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LUMINESCENCE AND PHOTOCHEMISTRY OF AZOLES (REVIEW)

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A review of the luminescence and photochemical properties of azoles and their relationship to their structures is given. The mechanism of the deactivation of the excited states of the molecules is discussed.

Azoles have recently found extensive application as dyes, effective luminophores [1, 2], scintillators [3-5], and active media for lasers [6, 7]. At the same time, their structural peculiarities are responsible for the interest in these molecules as models with which it is expedient to study the specific character of processes involving the deactivation of the electronically excited states of a broad class of compounds containing a C = N group [8, 9].

These circumstances have stimulated the development, particularly in the last decade, of intensive research on the luminescence and photochemistry of azoles.

The aim of the present review was to critically examine the most important, from the point of view of the authors, problems associated with the deactivation of the excited states of azole molecules.

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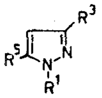
Structure and Luminescence Properties of Azoles.

Simple Azoles and Their Derivatives

Research on the luminescence properties of the simplest azole molecules has been carried out for structures I-V. It should be noted that unsubstituted molecules of this type do not have absorption bands in the longer-wave region above 230-240 nm [10, 11]. No data on the presence of the corresponding fluorescence in the UV region are available. At the same time, phosphorescence is observed at extremely low temperatures in the visible region of the spectrum only for V (see below).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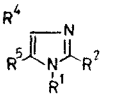
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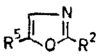
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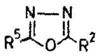
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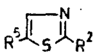

V

$R^1 = C_6H_4X$; $R^2, R^3, R^4, R^5 = Ar$, $C_6H_4-C_6H_5$, $C_6H_4-CH{=}CH-Ar$ etc.

Pyrazoles (I). Grandberg, Tabak, and Kost have made a qualitative study of the fluorescence of 1,3,5-trisubstituted I in the crystalline state [12] and in solutions [13]. Conjugation of the π systems when $R^1 = Ph$ leads to a strong bathochromic shift and an increase in the intensity of the long-wave absorption band and also to the development of intense fluorescence. When substituents R^5 are introduced (when $R^1 = Ph$), the reverse effect accompanied by a decrease in the fluorescence intensity is observed in the absorption spectra in the order $H < C_6H_5 < OH \sim NH_2 < Cl < NHCOCH_3 < CH_3 < COOH$. This "ortho effect" is a consequence of disruption of the coplanarity of the benzene and five-membered rings accompanied by an increase in the angle in the indicated order of substituents.

According to the data in [14], the pyrazole and phenyl rings in 1,3,5-triphenylpyrazole molecules also do not constitute a single π system. The longest-wave transition in the absorption ($\nu_{max} \approx 37{,}000$ cm^{-1}), which is responsible for the fluorescence ($\nu_{max} \approx 27{,}000$ cm^{-1}, $\tau_f = 0.9$ nsec, $\varphi_f \sim 0.05$) and phosphorescence ($\nu_{max} = 21{,}000$ cm^{-1}, τ_p 2 sec), is due, according to the results of quantum-mechanical calculations, to charge transfer from 3-Ph through the heteroring to 1- and 5-Ph. The anomalous Stokesian shift ($\sim 10{,}000$ cm^{-1}) and the absence of mirror-image symmetry between the excitation and fluorescence bands indicate substantial differences in the electron configurations of the ground and fluorescent states.

Imidazoles (II). Contradictory data on the position of the fluorescence band of 2,4,5-triphenylimidazole (λ_{max} 390 nm [4] or 440 nm [15]) under substantially different and difficult-to-compare conditions have been presented.

The relationship between the spectral-luminescence characteristics of 1,2,5-triphenylimidazole (C_6H_4X) and primarily para substituents X has been investigated [16]. It was established that the introduction of substituents in 1-Ph does not substantially change either the absorption spectra (λ_{max} 290 nm) or the spectral-luminescence characteristics (λ_{max} 370 nm, $\varphi = 0.4$-0.5). The effect of substituents in other phenyl rings on the absorption spectra leads to a bathochromic effect from the acceptors in the 2 position or from the donors in the 5 position. However, in this case the luminescence remains practically unchanged, except for special cases (Br or an NO_2 group) in which there is a substantial decrease in the quantum yield due to intensification of the intercombination conversion.

Oxazoles (III) and Oxadiazoles (IV). 2,5-Disubstituted oxazoles, particularly 2,5-diaryl-substituted oxazoles (PPO) and oxadiazoles (PPD), have been studied in greatest detail. The data for solutions presented in Table 1 provide evidence that the longest-wave transition in the absorption and the corresponding transition in the emission in the PPO and PPD molecules pertain to transitions of the $S_0 \rightleftharpoons S_{\pi\pi^*}$ type. The large values of the oscillator forces (f) and the fluorescence quantum yields (φ_f), the short fluorescence lifetimes (τ_f), and the spectral shifts in solvents that are characteristic for $\pi\pi^*$ transitions lead to this conclusion. Judging from the long phosphorescence lifetime (τ_p), the lower triplet state (T_1) also pertains to a transition of the $\pi\pi^*$ type. Similar data that attest to the $\pi\pi^*$ nature of the lower electronically excited states have been obtained for the gas phase [22]. The $S_0 \rightleftharpoons S_1^{\pi\pi^*}$ electron transitions are localized on the π system of the entire molecule [23] and are associated with redistribution of the electron density along the long axis of the molecule [24]. In the III molecule the $S_0 \rightleftharpoons S_{\pi\pi^*}$ transition is associated with transfer of electronic charge in the 2-phenyl → heteroring → 5-phenyl direction and, as a consequence, with a substantial change in the dipole moment during excitation to the $S_1^{\pi\pi^*}$ state [18] (Table 1). In the IV molecule symmetrical redistribution of the electron density (from 2- and 5-Ph to the heteroring) does not lead to an appreciable change in the dipole moment during excitation (Table 1). In addition, an increase in the number of nitrogen atoms (from PPO to PPD) leads to a short-wave shift of ~ 2900 cm^{-1} of the absorption bands and 2300 cm^{-1} of the luminescence bands both in the gas phase [22] and in

TABLE 1. Spectral-Luminescence Characteristics of 2,5-Diaryloxazoles and Oxadiazoles*

Compound	φ_f			f		τ_f^0, nsec			τ_p, sec 77°K	φ_p	φ_T	$E_{S_1} \cdot 10^3$, cm^{-1}	$E_{T_1} \cdot 10^3$, cm^{-1}	$k_f \cdot 10^8$, sec^{-1}	k_p, sec^{-1}	k_p^1, sec^{-1}	$k_T \cdot 10^8$, sec^{-1}	μ_y, D	$\mu_{e_{S_1}}$, D
	EET	C	M	C	M	EET	C	M											
PPO	0,53	0,75	0,64	1,28 1,70	1,70	1,4	1,7	3,3	—	—	0,46	27,5	—	2,5 —	—	—	2,7	1,55	6,4
PPD	0,9	0,88	0,8	1,08	1,70	1,35	2,4	4,0	0,8	0,04	0,10	28,55	20,0	3,0 6,0	0,05	1,2	0,66	3,5	3,0
PPO-N$(CH_3)_2$	0,62	0,85	0,94	1,53	1,9	1,4	2,5	2,2	$5 \cdot 10^{-2}$	10^{-4}	0,38	24,35	—	4,6 4,4	$5,2 \cdot 10^3$	2,0	2,7	—	8,2
PPD N$(CH_3)_2$	0,43	0,75	0,4	1,9	2,9	1,4	2,4	1,7	2,0	$8 \cdot 10^{-3}$	0,57	24,55	19,2	3,5 3,0	$9,3 \cdot 10^3$	0,5	4,0	—	1,5

*Symbols and abbreviations: EET is ethanol–ether (2 : 1), C is cyclohexane, M is methanol, φ_f is the fluorescence quantum yield, τ_p is the lifetime of the phosphorescent state, f is the oscillator force, τ_f^0 is the natural lifetime of the fluorescent state, φ_p is the phosphorescence quantum yield, k are the rate constants, and μ is the dipole moment.

solutions [21] (Table 1). In this case the form of the bands is determined primarily by the progressions of the frequencies of the stretching vibrations of the five-membered rings of the PPO and PPD molecules [25].

