Translated from *Uspehki Khimii*, **61** 1243–1267 (1992) U.D.C. 541.14

The photochemistry of coumarins

N A Kuznetsova, O L Kaliya
Institute of Organic Intermediates and Dyes, Moscow

ABSTRACT. **The luminescence-spectroscopic properties, photophysical characteristics, and the most important photochemical reactions of phosphors of the coumarin series and natural furocoumarins are examined.**

The bibliography includes 130 references

Contents

I. Introduction 683
II. Spectra and excited states 683
III. Photochemical properties 687

I. Introduction

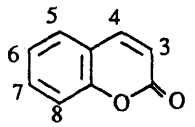
Superb luminescence in the blue-green part of the spectrum is characteristic of the majority of coumarin derivatives. By virtue of this property, coumarins have found extensive applications as optical bleaching agents,[1] in the creation of active media for tunable lasers,[2] and as luminescence labels.[3] Furocoumarins or psoralens are epidermal photosensitisers and are used in the phototherapy of skin diseases.[4] Coumarin derivatives are also of interest for the creation of photochromic materials.[5] Numerous studies devoted to the synthesis, properties, and applications of compounds of this class have been published recently. The principal methods of synthesis, reactivities, and lasing characteristics of 7-aminocoumarins have been recently reviewed.[6] Since the main applications of coumarins involve the transformation of radiation, photochemical studies are of decisive importance in the search for their new more effective and photostable derivatives. The luminescence-spectroscopic properties of coumarins are briefly analysed in the present review and a systematic account is given of data on their photochemistry, mainly those published in the literature during the last ten years.

II. Spectra and excited states

1. Absorption and fluorescence spectra

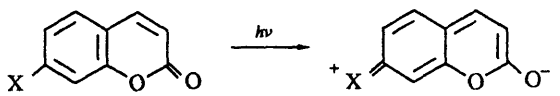
Our aim was not to carry out an exhaustive survey of the luminescence-spectroscopic properties of all the known coumarin derivatives.[7–11] We shall confine ourselves to the most general features of their dependence on the structure of the dye.

The luminescence-spectroscopic properties of coumarins are determined by the relative positions of the lowest electronically excited states of the $n\pi^*$ and $\pi\pi^*$ type. The unsubstituted coumarin does not fluoresce—it has a singlet lowest excited state of the $n\pi^*$ type with an energy of 3.4 eV.[12]



Coumarin

The most common phosphors among the compounds considered are 7-amino- and 7-hydroxy-derivatives. The introduction of an electron-donating substituent in the 7-position in coumarin has only a slight effect on the energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ states, while the energies of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states diminish appreciably under these conditions as a consequence of the conjugation of the electron-donating substituent with the aromatic system and they become the lowest states[12] with a considerable contribution by the state with intramolecular charge transfer owing to the promotion of an electron from the electron-donating substituent to the carbonyl group:



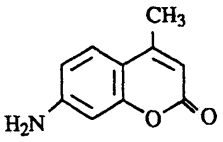
X = NR_2, OR.

The polarisation of the molecule on excitation is also indicated by the greater bathochromic shift of the fluorescence bands of 7-aminocoumarins relative to the absorption bands with increase in solvent polarity.[7] The estimated change in the dipole moment on excitation to the S_1 state is $\Delta\mu$ = 6.84 and 8.02 D for 7-amino and 7-diethylamino-4-methylcoumarins respectively.[13]

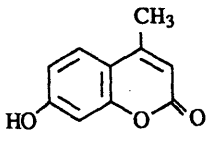
The data presented in Table 1 for certain coumarins illustrate the following characteristics of the influence of structural factors on the electronic absorption and fluorescence spectra. In comparing the spectroscopic parameters, account must be taken of the fact that the methyl group in the 4-position of the 4-pyrone ring does not affect the positions of the long-wavelength bands.

1. It has been demonstrated in relation to aminocoumarins with different positions of the amino-group in the molecule (Table 1) that the maximum bathochromic shift of the absorption spectra is observed when an electron-donating substituent is introduced in the 6 and 7-positions (the effect of substitution in the 6-position is

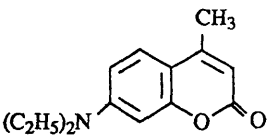
greater[20]) as a consequence of the greater stabilisation of charge transfer on excitation.



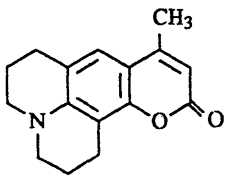
Coumarin 120



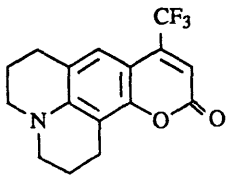
4-Methylumbelliferone



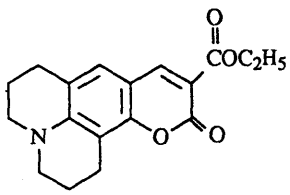
Coumarin 1



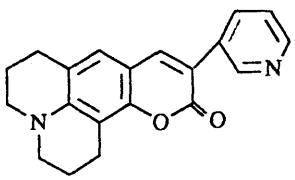
Coumarin 102



Coumarin 153



Coumarin 504



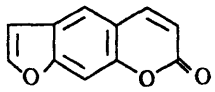
Coumarin 510

2. The bathochromic shifts of the absorption and fluorescence spectra depend on the electron-donating properties of the substituent. Thus the amino-group is a stronger electron donor than the hydroxy-group and has a greater effect than the latter on the energy of the S_1 state of coumarin. Alkylated amino-groups intensify the electron-donating properties of the substituent and lead to a further successive shift of the absorption and fluorescence bands of coumarins 120, 1, and 102 to the long-wavelength region.

3. The introduction of an electron-accepting substituent, for example, the trifluoromethyl, ethoxycarbonyl, aryl, heteroaryl, and other groups, into the pyrone fragment of the molecule induces an even greater shift of the absorption and fluorescence maxima into the red region as a consequence of the further enhancement of the degree of charge transfer. This conclusion is confirmed by the spectroscopic data presented in Table 1 for coumarin 102, on the one hand, and for coumarins 153, 504, and 510, on the other. The introduction of electron-donating substituents into the pyrone fragment of 7-aminocoumarins results in the opposite effect.[21]

The above features refer to the influence of structural factors on the absorption and fluorescence of neutral forms of coumarin derivatives, the acid–base reactions of which make it possible to expand considerably the spectral range of luminescence.[22–25]

Furocoumarins (derivatives of psoralen), exhibiting a photo-therapeutic effect, are of considerable interest.



Psoralen

The absorption spectra of the majority of furocoumarins are similar to that of psoralen, the lowest excited $S_{\pi\pi^*}$ state of which lies somewhat below the $S_{n\pi^*}$ state.[4]

Table 1. The luminescence spectroscopic parameters of coumarins in ethanol.

