of dyes in the case of lamp excitation [45]. The improvement of the generation characteristics of a solution of rhodamine 6Zh when cyclooctatetraene is added does not occur as a result of interaction of the extinguisher molecule with the triplet state of the dye, but rather as a result of a decrease in the rate of the intercombination conversion of the rhodamine 6Zh molecule when it is surrounded by a coating made up of cyclooctatetraene molecules [120]. It has been proposed that fluorobenzene, chlorobenzene, bromonaphthalene, $MnSO_4$, $Mn(NO_3)_2$, $InCl_3$, $SmCl_3$, and $EuCl_3$ be used to decrease the population of the triplet state of rhodamine 6Zh [121]. The decrease in φ and the lifetime of the singlet state of the dye when these compounds are added is insignificant, whereas the analogous characteristics of the triplet state decrease substantially. The addition of $K_4[Fe(CN)_6]$ increases the generation efficiency of rhodamine 6Zh by a factor of two [122].

4. Photostabilities of Active Media

Decomposition of the working substance occurs during operation of dye-based lasers under the influence of the exciting light. Large losses are also associated with absorption of the generated radiation by the photochemical products. The quenching of the fluorescence of the active substance by the products may be substantial. The decomposition of a number of organic dyes used in lasers has been investigated. The action of intense pulse excitation on rhodamine 6Zh, rhodamine C, pyronine C, acridine orange, cresyl violet, dichlorofluorescein, and fluorescein sodium has been studied [123]. The absorption of solutions of dyes, which attests to their photodecomposition, decreases under the influence of irradiation. Similar studies were made with continuous irradiation [124] and it was found that rhodamine 6Zh, fluorescein, rhodamine C, acridine red, and pyronine C decompose. An increase in the generation energy of alcohol solutions of rhodamine 6Zh is observed when the UV part of the excitation at wavelengths shorter than 230 nm is filtered out [125]. A substantial increase in the photostability of solutions of the dye was noted simultaneously. Extinction of the fluorescence of rhodamine by the photodecolorization products was observed during a study of the photodecolorization of solutions of rhodamine 6Zh in ethanol [126]. In methanol the decomposition of rhodamine 6Zh during irradiation takes place in two successive steps, one slow and one fast [127]. The second step is initiated by the products of the first step. Oxygen slows down the decomposition. The photostability of rhodamine 6Zh increases when it is in a cooled solid matrix. When poly(methyl methacrylate) is used as the matrix at low temperatures, the photostability of rhodamine 6Zh increases several times [128]. This increase in the photostability is explained by an increase in the microscopic rigidity, which impedes diffusion of the decomposition products. A study of the processes involved in the photodestruction of ethanol solutions of rhodamine and oxazine dyes showed that the initial photodestruction process is photodecomposition under the influence of UV excitation irradiation with the subsequent formation of acetic and formic acids [129]. An intermediate in the irreversible decolorization of rhodamine 6Zh may be its half-reduced form, which is formed in the reaction of the excited dye molecule with the solvent [130]. Upon the whole, the photoreduction of rhodamine dyes in ethanol is a complex combination of photoelectric and dark forward and reverse processes, in some of which molecules of alcohol and its decomposition products participate.

Five products are formed when 7-diethylamino-4-methylcoumarin is irradiated in ethanol with a pulse lamp [131]:



The formation of products VII and VIII does not require the presence of oxygen. The addition of VII and VIII to a solution of 7-diethylamino-4-methylcoumarin does not affect the generation threshold of this solution. The reaction with the participation of oxygen leads to the formation of products IX, X, and XI. The addition of products IX and X to the generating solution, also does not affect the generation threshold. The addition of XI to a fresh solution of the dye markedly increases the generation threshold. Compound XI in 5% amounts affects the generation threshold in the same way as 250 flashes of the pulse lamp. Compound XI absorbs at 470 nm, at which generation of 7-diethylamino-4-methylcoumarin is observed. The increase in the generation threshold occurs primarily due to optical absorption by XI, rather than as a result of a decrease in the dye concentration. For coumarin dyes that contain a methyl group it is recommended that a) oxygen should be replaced by another nonoxidizing triplet state extinguisher, b) the CH_3 group should be replaced by a less reactive trifluoromethyl group, and c) the photochemically produced inhibitors of generation should be removed. In fact, it has been shown [132] that fluoro derivatives of coumarin dyes are more resistant to the action of the irradiation with an excitation lamp. It is assumed that the chief reason for the chemical and photochemical transformations of the molecules may be the same process, viz., opening of the pyrone ring, i.e., cleavage of the oxygen bridge in the coumarin structure [133]. The oxazine and xanthene dyes evidently should be regarded as the most stable dyes, while the polymethine dyes should be regarded as the most photochemically unstable dyes.