A sharp increase in the phosphorescence yield (φ_p) and a certain increase in the fluorescence yield (φ_f) are observed in the same order [18, 21, 22, 24]. One should note the contradiction in the data on the fluorescence quantum yields (for example, from 0.43 to 1.00 and from 0.13 to 0.31 for PPO and PPD in heptane, respectively [27, 28]) because of the nonobservance identical conditions and the failure to allow for the photochemical processes, the rates of which depend on the solvent and concentration. The data that we obtained for analogs of the PPO and PPD molecules with allowance for the indicated circumstances confirm the results in [18, 21, 22, 24] and cast doubt on the assumption of a decrease in φ_f in the indicated order of compounds [27-31].

Because of the $\pi\pi^*$ nature of the transitions, the introduction in the III and IV molecules of substituents with a regularly lengthening chain of conjugated bonds leads to a corresponding long-wave shift of the absorption and luminescence spectra. Diphenylyl, naphthyl, or phenanthryl substituents [3, 17, 20, 21, 25, 27, 32], as well as arylethylene substituents conjugated with the five-membered ring [31, 33-35], shift the spectra 10-70 nm. In the latter case only superimposition of the spectra of the fragments is observed when this sort of conjugation is absent [34, 36]. The introduction of complex naphthanhydride, N-phenylimide, and other substituents [37-39] and crosslinking of the PPO and PPD molecules through an ethylene group [31] substantially (up to 100 nm) shift the bands bathochromically. The data on the change in the fluorescence quantum yield (φ_f) as the length of the chain of conjugated bonds increases are contradictory: an increase [17, 20, 31, 35] and a decrease [3, 21, 32] in φ have been observed, particularly when substituents are introduced in the 5 position; this is explained by degradation of the energy of the closely situated electronic states in connection with the vibrations of heavy groups.

The introduction of donor substituents in the para position of 2- and 5-Ph PPD and PPO molecules [17, 40, 41], particularly $N(CH_3)_2$ and OCH_3, substantially shifts the absorption and luminescence bathochromically (up to 30 nm), raising the fluorescence yield by a factor of 1.5-2. Acceptor substituents have little effect on the position of the bands but lower the quantum yield considerably [up to 0 in the case of the 2-(p-nitrophenyl) derivative of PPD]. In contrast to PPD, the position of the substituents in the PPO molecule has practically no effect on the spectra [41].

The introduction of an $N(CH_3)_2$ group delocalizes the electron density distribution in the five-membered ring in the ground state (LCMO method [18]). The $R^2 \rightarrow \text{heteroring} \rightarrow R^5$ charge-transfer process during excitation [particularly in the $PPD{-}N(CH_3)_2$ molecule] leads to a considerable increase in the dipole moment in the excited singlet state (μ_e) (Table 1). In the opinion of Kutsina and co-workers, the difference in the Stokesian shifts, determined by the difference in μ_e, explains the different dependences of the φ values of the $PPO{-}N(CH_3)_2$ and $PPD{-}N(CH_3)_2$ molecules on the nature of the solvents (Table 1), which usually has little effect on the luminescence yields of the PPO and PPD molecules [30].

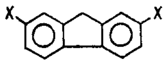
The universal molecular interactions in solvents of different natures (n 1.32-1.54; ε 1.97-38.8) lead to a bathochromic shift of the spectra as the polarity of the solvent increases only for unsymmetrically substituted molecules [30]. This shift increases in the substituent order $Cl < CH_3 < OCH_3 < N(CH_3)_2$; this is determined by the increase $\Delta\mu = \mu_e - \mu_g$ in the same series of molecules. In addition to this, specific interactions of individual solvents with some PPO and PPD molecules may lead to anomalous changes in the form, position, and intensity of the fluorescence bands [27, 42].

Thiazole (V) [11]. A structural phosphorescence band, excited (λ 210-310 nm) in the region of $n\pi^*$ absorption bands (λ_{max} 230 and 210 nm), is observed for thiazole at 380-500 nm in low-temperature (4 deg K) matrices [10]. Because of the absence of fluorescence, in conformity with the results of MO calculations ($E_{T_1} = 25{,}000$ cm^{-1}) and the τ_p value (~2 sec), the deactivation of the electronic excitation is interpreted as $S_1^{n\pi^*} \xrightarrow{1} T_1^{\pi\pi^*} \xrightarrow{2} S_0$. The decrease in the phosphorescence intensity in the series of matrices $Xe \sim SF_6 > Ar \sim CH_4 > Ne$ and the sharp decrease in the τ value in Xe (from 2 to $7 \cdot 10^{-2}$ sec) are explained by competition of processes 1 and 2 because of interaction with the matrix and the heavy atom effect, during which the existence of a temperature dependence of the rate of process 1 is indicated. In view of the nonexponential curve of attenuation of the phosphorescence, one notes the possibility of the existence of two triplets with different τ values (τ_1 and $\tau_2 \approx 1.3\ \tau_1$). Disappearance of the phosphorescence with τ_2 is observed in a magnetic field ($H \approx 28$ kOe).

Benzazole and Naphthazole Derivatives

As a result of the addition of a six-membered ring to the five-membered ring (VI), the absorption spectra are shifted substantially to the long-wave region as compared with the spectra of simple azoles.

TABLE 2. Spectral-Luminescence Parameters of Benzoxazole Derivatives

No.	Compound*	λ_{max}^{a}	$\varepsilon \cdot 10^{-3}$	λ_{max}^{f}	φ_f	$k_f \cdot 10^{-9}$, sec^{-1}	$(k_S+k_{ST}) \cdot 10^{-9}$, sec^{-1}	$\tau_T \times 10^3$, sec	φ_T
1	X—H	277	3,59	280 286 293	$\leqslant$0,05	0,06	$\geqslant$1,25	—	—
2	X—X	335	31,7	363 382 401	0,79	0,48	0,13	32	0,21
3	X—Ph	300	26,9	316 330 348	0,78	0,55	0,16	41	0,28
4	X—$(C_6H_4)_2$—X	339	65	380 423	0,96	0,90	0,05	52	0,03
5	X—$(C_6H_4)_4$—X	339	125	390 410	0,96	1,66	0,08	55	0,03
6		360	84	390 440	0,87	0,90	0,14	42	0,20

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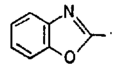
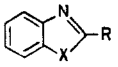
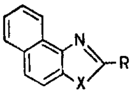
*X=

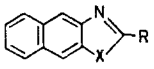




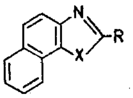
VI



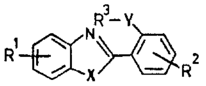
VIIa



VIIb



VIIc



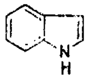
VIII

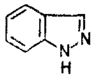
VI, VII X = O, S, N–R', R = H, CH_3, NH_2, C_6H_5, C_6H_4Hal (F, Cl, Br);
VIII R^1, R^2 = $N(CH_3)_2$, OCH_3, CH_3, NO_2, Cl, Br, COOH;
Y = O, S, NH, $NSO_2C_6H_4CH_3$-*p*; R^3 = H, Ac