Coumarin	Wavelength, nm		Fluorescence quantum yield	Refs.
	in absorption	in fluorescence		
3-Aminocoumarin*	324	–	–	[14]
6-Aminocoumarin	370	–	–	[15]
Coumarin 120	354	435	–	[16]
8-Aminocoumarin	300	–	–	[15]
6-Hydroxy-4-methylcoumarin	340	427	–	[17]
4-Methylumbelliferone	320	385	0,208	[18]
Coumarin 1	353	450	0,73	[16, 19]
Coumarin 102	387	473	0,95	[19]
Coumarin 153	421	531	0,38	[19]
Coumarin 504	436	480	–	[16]
Coumarin 510	452	–	–	[16]

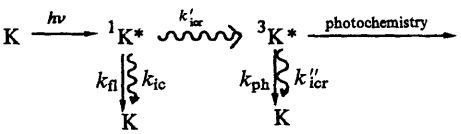
*Solvent — methanol.

2. The fluorescence efficiency

The fluorescence quantum yields of compounds of the coumarin series are determined both by internal factors (non-radiative internal conversion to the ground state and the intersystem crossing to the triplet state) and by external factors (interaction of the excited molecules with other molecules).

We shall consider the role of internal factors, which include the processes leading to the deactivation of excited states presented in Scheme 1.

Scheme 1



where K, $^1K^*$, and $^3K^*$ are coumarin derivatives in the ground, first excited singlet, and triplet states, k_l, k_{ph}, k_{ic}, and k_{icr} are the rate constants for fluorescence, phosphorescence, internal conversion, and intersystem crossing respectively.

It follows from Scheme 1 that a low fluorescence yield is observed in the case of predominant deactivation of the excited singlet state in non-radiative processes involving internal conversion to the ground state (k_{ic}) or intersystem crossing to the triplet state (k'_{icr}).

Theoretical calculations for 7-aminocoumarin derivatives showed that they belong to the fifth luminescence type of molecules with heteroatoms having higher energies of the $S_{\pi\pi^*}$ states relative to the triplet states of the $\pi\pi^*$ type.[12] Since the intersystem transition between these states is forbidden,[26] the population of the triplet levels (the main pathway leading to the loss of the energy of the fluorescent state of heteroaromatic compounds) is small in the case of 7-aminocoumarins (the quantum yield of the excited triplet states is $\varphi_T < 0.05$).[19]

The probability of intersystem crossing is determined, apart from the nature of the excited singlet and triplet states, also by the energy gap between them, increasing with decrease in the $S-T$ splitting. The energy gaps between the S_1 state and the triplet state closest to it have been calculated[12] for a series of 7-aminocoumarin derivatives. It was shown that, for compounds of the coumarin series, a relation is observed between the fluorescence quantum yields and the relative positions of the singlet and triplet states, in agreement with the ideas described.

The non-radiative deactivation via internal conversion is the second important pathway leading to the loss of the energy of the fluorescence states — it takes place mainly as a result of transitions between the vibronic levels of the S_1 and S_0 states and via hydrogen bonds. Comparison of the fluorescence quantum yields of coumarin 1 and coumarin 102 (Table 1) confirms the conclusion[27–29] that the fixation of the alkyl amino-group as a result of the incorporation of the alkyl substituent in a ring makes it possible to diminish the non-radiative excitation energy losses on rotation of the amino-groups in the excited state and permits a significant increase in the fluorescence quantum yield.

The deactivation of the fluorescent state via the hydrogen bond between 7-aminocoumarin and the solvent has been postulated to account for certain experimental data,[7,29] but it is apparently less effective than other pathways leading to the dissipation of excitation energy. Thus detailed studies have been made[13,19,27,30] of the dependences of the positions of the fluorescence bands, quantum yields, and lifetimes on the solvent polarity. It was found that in the case of 7-alkyl-aminocoumarins with a free amino-group, anomalously weak fluorescence, displaced to the red region, is observed in polar solvents. This phenomenon also occurs in solvents which do not form hydrogen bonds.[30] On the basis of these observations for 7-alkylaminocoumarins with a free amino-group, the following new model of the non-radiative deactivation of the excitation energy has been proposed. Two excited states with intramolecular charge transfer are postulated — a planar state which emits with a high efficiency and a "twisted" state, the degradation of the excitation energy of which is achieved mainly by a non-radiative pathway.[13,19,30,31] The activation barrier to the transition from the emitting planar state to the "twisted" state diminishes with increase in solvent polarity. For 7-aminocoumarins with a bound amino-group (coumarins 102, 153, etc.), only the planar excited state with intramolecular charge transfer can exist. With increase in solvent polarity, the fluorescence of such compounds shifts towards longer wavelengths and the efficiency and lifetime of the fluorescence change little under these conditions. In the case of 7-amino-coumarins with a free amino-group, there is a possibility of the formation of a non-luminescent "twisted" excited state in polar solvents, which is manifested by a significant decrease in the fluorescence efficiency and lifetime and its displacement towards longer wavelengths with increase in solvent polarity. For 7-amino-coumarins with a bound amino-group, the formation of a "twisted" non-luminescent excited state with intramolecular charge transfer is possible when the molecule contains other substituents capable of rotation.[32] It is noteworthy that the concept, developed in a number of studies,[13,19,30,31] that there are two types of excited states in coumarins with a free amino-group has not been confirmed experimentally in studies on the induced absorption and emission spectra of these compounds by picosecond spectroscopy.[33]

For coumarin derivatives with close lowest $\pi\pi^*$ and $n\pi^*$ states, the probability of non-radiative deactivation increases sharply as a consequence of vibrational interactions leading to a displacement of levels (the "proximity effect"). The effective non-radiative degradation of the excitation energy of 4-methylumbelliferone in aprotic media[18] and of furocoumarins[34] has been interpreted in terms of these ideas.

The fluorescent state energy deactivation processes, determined by external factors, including the interaction of the excited molecules with the molecules of quenching agents, are also extremely important. The oxygen present in solution, which induces the intersystem crossing to the triplet state by exchange interaction, is usually the cause of the quenching of the fluorescence of dyes of different classes.[35] Fletcher and co-workers[36] determined the relative fluorescence quantum yields (φ_{fl}) for a series of coumarin dyes in ethanol as a function of oxygen concentration. They established that the fluorescence of all the test compounds diminishes significantly in the presence of oxygen. For example, in the case of coumarin 1 the quantum yields φ_{fl} were 0.57, 0.79 and 0.85 in ethanol saturated with oxygen, air, and argon respectively.[36] Shakhverdov, et al.[35] noted high values of the constants for the quenching of the fluorescence of 7-aminocoumarins by oxygen ($k \geqslant 10^{10}$ litre mol^{-1} s^{-1}) accompanied by low rate constants for their intersystem crossing ($k_{cr} = 0.3 \times 10^7$ and 0.4×10^7 s^{-1} for coumarins 1 and 102), which is inconsistent with the quenching of the fluorescent state via the mechanism involving the oxygen-induced intersystem crossing to the triplet state. On the other hand, the rate constants for the quenching of the fluorescence of coumarin by oxygen agree with the relative positions of the states involving charge transfer from the dyes to oxygen.[35] On the basis of this relation, Shakhverdov, et al.[35] concluded that the mechanism of the quenching of the fluorescence of coumarin dyes by oxygen is based on donor–acceptor interactions.