5. Effect of the Structures of the Dye Molecules on Generation

Thus far, relatively little study has been devoted to the relationship between the structures and the generation characteristics of dyes. The literature contains data only on coumarin derivatives [133] and polymethine dyes [134]. Although coumarin itself does not generate, the introduction of electron-donor substituents (diethylaminohydroxy and acetoxy groups) in the 7 position of the coumarin ring leads to quite high generation efficiency. The introduction of electron-donor groups in the 3 and 5 and 5 and 7 positions of hydroxy(acetoxy)-coumarins does not change the spectral and generation properties substantially. The quantum yields and the position of the luminescence spectra of alkyl-substituted coumarins do not differ substantially from the analogous characteristics of 7-hydroxycoumarin. The introduction of strong electron-acceptor substituents (carbethoxy and acetyl groups) in the 3 position leads to a significant shift of the absorption spectrum to the long-wave region, while the luminescence spectra remain virtually unchanged. The generation efficiency of 7-hydroxy-3-carbethoxycoumarin is close to that of 7-hydroxycoumarin. A stronger electron-acceptor substituent in the 3 position leads to considerable deterioration of the generation efficiency due to pronounced overlapping of the absorption and luminescence spectra and to a decrease in the luminescence quantum yield and the photochemical stability.

In contrast to the compounds examined above, a shift of the luminescence and generation spectra to the longwave region is observed for 3-chloro- and 3-phenyl-substituted coumarins.

The magnitude of the losses due to absorption of the generation emission in the channel of the triplet levels depends on both the position of the spectrum of T—T absorption relative to the luminescence spectrum and on the magnitude of the probability of an intercombination transition. In the case of coumarin derivatives the introduction of auxochromic substituents, which shift the spectrum of the $S_0 \rightarrow S_1$ absorption, in the molecule leads to an even greater shift in the spectrum of the T—T absorption in the same direction. One of the reasons for the low generation efficiency of 7-hydroxy(acetoxy)coumarins in a neutral medium is the greater (as compared with the alkaline medium) overlapping of the luminescence and T—T absorption spectra. A comparative study of the generation properties of alkylaminocoumarins showed that alkylaminocoumarins are most efficient in the case of laser excitation, while acetoxycoumarins are most efficient in the case of laser excitation; this is probably associated with the high photostability of the latter. Whereas the introduction of alkyl substituents in the 3 position for the first and second groups leads to a small increase in the generation efficiency in the case of laser excitation, while the generation efficiency decreases in the case of lamp excitation, the reverse effect is observed for the third group. The introduction of a chlorine atom in the 3 position for the hydroxy derivative decreases its efficiency, while the efficiency is increased in the case of the acetoxy derivative. The considerable decrease in the generation efficiency for the bromo-substituted derivatives is probably associated with an increase in the singlet—triplet interconversion.

During a study of the luminescence properties of cyanines, merocyanines, merocyaninocyanines, and oxanines it was found that the luminescence quantum yields initially increase and then decrease as the polymeric chain of the cyanines is lengthened [134]. The maximum quantum yield corresponds to $n = 2$ and 3. The maximum generation efficiency in all cases corresponds to $n = 3$. It is characteristic that its value in this case is virtually independent of the nature of the heterocyclic residues. On passing from a tri- to a tetracarbocyanine the luminescence quantum yield decreases by two orders of magnitude, during which a substantial decrease in the generation efficiency is not observed. This fact constitutes evidence that the induced losses in this case depend only slightly on the luminescence quantum yield. The presence of various substituents in the meso position of the polymethine chain generally has a negative effect on the luminescence and generation properties of cyanines. Merocyanine, rhodacyanine, and oxanine dyes hold little promise for utilization as active media.