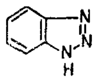
Benzoxazole and benzimidazole derivatives absorb at 300-400 nm and fluoresce intensely in solution at 320-450 nm. The fluorescence is characterized by a normal Stokesian shift and the presence of several bands of vibrational structure (for example, see Table 2). The spectral characteristics of the absorption and fluorescence of VI depend only slightly on the nature of the heteroatom [26, 43-45] but change substantially as a function of the R group. Aryl substituents with acceptor groups shift the spectra hypsochromically, whereas those with donor groups shift the spectra bathochromically. This sort of substituent effect leads to the concept that the nature of the long-wave electron transition is associated with redistribution during excitation of the electron density in a direction away from the C-aryl ring. A more accurate identification of the nature of the transitions is possible only on the basis of the results of quantum-mechanical calculations. The quantum fluorescence yields (φ_f) depend substantially on both the nature of heteroatom X and on the properties of substituent R without changing appreciably as a function of R^1 [26, 45]. Thus, in contrast to R, R^1, including Ph, practically do not interact with the π system of the heteroring. The substantial increase in the φ_f value in the order X = NH, O indicates the great possibility of stabilization of the structure during polarization of the system of conjugated bonds of the rings by the more electronegative oxygen atom as compared with the nitrogen atom. This leads to a decrease in the number of possible deformation vibrations and, consequently, to a decrease in the probability of emissionless processes.

Acceptor substituents in the 2-aryl derivatives decrease the φ_f values, whereas donor substituents increase them [45], although the opposite effect may also be observed in individual cases [26]. These phenomena may be associated with competitive changes in the probability of intercombination conversion in the case of variations of the S_1—T splitting and spin—orbital interaction with the introduction of the same donor or acceptor substituents (particularly halogens).

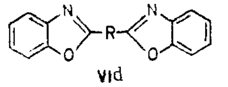
Spectral-polarization studies [46-48] of the absorption and fluorescence of the π-isoelectronic molecules benzimidazole VI (X = NH), indole VIa, indazole VIb, and benzotriazole VIc led to the conclusion that low-lying $n\pi^*$ states are absent in these molecules and that there is a similarity between the lower singlet $\pi\pi^*$ states and the $L_p{}^1$ and $L_a{}^1$ states of the naphthalene molecule. The lower triplet state also has $\pi\pi^*$ nature, as evidenced by the long lifetime ($\tau \simeq 1$ sec) and the phosphorescence polarization perpendicular to the plane of the molecule.


VIa


VIb


VIc

"Pairing" and the symmetrical addition of benzoxazole groups to the molecules of the polycyclic hydrocarbons stilbene and tolan sharply raise the fluorescence quantum yield and lead to a long-wave shift of the spectra of compounds of the VId type relative to unsubstituted benzoxazoles (Table 2) [26, 45, 49]. The increase in the first case is associated with a substantial increase in the probability of emissive transitions, whereas in the last two cases it is associated with a marked decrease in the probability of emissionless transitions; this is a consequence of possible structural changes in the stilbene and tolan molecules during excitation [49].


VId

$R = (-C_6H_4-)_n$, $n = 0\text{-}4$;

$-C_6H_4-CH=CH-C_6H_4-$;

$-C_6H_4-C\equiv C-C_6H_4-$

A study of the deactivation of the excited states of molecules of the VId type in a polystyrene matrix by pulse photolysis [49] made it possible to obtain important information regarding the spectral-kinetic parameters that characterize these processes (Table 2). In connection with the fact that the sum of the fluorescence (φ_f) and triplet (φ_T) quantum yields is practically unity, one should suppose that the principal pathway in the emissionless deactivation of the S_1 state is the intercombination conversion $S_1 \rightsquigarrow T_1$ (k_{ST}). Reiser and coworkers [49] assume that the direct spin–orbital interaction in the benzoxazole molecule between the $S_1^{\pi\pi^*}$ and $T_1^{n\pi^*}$ states is responsible for the rapid intercombination conversion ($k_{ST} = 10^9$ sec^{-1}). Direct spin–orbital interaction is excluded in complex systems (Table 2) owing to a change in the relative position of the $\pi\pi^*$ and $n\pi^*$ states, and the intercombination conversion is due to a spin–vibron interaction [50]; this leads to a decrease of one order of magnitude in the corresponding yields (φ_T) and rate constants (k_{ST}).

In this case it should be noted that "doubling" of the benzoxazole molecule and the addition to it of a phenyl group (compare Nos. 2 and 3 in Table 2) give approximately identical effects. However, the further accumulation of intermediate phenyl groups sharply increases the fluorescence quantum yield due to a decrease in the rate of the intercombination conversion (compare Nos. 1-3 and 4 and 5 in Table 2). As expected, disconnection of the phenyloxazole fragments (No. 6, Table 2) leads to results similar to those obtained in the case of simple "doubling" of the benzoxazole molecule.

The spectral-luminescence properties of arylnaphthoxazoles VIIa-c in solutions are determined to a considerable extent by the 2-arylbenzoxazole system of the molecule [44]. Two factors are most important. The first factor is the presence of a 25-30 nm long-wave shift in the spectra of VIIa,c and an even greater shift in the spectrum of VIIb relative to the VI molecule. The second factor is the substantial difference in the absorption and luminescence spectra (which are similar to the spectra of benzoxazoles VI) and the fluorescence quantum yields of VIIa,c from those observed for VIb. The latter fact makes it possible to assume that, as in the case of benzoxazoles, the oxazole ring is retained in the angular VIIa molecules, whereas an oxazoline ring rather than an oxazole ring is connected to the aryl system in the VIIb molecule; this suggests a naphthalene-like structure rather than a quinoid structure for the aryl portion of the molecule.

Molecules of VIII, in which transfer of a proton or a different molecular group in the excited state is possible, constitute a special class. A characteristic feature of these compounds is the presence, in addition to fluorescence in the UV region (~370-380 nm), of intense visible fluorescence ($\lambda_{max} \sim 440\text{-}520$ nm) with an anomalously large Stokesian shift (up to 10,000 cm^{-1}) in solutions in polar and nonpolar solvents and in the crystalline state. A bathochromic shift of the luminescence in the visible region is observed in the series X = NH, O, S [51]. The long-wave fluorescence in solutions was ascribed for these compounds (first in [8] and later in [52, 53]) to a form with a proton transferred to the nitrogen atom in the excited state, in analogy with the data in [54]. At the same time, the complex nature of the long-wave fluorescence bands and the dependence of their intensities on the polar properties of the solvents and the wavelength of the exciting light have been noted. The opinion that the fluorescing form is not the quinoid structure (VIIIa) but rather an exclusively dipolar structure with hydrogen covalently attached to the nitrogen atom (VIIIb) was later expressed for the crystalline state [55] and recently for solutions [56] without allowance for the above-noted complex nature of the luminescence.*

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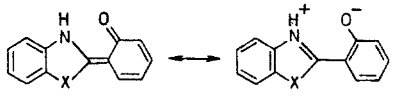
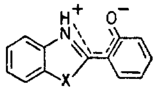
*It must be noted that in [56] this assumption was made on the basis of an insufficiently correct comparison of the absorption and fluorescence spectra recorded at different temperatures.