The quenching of the fluorescence of umbelliferone derivatives by inorganic ions has been investigated.[37–40] Since the results could not be explained by the heavy atom effect,[39] the most probable mechanism in this instance is believed to involve[39] quenching via electron transfer. The methyl group in the 4-position in the pyrone ring provides a partial shield to the quenching of the fluorescence of coumarin by halide ions.[39]

The rate constants for quenching by electron donors and acceptors increase with decrease in the free energy of electron transfer with participation of 7-aminocoumarins in the excited singlet state, and for donors with $E^{ox}_{1/2} < 1.0$ V and acceptors with $E^{red}_{1/2} > -1.5$ V (relative to the saturated calomel electrode) the rate constants for the quenching of 7-aminocoumarins in the S_1 state are close to diffusion rate constants.[41]

3. Excited triplet states

The triplet–triplet absorption spectrum of unsubstituted coumarin in ethanol, measured in several studies,[42–44] revealed the occurrence of an intense long-wavelength transition $T_1 \rightarrow T_3$ with a

maximum λ_{max} = 459 nm and a molecular extinction coefficient ε_T = 13000 litre mol^{-1} cm^{-1}. This transition is polarised in the molecular plane along the long axis of the molecule. A weak $T_1 \rightarrow T_2$ transition occurs at lower frequencies. The intersystem crossing quantum yield in water and the energy of the first triplet state of coumarin are φ_T = 0.054[45] and 262 kJ mol^{-1} [46] respectively. According to a theoretical study,[47] a strong polarisation of the bond between the third and fourth carbon atoms is characteristic of the T_1 state of coumarin. The lifetimes of the excited triplet states of both coumarin and its derivatives, which are in the microsecond range,[19,45,48] depend on the solution concentration. At low concentrations, the excited triplet states are degraded via a first-order process. For example, in the case of unsubstituted coumarin, the rate constant for this process in benzene is 2.6 × 10^5 s^{-1}.[45] With increase in coumarin concentration, τ_T diminishes as a consequence of the quenching of the triplets by interaction with the ground state and the rate constant for quenching via a second-order reaction is 1.5 × 10^8 litre mol^{-1} s^{-1} for coumarin in benzene.[4]

Laser-type 7-aminocoumarin has low yields of intersystem crossing to the excited triplet state (φ_T < 0.05;[19] for coumarin 1 in ethanol, φ_T = 0.006[49]). The phosphorescence lifetimes of these compounds at 77 K are in the range corresponding to several seconds,[42] which is characteristic of excited triplet states of the $\pi\pi^*$ type.

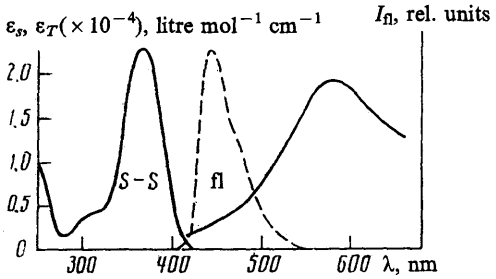


Figure 1. The $S-S$ and $T-T$ absorption and fluorescence spectra of coumarin 1;[42] I_{fl} = fluorescence intensity.

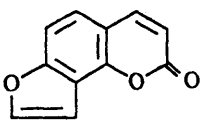
Fig. 1 illustrates the absorption spectrum of coumarin 1 in the excited triplet state obtained by pulsed laser photolysis.[42] Similar spectra have been obtained for a series of other 7-substituted coumarins. It is seen (Fig. 1) that the $T-T$ absorption of these compounds is represented by a broad band whose short-wavelength slope overlaps the luminescence spectrum. In order to estimate the loss of lasing energy in absorption by triplet levels, the molecular extinction coefficients for the $T-T$ absorption have been determined[50] in the region corresponding to the luminescence of the most important lasing coumarin dyes in ethanol.

As in the case of $S_0 \rightarrow S_1$ transitions, the methyl group in the 4-position in the pyrone ring does not alter the position of the maximum in the $T-T$ absorption spectrum, whereas the introduction of electron-donating substituents in the 7-position shifts the spectral maxima to the low-frequency region.[42] The characteristics of the $T-T$ absorption spectra of certain lasing coumarin dyes are[λ_{max}^{T-T}, nm (ε_T, litre mol^{-1} cm^{-1})]: coumarin 1—570 (15050),[51] coumarin 102—580 (14000),[48] coumarin 153 in benzene—580 (10000),[52] and 7-hydroxycoumarin in frozen alcohol—510 (18500).[44] The energies of the triplet levels determined by the energy transfer method using various triplet donors and acceptors are 240, 240, 210, and 217 kJ mol^{-1} for coumarins 1, 102, and 153 and 7-diethylamino-4-trifluoromethylcoumarin respectively.[48,51,52] As in the case of excited singlet states, the energies of the triplet levels of 7-aminocoumarins are lowered when the CH_3 group is replaced by the electron-accepting CF_3 group in the pyrone part of the molecule and T_1 therefore has the character of a state with charge transfer.

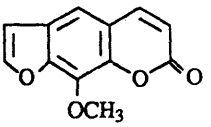
Table 2. Characteristics of the excited triplet states of furocoumarins in benzene.[34,53]

Furocoumarin	$\varphi_T \pm 10\%$	λ_{max}^{T-T}, nm	ε_T, litre mol^{-1} cm^{-1}	E_T, kJ mol^{-1}
Psoralen	0.03	450	8100	278
Angelicin	0.03	430	5500	–
8-Methoxypsoralen	0.01	480	10000	270
4,5',8-Trimethylpsoralen	0.21	450	7750	–
6,4,4'-Trimethylangelicin	0.13	450	6300	–
3-Ethoxycarbonylpsoralen	0.30	410	11500	271
3-Acetoangelicin	0.54	430	13200	–

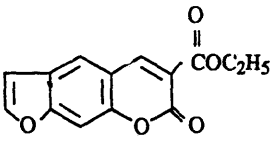
Like many aromatic carbonyl-containing compounds, furocoumarins or psoralens, which is another important group of coumarins, have $n\pi^*$ levels which are close to the lowest excited states of the $\pi\pi^*$ type.[34] This phenomenon, the so called "proximity effect", leads to intense non-radiative degradation of the excitation energy involving its transfer to both the ground and excited triplet states. The dependence of the efficiency of the non-radiative degradation on the relative positions of the levels is used to explain the characteristic features of the influence of the structure of furocoumarin on the quantum yield of the intersystem crossing, which are illustrated by examples in Table 2. The photophysical and spectroscopic parameters of the excited triplet states for a wide range of furocoumarins have been published in the literature.[34,54] The quantum yields of the intersystem crossing of furocoumarins vary within wide limits as a function of their structure—from 0.01 for 8-methoxypsoralen to 0.54 for 3-acetylangelicin (Table 2).