Approaches to the optimization of the structures of the molecules of polymethine dyes for generation have been formulated [135]. It has been shown that n must be 0, 1, 2, 3, 4, or 5 for the production of dyes that emit over the 5000-12,000 Å range. The fluorescence quantum yield is maximal when $n = 2$-3. When n is a constant, the effect of an increase in the fluorescence quantum yields is achieved through the addition to the terminal rings of substituents that have their own π-electron system, as well as through the incorporation of five- or six-membered rings in the polymethine chain. It was found that through the incoroporation of aromatic or heterocyclic substituents at the nitrogen atoms of the heterocycles, the Stokesian shift can be increased to 2000-2500 cm^{-1} as compared with the ordinary shift of 200-250 cm^{-1} with a corresponding decrease in the generation threshold of the system by a factor of three to four and an up to 50% increase in the efficiency of the transformation. The addition to the nitrogen atoms at the ends of the conjugation chain of substituents that have their own π-electron system, which can interact with the π-electron system of the polymethine chain, creates the possibility of purposefully changing the form of the absorption and fluorescence bands. One can thus increase the half-width of the fluorescence band and consequently the range of tuning of the generation frequency.

6. Effect of the Solvent on the Generation of Organic Compounds

The solvent is an important component of the active medium. One must therefore take the role of the solvent into account in the examination of the generation characteristics of the solution. By interacting with the excited molecules of the dye the solvent may both decrease and increase the generation energy and shift the generation to the longer or shorter wavelength region. In addition, the solvent determines the thermooptical properties of the solution, and this affects the characteristics of the resonator. It should be noted that the little study has been devoted to the effect of the solvent on the generation of dyes.

Water is the best solvent in lasers. This is due to the fact that water has a small temperature coefficient of its refractive index, on which the magnitude of the thermooptical distortions of the resonator during generation and consequently both the energy of the generated emission and its divergence depend to a significant extent. In a number of cases effective generation is absent in aqueous solutions because of various processes involving aggregation of the dye molecules. A typical example of this is rhodamine 6Zh, which dimerizes in aqueous solutions. It is known that the absorption band of dimers of rhodamine 6Zh is slightly broader than the band of the monomer, which is associated with a transition to the first excited state, and overlaps to a greater extent with the luminescence spectrum. Both of the indicated factors lead to a decrease in the intensification and consequently to an increase in the generation threshold. In addition, the aggregation process is accompanied by a decrease in the fluorescence quantum yield, which also has a negative effect on generation. However, if an organic solvent is added to aqueous solutions, the generation energy increases. It has been shown [136] that the maximum generation energy in the binary solvents dimethylformamide—water, isopropyl alcohol—water, and acetic acid—water is reached at a water content of 50%. The aggregation process evidently no longer plays an appreciable role in mixed solvents. Extremal dependences were also observed during a study of the generation of rhodamine 6Zh in aqueous ethanol mixtures [137]. The maximum generation energy is observed in a mixture consisting of 57% water and 43% alcohol. It is assumed that the addition of water increases the heat capacity of the solution and decreases the dependence of the refractive index of the solution on the temperature.

The aggregation of the dyes in aqueous solutions is also suppressed by the addition of organic detergents to the solutions. N,N-Dimethyldodecylamine N-oxide [10], hexafluoroisopropyl alcohol [17], N,N-dipropylacetamide [17], acetamide [138], and the surfactants Tween-60 and Tween-80 [30] are very effective in this respect [30]. Generation by lamp excitation developed when the last three compounds were added to an aqueous solution of rhodamine 6Zh. These additives evidently form a coating of hydrophobic dye molecules and thus separate them from one another and from water.

The degree of chemical purity of the dye solution affects the efficiency of generation substantially. During a study of the effect of impurities on the generation characteristics of solutions of various samples of rhodamine 6Zh, it was shown [139] that a comparison of the coefficients of absorption of solutions in the spectral generation region may serve as a criterion of sufficient chemical purity and laser efficiency of both the solvent and the dye. However, as demonstrated during a study of the effect of the degree of purity of various rhodamines on their generation characteristics, a comparison of the fluorescence quantum yields of the generating solutions may be a criterion of the laser efficiency when the coefficients of absorption indicated above are equal.

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