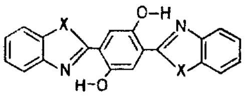
VIIIa VIIIb



VIIIc

A study of the absorption, fluorescence, and excitation spectra of 2-(o-hydroxyphenyl)benzoxazole (VIII, X, V = O, $R^1 = R^2 = R^3 = H$) and model fixed benzenoid and anionic structures in different solvents made it possible to establish [57] the nature of the fluorescence and phosphorescence bands of this compound. Thus the weak UV fluorescence was assigned to the benzenoid form of the VIII molecule, while the fluorescence in the visible region with a large Stokesian shift is emitted by anionic structure VIIIc and also by a structure with a hydrogen atom covalently bonded to the nitrogen atom; these structures are formed in high yields in the excited singlet state of the benzenoid form. The covalent "quinoid" structure, which is depicted in terms of resonance theory (VIIIa ⟷ VIIIb), has a significant dipole moment that depends on the polarity of the solvent and consequently substantially changes the configuration in polar solvents. This circumstance and the change in the relative contribution of the ionic and covalent structures also determine the dependence of the luminescence on the wavelength of the excitation and the polarity of the solvents. Moreover, the phosphorescence (at 77 deg K) pertains primarily to the emission of the $T_1^{\pi\pi^*}$ state of the anionic form.

It should be noted that an extremely pronounced bathochromic shift of the luminescence spectra (160, 110, and 270 nm for X = S, O, and NH, respectively) relative to the spectra of VIII ($R^1 = R^2 = H$; Y = O) is observed in the case of "doubling" of benzazole molecule VIIId [51].



VIIId

Fluorescence with an anomalously large Stokesian shift is also emitted when a proton is transferred from the nitrogen atom of the tosylamino group to the nitrogen atom of the azomethine group in the VIII (X = O; Y = $NSO_2C_6H_4CH_3$) molecule in the excited state [56, 58].

Finally, not only UV fluorescence but also visible fluorescence similar to the luminescence of the corresponding o-hydroxybenzoxazole [59] are observed in the case of the o-acyl derivative of VIII (R^3 = Ac; X = Y = O; $R^1 = R^2 = H$) [59]. As in the case of the corresponding o-hydroxybenzoxazole, the spectra of the excitation of visible and UV fluorescence in nonpolar solvents coincide, but the latter has a considerably higher relative intensity. Thus it can be concluded that migration of an acyl group from the oxygen atom to the nitrogen atom in the singlet excited state of the benzenoid form that is similar to the migration of a proton but occurs with a lower probability is present in this case. The results of a study of complexes of benzazoles with metals are extremely important for an understanding of the nature of their spectral-luminescence properties. The spectral-luminescence properties of Zn, Cd, Co, Ni, Cu, and Mn complexes of the chelate and molecular types with molecules of the VIII type were studied in [62-70]. It was established that the excitation and emission of the complexes occur in the π system of the ligand, and the most important characteristics of the spectral-luminescence properties are therefore determined primarily by the structure of the organic portion of the molecule. Thus all three types of fluorescence that are characteristic for the organic molecule are displayed in the case of the chelate complexes with benzoxazole [70]. This provides evidence for this sort of rearrangement of the chelate node in the electronically excited state; in addition to the benzenoid form, the organic portion of the molecule may be found in the ionic and "quinoid" forms. However, the metal complexing agent has a substantial effect on the spectral-luminescence properties and, first and foremost, on the overall luminescence quantum yield. In the case of nontransition metals the probabilities of emissionless transitions decrease sharply because of the rigidity of the chelate node, and this leads not only to a considerable increase in the overall fluorescence quantum yield (up to 0.9) in both the UV and visible regions but also to an increase in the lifetime and fluorescence quantum yield. The effect of the transition metal atom leads to a substantial increase in the probability of the $S_1 \rightsquigarrow T_1$ intercombination conversion; at the same time, effective transfer of energy from the T_1 state of the organic portion of the molecule to the d level of the transition metal ion is possible. These two factors lead to a sharp decrease in the overall luminescence yield in complexes with Cu, Co, Ni, and Mn.

The "migration" of the metal ion from the oxygen atoms to the nitrogen atoms in the chelate node takes place with a considerably lower probability than the analogous process for the proton in the free molecule, and this leads to a substantial increase in the relative intensity of the UV fluorescence in the case of the complex molecule. In addition, the luminescence quantum yield in the visible region is higher for complexes with a molecular structure than for chelate complexes because of the absence of fluorescence in the UV region as a consequence of the high probability of the formation of an anionic form in the excited state.

Thus both chelate and molecular complexes of benzazoles with nontransition metals are new extremely effective organic luminophores [71].

Excimeric Fluorescence

The fluorescence of excimers (excited dimers) has been observed and investigated in the case of molecules of the III and IV type. The first evidence for the existence of excimers of PPO in solutions (III, $R^2=R^5=$ Ph) was obtained in [72], and further evidence was subsequently obtained in [73-75].

Excimeric fluorescence excited at 313 nm (absorption of the monomers) develops in the form of a broad structureless long-wave band (with $\lambda_{max}>450$ nm) when the PPO concentration is increased to 10^{-2} mole/liter or higher vis-à-vis the characteristic absence of concentration changes in the absorption spectrum. The lifetime ($\tau=14.5\cdot10^{-9}$ sec) of this exponentially-attenuating fluorescence differs substantially from the lifetime of the short-wave monomeric fluorescence ($\tau=2.7\cdot10^{-9}$ sec), which also attenuates exponentially, and its relative intensity decreases as the temperature rises and the viscosity of the solvent increases. The development of long-wave fluorescence that has such characteristics indicates that stable (only in the excited state) molecular fluorescing complexes (PP*) (excimers), which decompose after deactivation of the excitation energy, as first demonstrated for pyrene in the classical research reported in [76, 77], are formed during excitation of the PPO molecule (P) to the singlet excited state (P*). Moreover, it has been established [73] that the excimeric fluorescence of PPO is quenched by dissolved molecular oxygen.

In a series of studies [78-80] Kutsina and co-workers used the method of measurement of the hysteresis of the luminescence phase relative to the phase of modulation of the exciting light in the monomeric and excimeric portions of the spectrum. In addition to confirmation of the fact of the formation of excimers, quantitative data that characterize the monomer–excimer kinetics of PPO and its derivatives were obtained in these studies. In particular, the rate constants for the formation (k_{em}) and decomposition (k_{me}) of the excimers and the emissionless (k_{lm}, k_{le}), emission (k_{Fm}, k_{Fe}), and total (k_m, k_e) rate constants of deactivation of the excited states of the monomeric and excimeric molecules were determined. The probability of collisions (p) and "meetings" (P) of the monomeric molecules that lead to the formation of an excimer in the solvent cage was also estimated. The dependence of these parameters and the quantum yields of monomeric (φ_m) and excimeric (φ_e) fluorescence on the substituents was also traced (Table 3). It was shown that the efficiency of the process involving the formation of the excimer decreases as the volume of the substituent increases in the order Cl → $N(CH_3)_2$.

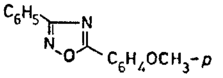
The effect of the ε values of solvents on the thermodynamic properties of the formation of PPO excimers has been studied [81]. The temperature dependences of the fluorescence spectra of solutions at various concentrations in cyclohexane, dioxane, benzyl alcohol, methanol, and ethanol made it possible to evaluate the effect of solvents on the change in the free energy of the enthalpy and entropy during the formation of the excimers. It was established that these values decrease considerably in the case of strongly polar solvents ($\varepsilon>20$). This fact is associated with the substantial role played by charge transfer between the monomeric molecules during photoassociation and, consequently, with the large dipole moment of the excimer ($\mu=6$ D). The effect of a polar solvent reduces to weakening of the interaction between the unexcited and excited monomeric molecules, which have oppositely directed dipole moments, and, consequently, to an increase in the distance between them, and, as a result, to a decrease in the changes in the thermodynamic parameters during photoassociation.