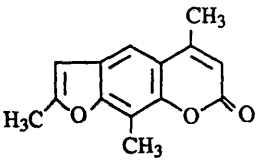
Angelicin



8-Methoxypsoralen



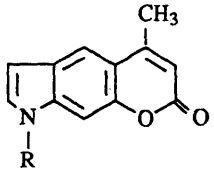
3-Ethoxycarbonylpsoralen



4,5',8-Trimethylpsoralen

The introduction of a methyl group increases φ_T. For example, φ_T = 0.21 for 4,5′,8-trimethylpsoralen, whereas the intersystem crossing yield for unsubstituted psoralen is much lower, amounting to 0.03. Similarly, 6,4,4′-trimethylangelicin has φ_T = 0.13, while angelicin itself has φ_T = 0.03. The yields φ_T increase also when an additional carbonyl group is introduced into the furocoumarin molecule. Thus the intersystem crossing quantum yield increases from φ_T = 0.03 to φ_T = 0.30 and 0.54 when the hydrogen atom in the 3-position in psoralen and angelicin is replaced by the ethoxycarbonyl and acetyl groups respectively. The molar extinction coefficients also increase on passing to furocoumarins containing an additional conjugated carbonyl group. The energies of the triplet levels of furocoumarins decrease when both electron-donating substituents and groups containing a carbonyl moiety conjugated with the aromatic system are introduced into the molecule (Table 2).

The pyrrolocoumarins (I) and (III), which have been synthesised recently,[55] are structurally similar to psoralenes.



R = H(I), CH_3(II), C_2H_5(III)

The photophysical behaviour of these two groups of compounds also has much in common. Whilst exhibiting only a weak fluorescence ($\varphi_{fl} \simeq 10^{-2}$), pyrrolocoumarins phosphoresce intensely in the range 480–600 nm. The triplet–triplet absorption spectrum of compound (I) contains bands with maxima at λ_{max}^{T-T} = 380, 500, and ~600 nm.[55] The lifetimes of the excited triplet states of pyrrolocoumarins are typical for coumarins and amount to ~5 μs. Experimental data[55] indicate an intense intramolecular charge transfer on excitation of compounds (I)–(III) as a consequence of the pronounced electron-donating properties of the pyrrole ring.

4. Generation of singlet oxygen

An important characteristic of coumarins is the quantum yield in the generation of singlet oxygen by these compounds. It has been suggested that the phototherapeutic effects of furocoumarins, which are epidermal photosensitisers and are used in the phototherapy of many skin diseases, may be partly due to the formation of $^1\Delta_g$ singlet oxygen ($^1O_2$).[56,57] The lasing 7-aminocoumarins are oxidised by singlet oxygen via a self-sensitised oxidation mechanism.[58,59] For the quantitative estimation of the efficiency of both the processes listed above as well as others occurring with participation of $^1O_2$ generated by coumarins, it is essential to know the quantum yield of singlet oxygen ($\varphi_{^1O_2}$).

$^1O_2$ is usually formed when excitation energy is transferred from the T_1 level of the sensitiser (coumarin) to oxygen in the triplet ground state:

$$^3K^* + {}^3O_2 \rightarrow K + {}^1O_2.$$

The energies of the triplet levels of coumarin and its derivatives (see above) exceed the energy of $^1\Delta_g$ singlet oxygen (94.4 kJ mol^{-1}), so that the energy transfer process considered is feasible. The quenching of the excited triplet states of coumarin by oxygen proceeds, like that of the majority of other compounds, with rate compounds close to the diffusion-controlled limit and leads to the formation of $^1O_2$.[60]

$\varphi_{^1O_2}$ for unsubstituted coumarin, which has been determined by a comparative method from the luminescence of the singlet oxygen generation, is ~0.015 in D_2O and 0.03 in CH_3OH.[61] Knox, et al.[34] determined the quantum yields in the generation of $^1O_2$ for a series of furocoumarins in benzene. The yields $\varphi_{^1O_2}$ for some of them are presented in Table 3, which shows that the efficiency of the generation of $^1O_2$ by furocoumarins may be various. It has been established that $\varphi_{^1O_2}$ is determined not only by the quantum yields of the excited triplet states of furocoumarins but also by the probability of the formation of $^1O_2$ when their T_1 states are quenched by oxygen ($\theta_{^1O_2}$), which varies in the range 0.1 to 1 for many of the furocoumarins investigated (Table 3).

Table 3. Characteristics of the generation of singlet oxygen by furocoumarins in benzene.[34]

Furocoumarin	$\varphi_{^1O_2}$ ±10%	$\theta_{^1O_2}$ ±25%
Psoralen	0.01	0.33
Angelicin	0.01	0.33
8-Methoxypsoralen	0.004	0.40
5,8-Dimethoxypsoralen	0.004	0.10
4,5′,8-Trimethylpsoralen	0.08	0.38
6,4,4′-Trimethylangelicin	0.02	0.16
3-Ethoxycarbonylpsoralen	0.30	1.00
3-Acetoangelicin	0.40	0.73

The quantum yields in the generation of $^1O_2$ by the lasing 7-aminocoumarins are low—the values for coumarins 1 and 102, determined using rubrene as the trapping agent for $^1O_2$, are 0.08–0.025 in benzene.[62]

III. Photochemical properties

1. Electron and proton phototransfer

The phototransfer of an electron is postulated as the primary elementary step in many photochemical reactions of coumarin derivatives. This aspect of the problem will be dealt with in the corresponding Sections of the review.

As noted above, the excited singlet[37–41] as well as triplet[41] states of coumarins are quenched by electron donors and acceptors. The acceleration of the destruction of coumarin and psoralene triplets in the presence of thymine and other DNA bases as well as aminoacids, in particular tryptophan, has also been interpreted as quenching via an electron transfer mechanism.[45] However, the attempts to detect coumarin radical-ions as the products of the total electron transfer were unsuccessful in these experiments.[41,45] Only in the study of the quenching of the excited triplet states of coumarin and 4′,5′-dihydropsoralen by tryptophan using pulsed laser photolysis was a relatively long-lived absorption detected and was tentatively

assigned to absorption by the mixture of the coumarin radical-anion and the tryptophan radical-cation.[45]

Reliable data for the absorption spectra of the radical-ions of coumarin derivatives were obtained by the pulsed radiolysis method.[45,53,63] The electronic absorption spectra of the radical-anions of coumarins and psoralens in water show an intense absorption peak in the vicinity of 360 nm and a broad structureless band in the wavelength range above 500 nm with a diffuse maximum near 600 nm ($\varepsilon \simeq 2000$ mol litre^{-1} cm^{-1}).[45,53] The radical-cations of coumarins absorb at shorter wavelengths: $\lambda_{max}^{abs} = 460$ nm for the coumarin 153 radical-cation in cyclohexane[63] and $\lambda_{max}^{abs} = 480-500$ nm for the radical-cations of psoralen and its derivatives in aqueous solution.[53]