The existence of excimeric fluorescence in molecules of the IV type was detected and studied in [61, 82-84]. Of course, from theoretical considerations it was concluded that 2-phenyl-4-diphenylyloxadiazole (PDD) (IV, $R^5=$ 4-diphenylyl, $R^2=$ Ph) and PPD (IV, $R^2=R^5=$ Ph) molecules are not inclined to undergo photoassociation in view of the existence of the repulsed dipoles of the ground and excited singlet states of these molecules [85]. However, excimers have been observed at high concentrations and low temperatures for certain highly soluble PDD derivatives [82] and distinctly displayed excimeric fluorescence was observed in [83] for molecules of the IV [$R^5=$ 4-diphenylyl, $R^2=CH_3$, CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$] type, regardless of the volume of substituent R^2 even at room temperature ($c>1.66\cdot10^{-6}$ mole/liter).

It has been shown that IV molecules with o-hydroxyphenyl substituents ($R^2=R^5=C_6H_4OH$) form the usual dimers, which are displayed in the absorption spectra [61, 84]. The fluorescence spectra depend substantially on the concentration, temperature, and solvent and are due to the existence of three emission centers – the excited dimers (ν_{max} 27,000 cm^{-1}), the monomeric anions (ν_{max} 25,000 cm^{-1}), and associates of the excimer type (ν_{max} 20,000 cm^{-1}).

TABLE 3. Parameters Characterizing the Excimeric—Monomeric Fluorescence of PPO and Its p-Substituted Derivatives

Compound	k_{FM}	k_m	k_{Fe}	k_e	k_{me}	$k_{em} \cdot 10^8$, liter · mole^{-1} · sec^{-1}	φ_m	φ_e	P	p
	(· 10^8), sec^{-1}									
PPO	6,1	7,8	0,8	1,4	1,0	62	0,75	0,57	0,925	0,028
PPO-Cl	3,3	4,6	0,4	0,5	1,6	53	0,72	0,67	0,790	0,018
PPO-OCH_3	6,3	8,2	1,1	2,2	3,2	58	0,77	0,55	0,865	0,022
PPO-$N(CH_3)_2$	7,2	9,6	2,2	3,5	1,5	57	0,75	0,36	0,850	0,021



IX

The quenching of the fluorescence ($\varphi = 0.49$) of the IX molecule (A) in acetonitrile in the presence of various quenching agents (Q) is explained by the formation of A*Q exciplexes (i.e., complexes of the excited IX molecule and the quenching agent molecule in the ground state) primarily via a charge-transfer mechanism [86]. In this case the Q molecule is an electron donor (for example, 2,4-dimethyl-2,4-hexadiene, tetrahydrothiophene, or isoprene), and the electron acceptor is the azole molecule A* excited to the lower singlet state. The formation of exciplexes via this mechanism is proved by the existence of the characteristic relationship between the constant for the quenching of the fluorescence of the IX molecule and the ionization potential of the Q molecules.

Emissionless Transfer of the Electronic Excitation Energy

The phenomenon of the emissionless transfer of the electronic excitation energy lies at the foundation of extremely widespread methods for the study of the mechanisms of deactivation of excited states and practical methods for the sensitization of luminescence and photochemical reactions of organic molecules.

The main principles of the phenomenon of emissionless energy transfer between organic molecules are discussed in numerous original and review papers (for example, see [87-89]). One should note only that energy transfer can be realized via inductive-resonance (for example, singlet—singlet transfer) or exchange-resonance (for example, triplet—triplet transfer) mechanisms both between different molecules (intermolecular transfer) and between individual fragments of a single molecule (intramolecular transfer). In this case for the realization of effective transfer it is necessary that the deactivated energy level of the donor molecule (D) be situated no lower than the excited energy level of the acceptor molecule (A) and that the distance between D and A not exceed 70-80 Å for the singlet—singlet energy transfer or 15-20 Å for the triplet—triplet energy transfer.

Studies [90-93] have been devoted to the proof of the realization of intermolecular energy transfer and the investigation of its efficiency in resins, polymeric matrices (PS and PMMA), and solutions.

The principal evidence for the existence of a singlet—singlet energy transfer is the regular (in conformity with transfer theory) decrease in the intensity of the fluorescence of structurally different excited donors and the increase in the intensity of the fluorescence of acceptors as the concentration of the latter increases. The relative change in the intensity of the fluorescence of the donor and acceptor, which determines the efficiency of energy transfer, also depends, in conformity with the theory of energy transfer, on the magnitude of the integral of overlap of the absorption spectrum of the acceptor and the fluorescence spectrum of the donor, on the quantum yield, and on the fluorescence lifetime of the donor and the absorption intensity of the acceptor [$\varepsilon(\nu)$].

The efficiency of energy transfer, which is determined by the transfer coefficient from the formula $K_{DA} = 1 - S_D/S_{OD}$ (where S_D and S_{OD} are the integral intensities of the fluorescence of the donor in the presence and absence of an acceptor, respectively) (Table 4), increases substantially in resins, PMMA, PS, and frozen solutions as compared with liquid solutions and also depends on the character of the solid matrix. This dependence was explained by Krasovitskii and co-workers [90, 91] by competition between energy transfer and emissionless deactivation of the energy in the donor molecule. The phenomenon of intermolecular energy transfer makes it possible to create special compositions of luminophores with considerably increased intensity of the long-wave component of the spectrum that corresponds to the fluorescence of the acceptor [90].

Intramolecular energy transfer between individual unconjugated fragments of molecules, one of which has an azole structure, was studied in [91, 93, 94]. It was shown that efficient intramolecular singlet—singlet energy transfer from the oxazole fragment (PPO) to the corresponding acceptor fragment is realized in most

TABLE 4. Efficiency of Inter- and Intramolecular Energy Transfer*

No.	Donor	Connecting bridge (para)	Acceptor	Acceptor concn., c $\cdot 10^{-4}$ mole/liter	K_{DA}	Solvent	Literature
1	X	—	MBA	8	0,64	Polycondensation resin	92
2	MBA	—	XI	4,4	0,80		92
3	PPO	—	DPSP	5,0	0,44 0,20	PMMA Toluene	91
4	PPO	—	DSB	5,0	0,13	Toluene	91
5	PPO	—	XII	1,0	0,20 0,11	PS Toluene	93
6	PPO	$-CH_2O-$	XII	—	0,36	Toluene	93
7	PPO	meta $-CH=CH-$	DPSP	—	0,44 0,39	PMMA Toluene	91
8	PPO	meta $-CH=CH=$	DSB	—	0,10	Toluene	91
9	APT	$-(CH_2)_3-$	XIII	—	0,94	Ethanol	94
10	APU	$-(CH_2)_3-$	XIII	—	0,60	Ethanol	94

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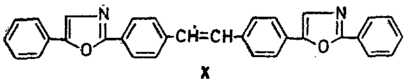
*Abbreviations and symbols adopted in the table: DPSP is 1,5-diphenyl-3-styrylpyrazoline, MBA is 3-methoxybenzatrone, DSB is 1,4-distyrylbenzene, APT is 3-aminopropylthymine, and APU is 3-aminopropyluracil.

cases (Table 4, Nos. 6-8). The efficiency of this transfer, particularly in nonpolar solvents (toluene), is appreciably higher than for intermolecular transfer (for example, compare Nos. 3 and 7 and 5 and 6); this is explainable if one takes into account the fixed (and evidently favorable) mutual orientation of the fragments in the case of the intramolecular process. At the same time, in PMMA (Nos. 3 and 7), despite the chaotic (although rigid) mutual orientation of the molecules, the efficiencies of the intermolecular and intramolecular energy transfers do not differ. The diazole fragment is an acceptor of the energy, which is transferred efficiently via a singlet–singlet mechanism from the excited ($\lambda \simeq 270$ nm) thymine (APT) or uracil (APU) fragments (Table 4, Nos. 9 and 10) at extremely high rates ($k = 10^{12}$-10^{13} mole^{-1} $\cdot$ sec^{-1}) [94].