Proton phototransfer has been investigated for many, mainly lasing, coumarin dyes. New ionic forms formed in this process exhibit an effective luminescence in a whole series of instances, which makes it possible to plan significantly the laser tuning range. The spectra and structures of photoprotolytic forms have been identified and the kinetics of the proton phototransfer reactions have been investigated for 7-hydroxycoumarin[22,64,65] and its 4-methyl[22,64] and 4-trifluoromethyl derivatives[23] as well as esculin (6,7-dihydroxy-coumarins to the S_1 state intensifies sharply the acid properties of the hydroxy-group and the basic properties of the carbonyl oxygen, which determines the direction of the proton phototransfer. Whereas the CH_3 substituent in the 4-position in the pyrone ring does not alter the efficiency of the formation of the various protolytic forms, the CF_3 group has a marked influence on this reaction with abstraction, addition and transfer of a proton in hydroxycoumarins. By virtue of the inductive effect of the trifluoromethyl group, in the excited singlet state there is an appreciable increase in the probability of the abstraction of a proton from the hydroxy-group, but its addition to the carbonyl group is hindered. In the case of 3-hydroxycoumarin, there is insufficient time for the attainment of the protolytic equilibrium in the excited state owing to the rapid degradation of the excitation energy.[67]

The acid–base forms of aminocoumarins luminesce much less effectively than the neutral forms.[14,25] We shall consider the characteristics of the photocatalytic reactions of the familiar lasing dye coumarin 102. On protonation of the coumarin 102 molecule, the amino group is the first to be protonated in the ground state and is followed by the carbonyl group.[24] In the fluorescent S_1 state, the proton-accepting capacity of the carbonyl group increases appreciably and the order in which the groups are protonated changes. It has been suggested[24] that, during the lifetime of the excited state in acidified solutions of coumarin 102, a proton is abstracted from the nitrogen atom of the amino-group and is added to the oxygen atom of the carbonyl group after transfer through the surrounding medium.

7-Aminocoumarins have been divided into three groups in terms of their photoprotolytic properties:[25] (1) coumarins 102 and 120 as well as others in which a proton adds adiabatically to the carbonyl oxygen; (2) 7-aminocoumarins containing a CF_3 substituent in the 4-position in the pyrone ring, where the proton phototransfer is accompanied by the loss of excitation; (3) 7-alkylaminocoumarins whose photoprotolytic forms do not luminesce owing to the disruption of the planar configuration of the cation by the mobile alkyl groups attached to the nitrogen atom.

It is noteworthy that the proton phototransfer reactions are fully reversible: the loss of excitation is accompanied by the rapid conversion of the dye into the initial form.

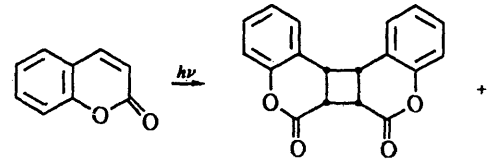
2. Phototransformation of the chromophore

Photochemical reactions leading to the disruption of the benzo-pyrone fragment, which serves as the chromophore in compounds of the coumarin type, are included among the phototransformations of the chromophore. The absorption and luminescence in the visible and near UV regions of the spectrum disappear under these conditions. This part of the review will deal with the reactions involving the opening of the pyrone ring, the photochemical reduction, as well as reactions involving the [2 + 2]photocyclo-addition to the double bond between the third and fourth carbon atoms, which are extremely characteristic of coumarins.

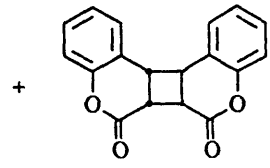
(a) [2 + 2]Photocycloaddition reactions

Photodimerisation. Coumarins, which are cyclic esters [lactones?] of α,β-unsaturated carboxylic acids, show an extremely great tendency to undergo reactions involving photocycloaddition to the 3,4-bond of the pyrone ring, in which cyclobutane adducts are formed. Such reactions include photodimerisation. The photo-dimerisation of coumarin has been the subject of numerous investigations.[68–71] The principal conclusions reached in such studies can be formulated as follows.

Mainly two out of the four possible stereoisomers are formed as the products of the photodimerisation of coumarin in solution:



(IV)



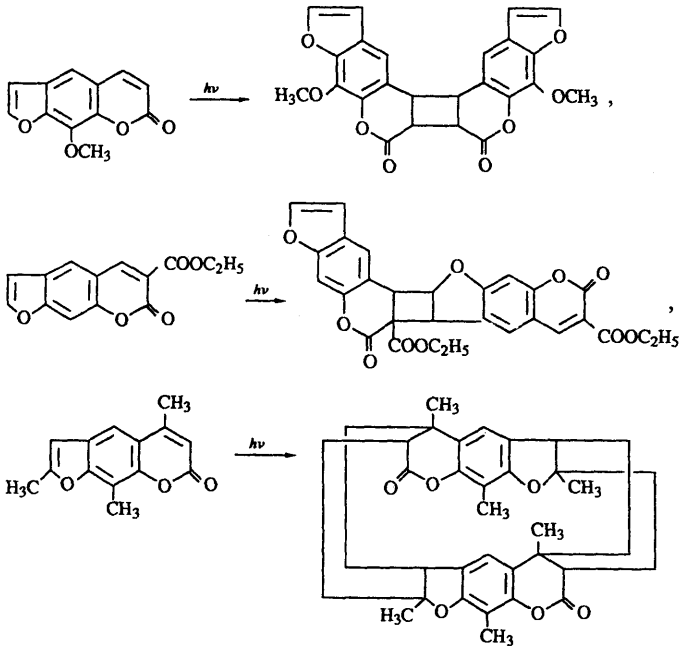
(V)

The "head to head" *endo*-dimer (IV) is the main product of the extremely inefficient reaction of coumarin in the excited singlet state ($\varphi \simeq 10^{-3}$ in water at a coumarin concentration of 0.01 M and $\varphi < 10^{-5}$ in methanol and benzene[70]). The "head to head" *exo*-adduct (V) is formed from the excited triplet state with an average efficiency ($\varphi \simeq 0.1$ on sensitisation with benzophenone[69]). The reaction in the excited singlet state is catalysed by Lewis acids. Thus the quantum yield of the *endo*-dimer in dichloromethane (coumarin concentration 0.2 M) increases from 10^{-3} to 0.16 in the presence of BF_3.[71]

The *endo*-orientation of the product obtained from the excited singlet state and the *exo*-orientation of the product obtained from the excited triplet state in the photodimerisation reaction persist also for substituted coumarins. Studies have been performed in relation to compounds containing alkyl, alkoxy-, acetoxy-, chloro-, phenyl, and cyano-substituents in the 3-, 4-, 6-, and 7-positions.[72,73] Depending on their structure, coumarin derivatives dimerise via both excited singlet and triplet states. Thus, whereas in the case of 4-substituted derivatives the photoreaction takes place via the triplet on direct excitation, the multiplicity of the reactive excited state of coumarins substituted in the 7-position depends on the nature of the

substituent. A dual behaviour is characteristic of 4,7-di-substituted derivatives—the reaction proceeds simultaneously via states of different multiplicity.[72–74] The methyl group in the 4-position in the pyrone ring does not prevent photodimerisation,[72,75] but the familiar lasing dye 7-diethylamino-4-methylcoumarin (coumarin 1) does not dimerise under the reaction conditions, undergoing another photochemical transformation involving the photochemical oxidation of the diethylamino-group.[75] 3,4-Disubstituted coumarins do not form dimeric cyclobutane photoadducts, probably as a consequence of steric hindrance.[75] In aqueous micellar solutions, the nature of the products has not changed but a decrease in the rate of photochemical reaction is observed for coumarin itself,[70] whereas in the case of its substituted derivatives the rate increases.[72]