Information on triplet–triplet absorption in these molecules becomes necessary for the utilization of a number of azoles as laser dyes. At the same time, because of the low yield of the formation of triplet states during direct excitation (a large fluorescence quantum yield), the population of the lower triplet state is extremely small. The phenomenon of triplet–triplet energy transfer to the PPO molecule therefore was used to record the spectra and determine the extinction (ε_T) of the triplet–triplet absorption of the PPO molecule by means of pulse photolysis [95]. The naphthalene molecule (c 10^{-3} mole/liter), which efficiently populates the triplet of the PPO molecule (c 10^{-6} mole/liter) (the rate constant of the T–T transition is $k \simeq 9.2 \cdot 10^9$ mole^{-1} $\cdot$ sec^{-1}), was used as the triplet energy donor. The T–T absorption spectrum obtained in this way is a broad band that ranges from 350 to 600 nm with λ_{max} 500 nm and ε_{max}^T 28,400 ± 1500 liters $\cdot$ mole^{-1} $\cdot$ cm^{-1}.

Quasi-Line Luminescence Spectra (Shpol'skii Effect)

The investigation of the quasi-line spectra observed at low temperatures (77 deg K) usually in frozen solutions of n-alkanes opens up great possibilities in the study of the relationship between the electronic spectra and the peculiarities of the electron and three-dimensional structures of organic molecules. This pertains to the determination with a high degree of accuracy of the frequencies and intensities of the purely electron transitions, and the number and frequencies of the normal vibrations of molecules that are directly related to their structure and symmetry. A unique possibility for the exposure of the localization of the electron transition in the molecule appears in this case. In addition, analysis of the "multiplicity" makes it possible to form a judgment regarding the interaction of the molecules with the crystal lattice of the solvent.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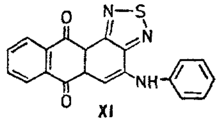
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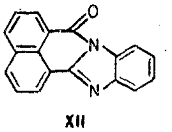
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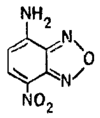
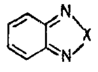

XIII

Some of these possibilities have been used in the study of the Shpol'skii effect in azoles.

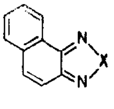
2,5-Diaryloxadiazoles (IV) [97] display, primarily in hexane, distinctly expressed quasi-line fluorescence spectra with progression of the skeletal "breathing" vibrations of the oxadiazole ring (ν 1510-1570 cm^{-1}). Since the character of the vibrational structure in phenyl-substituted derivatives is independent of the substituents in the phenyl ring and is determined, as in the case of arylethylenes, by the intermediate bridge group ($\nu_{C=C}$ 1600-1650 cm^{-1}), Nurmukhametov and co-workers [97] have drawn a conclusion regarding the related nature of the electronically excited states in these classes of molecules in connection with the identical character of the π conjugation.

In addition, as in the case of β-naphthylethylenes, progressions corresponding to the vibrations of the naphthalene ring [ν 1630 cm^{-1}; 1375 cm^{-1} (with respect to phosphorescence)] are displayed in the case of 2-(β-naphthyloxadiazole) molecules; this provides evidence for primary localization of the electronic excitation on the naphthalene fragment in both types of molecules.

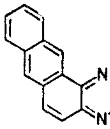
The quasi-line spectra of aromatic compounds with oxa-, thia-, and selenadiazole rings (XIV-XVI) consist of more than 100 quasi-lines and make it possible to establish the relationship between the electronic spectra and the structure of the molecule [98-102].



XIV



XV



XVI

XIV-XVI X=O,S,Se

As one should have expected, the frequency of the purely electronic S* → S$_0$ transition decreases as the π system becomes larger on passing from XIV to XVI and also in the order O, S, Se. The latter is explained qualitatively by a change in the energy of the orbital with the unshared pair of electrons of the X atom conjugated with the π system. Despite the overall shift of the electronic bands, the quasi-line fluorescence and phosphorescence spectra (τ = 2-3 sec) of compounds with X = O, S, Se have similar structures that are determined primarily by the identical vibrations in this series of molecules. The vibrations are divided into two distinctly different groups. The first group of vibrations is associated with the heteroring, and their frequencies decrease in the order O, S, Se; this is associated with the increase in this order of the mass of the heteroatom and the polarizability of the unshared pairs, as well as with the decrease in the electronegativity of the X atom. The second group of vibrations, the frequencies of which are practically independent of atom X, is characteristic for aromatic molecules that contain one ring less than the corresponding azole molecules. Hence the authors conclude that the ring adjacent to the heteroring has an o-quinoid structure. The origin of the distinctly expressed multiplicity in the Shpol'skii spectra, which depends substantially on the solvent (hexane, heptane, and octane), has not been ascertained.

A peculiarity of the structures of benzoxazoles and naphthoxazoles (VI and VIIa, c, where X = O, R = Ph, C_6H_4-Ph, and CH=CH-Ph) is the existence of an oxazole ring that includes a C = N group and a bridge oxygen atom, which ensures the planar structure of the molecule and its π-isoelectronic character with respect to the corresponding arylethylenes. In this connection, the oxazole ring plays a substantial role in the formation of the electronic-vibrational spectra of molecules of the type under consideration [103-105]. This is manifested in the presence in the fluorescence spectrum of intense quasi-lines [103, 104] that form a progression associated with the vibrations of the C = N group, which determines the contribution of the oxazole ring to the π system of the molecule. In addition, frequencies of stretching vibrations (for example, of the C = C group in the compound with R = CH = CH-Ph) and of the deformation and stretching (C-H) vibrations of phenyl rings appear in the spectra. The great similarity in the spectra of phenylbenzoxazoles and arylethylenes confirms the isoelectronic character of their π systems [106]. The vibrations of the naphthalene ring (ν 1405 cm^{-1}) show up more actively in the spectra of naphthoxazoles VIIIa, c, and the lines associated with the vibrations of the oxazole ring ($\nu \simeq$ 1550 and 1610 cm^{-1}) are weakened; this provides evidence for substantial localization of the electron transition in the naphthalene fragment.

Vibrational analysis of the quasi-line fluorescence spectra of VI (R = Ph, X = O, S) [105] shows that activity of the same vibration as in the transition that determines the fluorescence ($S_1^{\pi\pi^*} \rightarrow S^0$) [103] is displayed in the $T_1^{\pi\pi^*} \rightarrow S_0$ electron transition (to which Olszowski and co-workers [103] ascribe the phosphorescence with τ = 0.1 sec). This provides evidence for identical participation of the same molecular fragments in both transitions.

Chemiluminescence

Chemiluminescence (CL) is low-intensity luminescence that develops as a result of conversion of a portion of the chemical energy to energy of electronic excitation of the molecules of the reaction products and their subsequent deactivation by the emission of light.

The CL of azoles was detected in 1877 [107] in the case of the II ($R^2 = R^4 = R^5 = Ph$) molecule (lophine) by oxidation with molecular oxygen in 1 N ethanolic KOH solution at room temperature.

However, it was established only recently [108, 109] that in this reaction, the chemiluminescence, the spectrum of which is a broad band at 465-660 nm (λ_{max} 545 nm), develops during deactivation of the excited peroxide molecules formed in the reaction of lophine free radicals with molecular oxygen. The electrochemiluminescence (ECL) that develops in a variable high-frequency (up to 10^5Hz) electrical field during transfer of an electron from the anion radical of the PPD (IV, $R^2 = R^5 = Ph$) molecule to the thianthrene (TH) cation radical in acetonitrile has been investigated [110]. The ECL mechamism includes not only electron transfer but also possibly the formation of exciplexes (PPD and TH), as well as T—T annihilation. The ECL yield is no more than 10^{-4} of a photon per electron transfer act.

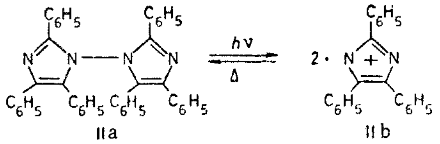
The peculiar sensitization of CL has been studied in the reaction of dicyclohexylperoxydicarbonate with N,N-dimethylaniline (DMA) [111]. The CL yield (λ_{max} 400 nm) increases as compared with DMA by a factor of 10^3 when azole substituents are included in the para position of the DMA molecule [PPO—$N(CH_3)_2$ and PPD—$N(CH_3)_2$]. Comparative studies have shown that the increase in the CL yield occurs as a result of transfer of the reaction energy to the fluorescent fragment of the product molecule, evidently at the instant that it is formed.

Photochemical Reactions of Azoles

The planar cyclic structure of simple azoles and benzazoles as compared with their analogs that contain an exocyclic C = N group leads to a substantial decrease in the $S_1 \rightarrow T_1$ intercombination conversion and exclusion of trans—cis isomerization relative to the C = N bond, which takes place primarily in the triplet state [112, 113]. Although these factors also promote an increase in the luminescence yield, they nevertheless reduce the photostability of the molecules, increasing their reactivities through primarily intermolecular photoreactions. The photochemical stabilities of these luminophores depend substantially on the external conditions and the concentrations of the solutions. Thus irradiation of PPO, PPD, and POPOP in solutions and particularly in polymeric matrices leads to a substantial attenuation of the luminescence following a law that differs from exponential attenuation [114-117]. In this case irradiation for 30 min leads to a 70% decrease in the fluorescence intensity, and the band of —C—O—C— stretching vibrations (1300 cm^{-1}) that is characteristic for the oxazole ring vanishes in the IR spectra. The rate of the photoreaction depends on the number of heterorings in the molecule. In their totality, these data lead to the assumption of the formation of nonluminescing photodimers at a rate that is determined substantially by the external conditions.

The kinetics of the photoconversion of PPO and PPD derivatives in PMMA have been investigated by phosphorescence spectroscopy [118, 119]. An intermediate photoelectrically unstable product, which is converted after absorption of a quantum of light to the final product with characteristic phosphorescence (λ_{max} 520 nm, τ_p 0.4 sec), is formed as a result of a photoreaction proceeding through the triplet state of the starting molecule.

Dimer IIa, which has photochromic properties, was obtained by oxidation of 2,4,5-triphenylimidazole in the presence of sodium ferricyanide [120, 121]:



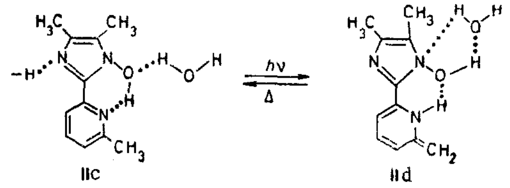
IIa IIb

Photocoloration is a consequence of a decrease in the intensity of the absorption band with λ_{max} 277 nm and the formation of new absorption bands in liquid solutions with λ_{max} 345, 526, and 551 nm and in frozen solutions with λ_{max} 352, 540, and 575 nm [121]. It has been shown by ESR spectroscopy that the coloration is associated with the formation of cation radicals IIb; the kinetics of the reverse dark reaction of recombination of the radicals have been studied [122, 123]. This dark reaction of decolorization in liquid solutions proceeds with an activation energy of ~14 kcal/mole [120] and is a second-order reaction [122, 124] only at low IIa concentrations ($< 10^{-4}$ M). When the concentration is increased to 10^{-4} M, the reaction order changes to $^3/_2$; this probably constitutes evidence for the presence of complexing between the dimer molecules and the radicals [124]. Decolorization, i.e., recombination of the radicals, also proceeds photolytically in frozen alcohol solutions (77 deg K) with an extremely low quantum yield [125]. The results obtained during a study of the photochromic reaction in solutions and in the crystalline state at room temperature and low temperatures [121, 123, 126, 127], together with the results obtained in [128], are explained on the basis of an equilibrium scheme that depends substantially on the temperature [126, 127]; in this scheme the nonphotochromic dimers, which give coloration without irradiation (R_2^1), triphenylimidazole radicals ($R^{\cdot}$), which are responsible for the color, and the photochromic dimers (R_2'), which give coloration only during irradiation, exist in equilibrium. Decomposition to give $R^{\cdot}$ radicals with a quantum yield (φ) of ~0.9-1.0 [127] occurs primarily in the singlet excited state (R_2^{1*}) of the dimer [124].

$$\begin{tikzcd}
R_2 \arrow[r, shift left] & 2R\cdot \arrow[l, shift left] \arrow[r, shift left] & R_2' \arrow[l, shift left] \arrow[dl, "h\nu"] \\
 & R_2'^{1*} \arrow[u] &
\end{tikzcd}$$

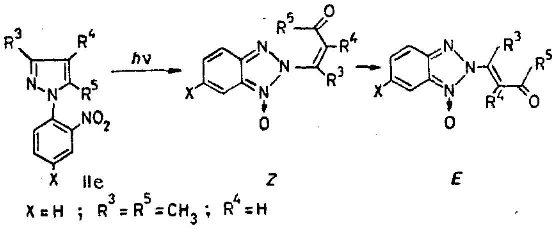
In this case Maeda and Hayshi [126] and Prokhoda and Krongauz [127] assume that the R_2 and R_2' dimers have substantially different structures. To explain the long-wave shift of the absorption bands of the colored form at low temperatures [121, 126] it has been proposed that the "low-temperature" (<150 deg C) photoradicals ($S^{\cdot}$) differ from the "high-temperature" (>−20 deg C) photoradicals ($R^{\cdot}$) with respect to their more nearly planar conformation. Different radicals ($R^{\cdot}$ and $S^{\cdot}$) are formed in the crystalline state, as in solutions, at various temperatures; however, in contrast to the solutions, the formation of nonphotochromic dimers R_2 is not observed. It has been shown that in proton-donor solutions the excited molecules and radicals ($R_2'^{*}$ and $R^{\cdot *}$) are capable of detaching hydrogen from the solvent, which leads to the irreversible formation of 2,4,5-triphenylimidazole [124, 125]. This photoreaction and other processes associated with the high reactivity of the radicals [129-131] constitute the reason for the strongly expressed photochemical instability of photochromes of this type.