Furocoumarins can dimerise via both the pyrone and furan fragments[76–79] to form dimers of different types, for example:

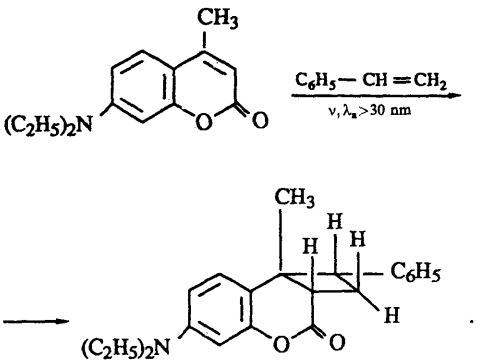


In contrast to the liquid phase, in the solid state coumarin exhibits a fairly high photostability and does not form dimeric cyclobutane adducts on irradiation.[80] A characteristic feature of the solid-phase reaction is the restriction of the movement of the molecules and a greater influence of their disposition in the crystal on the course of the process. The packing in individual crystals unfavourable for photodimerisation can be modified in mixed crystals, for example, with phenanthrene or antipyrine.[80] In mixed crystals, photodimerisation of this kind becomes geometrically feasible and a mixture of the photodimers (IV) and (V) is formed, containing mainly the "head to head" *endo*-dimer (IV).

The relation between the structure of the crystals and reactivity was investigated for a series of coumarin derivatives.[81,82] The limiting distance between the centres of the reaction bonds in the photoreactive crystals is 4.2 Å.[81] For small deviations from the disposition of molecules favourable for photodimerisation, of the kind which occur, for example, in the case of 7-chlorocoumarin where the distance between the reacting bonds in the crystals is 4.454 Å or 7-methoxycoumarin in the crystals of which the reacting bonds have been rotated by 65° relative to one another, the topochemical reaction can proceed with a high yield (~90%).[82]

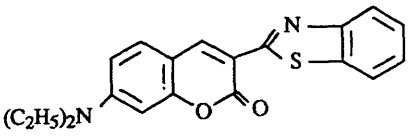
The photodimerisation of coumarin is reversible: on irradiation with short-wavelength light, the dimers are reconverted into the initial compounds, while on exposure to polychromatic sunlight a photostationary equilibrium is established between coumarin and its dimer.[83]

Photocycloaddition of olefins. The [2 + 2]photocycloaddition of olefins to coumarins usually takes place more effectively than the photodimerisation of the latter. In the presence of olefins, the photodimerisation can be actually inhibited as a consequence of the preferential reaction with olefins.[84] 7-Aminocoumarins, which do not tend to form photodimers,[75] react with olefins to form cyclobutane adducts.[85–88] As a result of the reaction occurring regiospecifically via the excited singlet state, mainly "head to tail" cyclic [2 + 2]adducts are formed. For example, coumarin 1 reacts with styrene in acetonitrile at reactant concentrations of 10 and 0.08 M respectively to form a "head to tail" type isomer with the *endo*-disposition of the phenyl substituent,[86] the quantum yield being 0.041:



The presence of an electron-donating group in the 4-position accelerates the process.[87,88] These results as well as the data of other workers concerning the reactivity of 4-hydroxycoumarin[89] and 3-acetylcoumarin[90] show that the substituents in the 3- and 4-positions in the pyrone ring do not prevent the formation of [2 + 2]photoadducts with olefins.

The lasing dye coumarin 6 in solutions in the presence of diphenylpolyenes generates stimulated radiation under the influence of a light pulse and is simultaneously decolorised in the [2 + 2]photocycloaddition reaction.

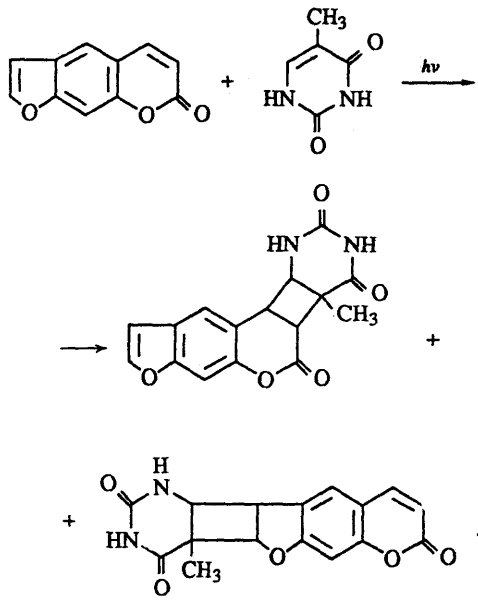


Coumarin 6

Active media having this composition have been proposed for lasers of a new type operating in the decolorisation wave regime with the lasing zone moving in the solution.[91]

Furocoumarins also form photoadducts with olefins,[92] while in biological systems they add under the influence of light to thymine in nucleic acids, to unsaturated acids, and to lipids and proteins,[93–96] and the reaction can involve not only the pyrone but also the furan

ring. Thus both types of psoralene–thymine monoadducts have been isolated:[97–99]



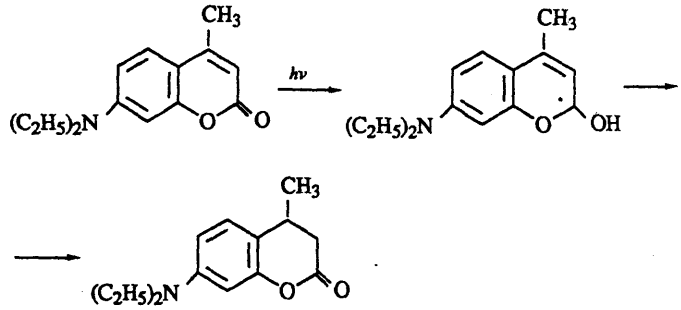
It is nowadays generally accepted that the therapeutic action of furocoumarin combined with irradiation by near UV light is due to the photochemical formation of interstrand cross-links in DNA via the successive cycloaddition of the furocoumarin to the pyrimidine bases of two DNA strands. The presence of such cross-links suppresses the hyperactive synthesis of DNA associated with psoriasis.[4] The breakdown of conjugation in the psoralen molecule on formation of a monoadduct via the pyrone ring induces a marked hypsochromic shift of the absorption, whereas the product of the addition of thymine to the furan ring absorbs radiation in almost the same way as psoralene—up to 380 nm.[97,98] Accordingly, it is clear that the interstrand cross-linking of DNA is possible only under the conditions of the initial addition of psoralene to the furan fragment, since only then can the system retain its ability to be activated by near UV light. It is noteworthy that in solution the reactivity of furocoumarins in the photocycloaddition reaction is much higher for the double bond of the pyrone ring than for that of the furan ring.[92] Since furocoumarins add to DNA in the opposite order in biological systems, it has been suggested that the mode of photocycloaddition is determined in this instant by non-valence interactions.

The [2 + 2]photocycloaddition of olefins to coumarins can occur, like the photodimerisation of the latter, both via the excited singlet and excited triplet states, depending on the structure of the substrate. Thus experimental data show that in the case of 7-aminocoumarins the excited singlet state is reactive,[85–87] while in furocoumarins it is the excited triplet state.[92,100]

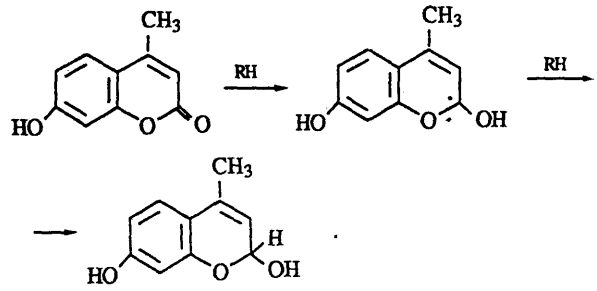
The similarity between the [2 + 2]photocycloaddition of olefins and [2 + 2]photocyclodimerisation is also manifested by the fact that both reactions are reversible—under the influence of short-wavelength light the cyclic adducts are reconverted into the initial compounds.[95,98]

(b) Other photochemical reactions of the chromophore

There are few data on the photodegradation of the chromophore in coumarin dyes in photochemical reduction reactions. When coumarin 1 is irradiated in deoxygenated acetonitrile, the product of the hydrogenation of one of the double bonds is formed, judging from mass-spectrometric data, in a low yield as a side-product.[49,101] Jones and co-workers[49,101] suggested that the 3,4-bond of the pyrone ring is reduced. In their view, the photochemical reaction proceeds via the excited singlet state by a bimolecular mechanism, which includes the ketyl radical disproportionation stage:

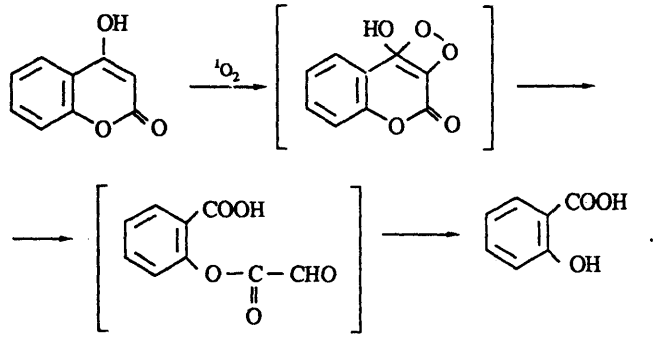


On the other hand, the reduction of the carbonyl groups has been postulated[102] for the analogous product of the photolysis of 4-methylumbelliferone:



The different views concerning the mode of photochemical reduction of the chromophore in coumarin derivatives indicate that the process has been studied inadequately and that a detailed analysis of the products is necessary in order to elucidate their structure unambiguously.

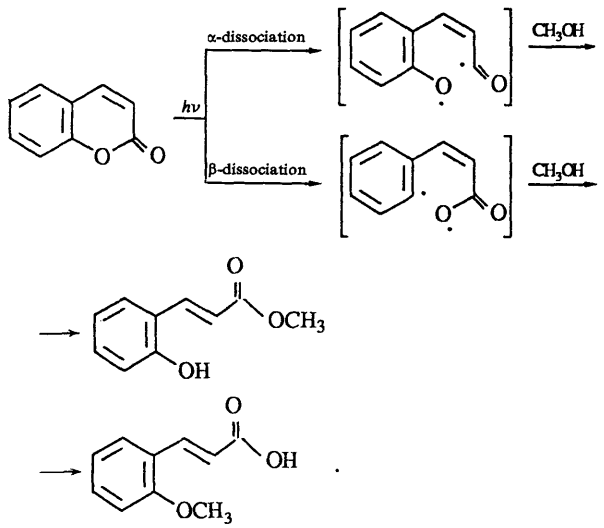
The photodegradation of the heterocycle with participation of singlet oxygen is known to occur for coumarins containing a hydroxy-group in the 4-position:[103]



The electron-donating hydroxy-group in compounds of this type activates the 3,4-double bond in reactions with $^1O_2$, which is particularly necessary for coumarins containing a carbonyl group, a powerful electron acceptor, next to the double bond. The hydroxy-group in the 3-position does not activate coumarin, since it forms an intramolecular hydrogen bond with the carbonyl oxygen. Like other

substituted derivatives, 3-hydroxycoumarins, with the exception of those containing a hydroxy-group in the 4-position, are not oxidised by singlet oxygen.[103]

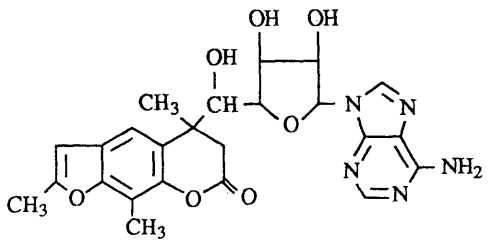
The opening of the pyrone ring can be initiated by the α- and β-dissociation of the C—O bond (relative to the carbonyl group).[104] The final products are formed in the reactions of biradicals with solvent molecules:



The α- and β-dissociation products are formed via states of different multiplicity—singlet and triplet respectively, α-dissociation being more probable.

The analogous ring opening reaction in derivatives of 3,4-dihydrocoumarin proceeds via α-dissociation. The quantum yield of this photochemical reaction is high and amounts to, for example, $(7.4 \pm 0.5) \times 10^{-2}$ for unsubstituted 3,4-dihydrocoumarin.[105]

The only known example of photoaddition to coumarins without the formation of cyclobutane derivatives is the photoaddition of adenosine to trimethylpsoralene.[106] The photoadduct has the following structure:

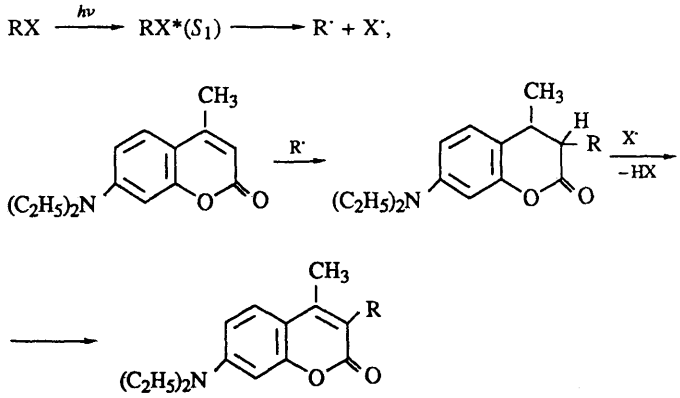


3. Photochemical reactions of the substituting groups

It was noted above that unsubstituted coumarin does not fluoresce and that the best phosphors of the coumarin series have electron-donating substituents in the 7-position. Other groups usually cause a shift of the fluorescence to the required spectral region and increase solubility, photostability, affinity for fibres, etc. In the light, the substituting groups can enter into various photochemical reactions. We shall consider the most important of these.