Yet another diversity is observed in the case of a compound of the II type in aqueous solutions ("aquo photochromism") [132, 133] and is associated with proton transfer with the participation of water molecules:



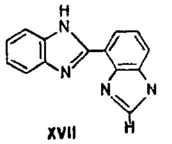
Photoproduct IId absorbs at 600-700 nm and is converted to IIc when it is heated to 105 deg C for a long time or is subjected to IR irradiation.

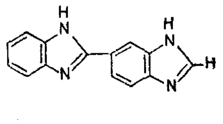
Irreversible photochemical reactions play a significant role in the photochemistry of azoles. The photochemistry of imidazoles and pyrazoles [134, 135], particularly the photooxidation of alcohol solutions of IIe, which leads to the formation of Z and E isomers through intermediate diradical structures, has been examined:



Photoirradiation of 1,2,3-thiadiazole 2-oxide leads to the formation of 1,2,3-thiadiazole 3-oxide [60].

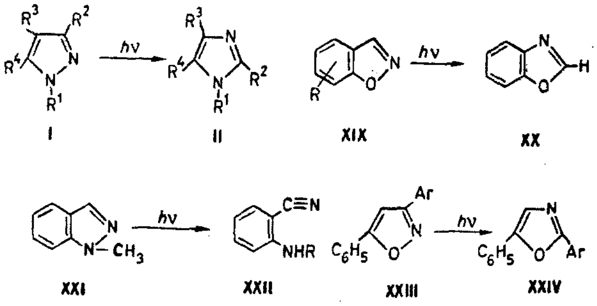
Products containing an α-cyanoethyl group are formed through an electronically excited complex as a result of photoaddition [136] of acrylonitrile to an N-unsubstituted imidazole (II, $R^1 = H$). An adduct – a tetrahydrofuro [2,3-b]azetidino[2,1-b]-1,3,4-oxadiazole derivative – is formed in the direct and benzophenone-sensitized photoreactions [127] of 2,5-disubstituted molecules IV with furan. Finally, the somewhat unusual photodimerization of benzimidazole to give dimers XVII and XVIII, probably through intermediate excited radicals, has been observed [138].


XVII


XVIII

The photocyclization of 4,5-diphenyl- (IIf) and 2,4,5-triphenyl-substituted imidazoles (IIg) [139] to 9,10-phenyltriimidazole (FIM) and its 2-phenyl derivative, respectively, gives the products in low quantum yields (~ 10^{-3}); the yields decrease when the solutions are degassed. Both photoreaction possibly include steps involving the addition of a hydrogen atom from the solvent, cyclization proper, and the loss of a hydrogen atom by the cyclization product; the reaction IIf → FIM proceeds through the $S_1^{\pi\pi^*}$ state of the IIf molecule. Photocyclization has also been used for the preparation of a number of azoles from aromatic aminonitriles, related systems [140], and o-substituted benzalanilines [141].

A number of photorearrangements, for example, I → II, XVII → XVIII, XIX → XX, XXI → XXII [142], and 2 → 4 rearrangement in phenyloxazoles [143], and rearrangement of benzisoxazole to benzoxazole, have been studied:



I, II, XIX, XX, XXI, XXII, XXIII, XXIV

The mechanism of the photorearrangements of indazoles, benzotriazoles, and benzisoxazoles has also been studied [145, 146] by ESR, IR, fluorescence, and pulse spectroscopy, and the mechanism of the phototransformations of 2-aryloxybenzazoles to 2-[2- and(or)-4-hydroxyphenyl]benzazoles was investigated in [147]. It has been shown that all of the described reactions take place primarily in the first singlet excited state of the starting molecule through different intermediate structures (for example, azirine [143], the isonitrile [144], radicals [145], and other structures [147]).

Decomposition products have been detected in the photolysis of 1,2,3-thiadiazole [148], and nitrobenzene, which is formed through a diradical structure in which a proton is transferred intramolecularly from the hydroxyl group, has been obtained by photolysis of 1-hydroxy-1,2,3-benzotriazole [149].

The photoreactions of complexes of various metals with molecules of the VIII type [where X = NH, R = H, Y = $O(L_1)$, or N−$Ts(L_2)$] have been studied [66-69]. These photoreactions and reversible dark reactions, particularly in the case of L_2, have intermolecular character, as evidenced by the concentration dependences of the reaction rates and the spectral-luminescence data.

The above-described photochemical properties of azoles make it possible to work out new methods for the preparation of practically useful compounds [148, 149] as well as new promising photochromic preparations [126, 127, 133].

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SYNTHESIS OF 3,4,6-TRIARYL-2-PYRONES

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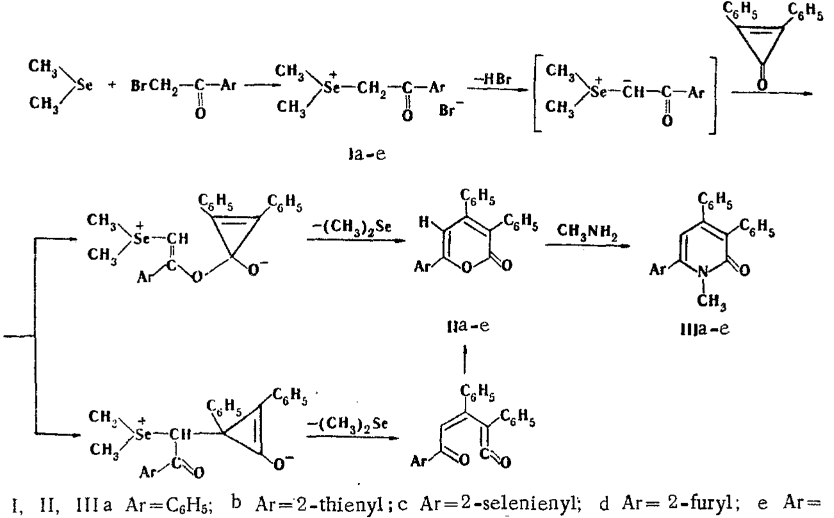
A preparative method was worked out for the synthesis of 3,4,6-triaryl-2-pyrones by 1,3-dipolar cycloaddition of selenium arylacylmethylides to diphenylcyclopropenone.

It is known that the reaction of stable selenonium ylides with acetylenedicarboxylic acid esters is a convenient preparative method for the synthesis of tetrasubstituted furans [1]. In the present research selenium ylides were used in the synthesis of α-pyrones. It is shown that 1,3-dipolar cycloaddition of reactive selenium carbonylylides to an active dipolarophile – diphenylcyclopropenone [2] – is a convenient preparative method for the synthesis of 3,4,6-triaryl-2-pyrones.

Since selenium monocarbonylylides are unstable under ordinary conditions and decompose readily to give carbenes and, subsequently, the corresponding cyclopropanes [3], stable selenonium salts – aracyldimethylselenonium bromides – were used as the starting compounds for the synthesis of the 2-pyrones. These salts were deprotonated by a methanolic solution of potassium hydroxide and underwent smooth conversion to the corresponding monocarbonylylides, which were subjected, without isolation, to reaction with diphenylcyclopropene.

1,3-Dipolar cycloaddition may begin with attack by the dipolarophile either at the ylide carbon atom or the oxygen atom. Since it is known [4] that the negative charge in phenacylmethylides is shifted to a considerable extent to the oxygen atom, it may be assumed that attack by the dipolarophile at the oxygen atom with subsequent ring closure will be the most likely pathway:



I, II, IIIa Ar=C_6H_5; b Ar=2-thienyl; c Ar=2-selenienyl; d Ar=2-furyl; e Ar=1-methyl-2-pyrrolyl

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