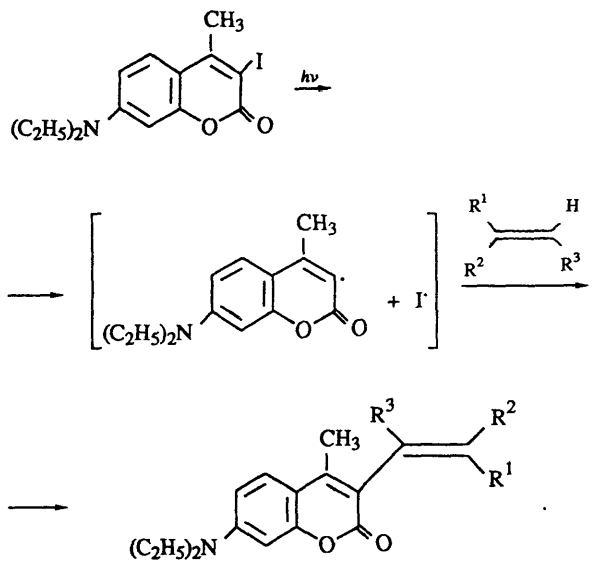
(a) Photosubstitution

The photosubstitution reactions of coumarin derivatives have been investigated in relation to the most readily available dye coumarin 1. Photosubstitution via a radical mechanism involves the 3-position when coumarin 1 is irradiated in the presence of reagents containing photolabile chemical bonds (alkyl and aryl halides, dioxane pyroxide, nitromethane):[107]



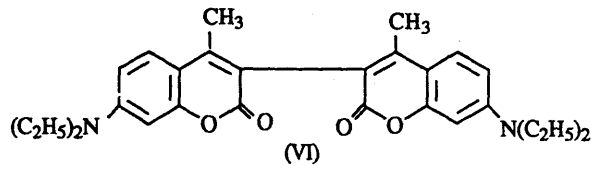
The yields of the photochemical reaction products are 10—30%. In conformity with the bond energies in the series of alkyl or aryl halides. the use of iodo-derivatives is most effective for substitution reactions. The study of the influence of the nature of the substituent in the 4-position in the pyrone ring showed that both electron-donating and electron-accepting substituents accelerate the process, apparently stabilising the radical centre in the intermediate.[108]

When 3-iodocoumarins containing the photolabile C—I bond were used in the presence of substituted benzene derivatives as well as olefins, a series of new 7-aminocoumarins were obtained containing an aryl[109] or unsaturated substituent[110] in the 3-position. The photochemical reaction proceeds via the excited singlet state of the substrate in accordance with the following most probable mechanism:



The reactions with monosubstituted benzenes result in the formation of *ortho*- and *para*-isomeric products, the efficiency of the photosubstitution decreasing on passing from electron-donating to electron-accepting substituents.[109]

The biscoumarin (VI) was obtained from coumarin 1 and its 3-iodo-derivative under similar conditions.[107]



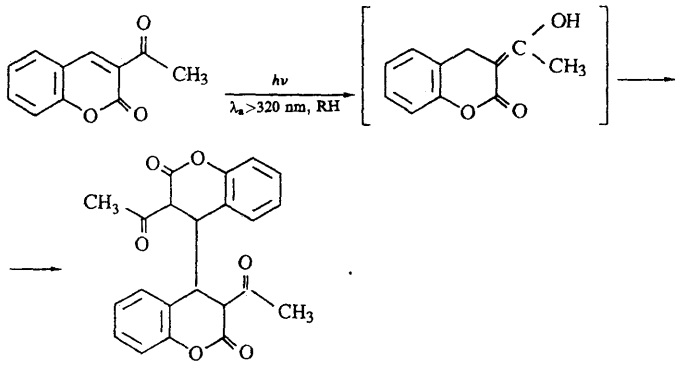
(VI)

On irradiation of 7-aminocoumarins in chlorine-containing solvents, 3-chloro-substituted derivatives are also formed via the radical photosubstitution mechanism with participation of chlorine atoms, which attack the unoccupied 3-position in the substrate molecule.[111]

Photosubstitution of coumarins by the radical-ion mechanism has not been investigated. According to preliminary data,[107] it is not selective and involves not only the 3-position but also other positions subjected to attack by the radical-ion.

The formation of a 3-hydroxy-derivative from coumarin 120 in the reactions of the latter with singlet oxygen has been postulated.[112,113]

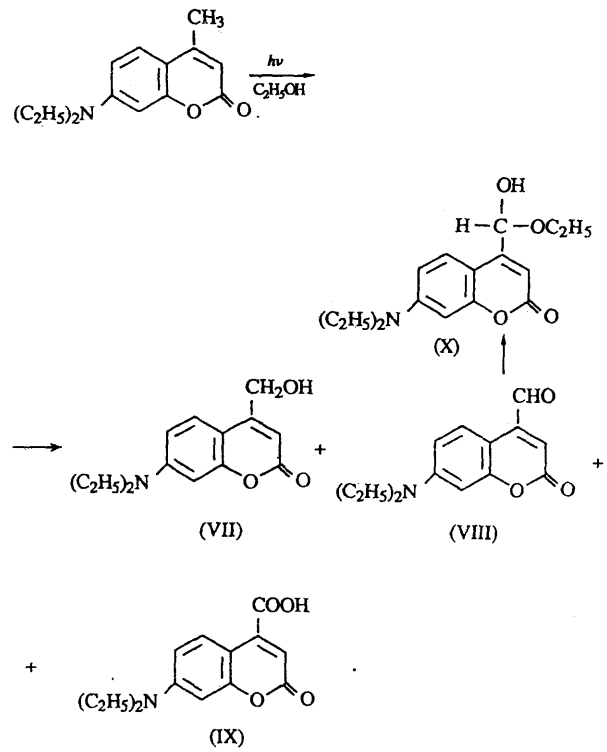
In connection with the discussion in this Section of the review of the mechanism of the formation of the biscoumarin (VI), we may note that 3,3'-diacetyl-3,3',4,4'-tetrahydro-4,4'-biscoumarin is formed in accordance with an unusual mechanism via the reduction of a substituent and the isomerisation and recombination of radicals:[90,114]



(b) Photochemical oxidation of alkyl substituents

Many coumarin phosphors contain a methyl group in the 4-position in the pyrone ring. Compounds of this type include coumarins 1 and 102, which have found extensive applications in the laser technique.

Winters, et al.[115] established for the first time that, when active lasing media based on alcoholic solutions of coumarin 1 are irradiated with light from pulsing pumping lamps, the methyl group in its structure is oxidised to the corresponding alcohol, aldehyde, and acid:

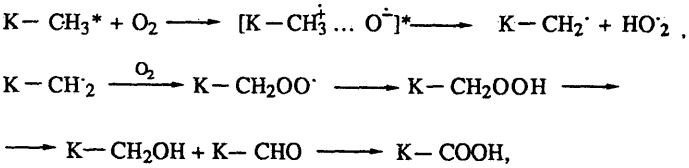


(VII) (VIII) (IX) (X)

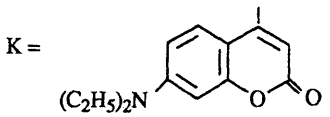
The accumulation in the solution of the products of the photochemical oxidation of the methyl group leads to an increase in the absorption by the lasing medium in the region corresponding to the luminescence of coumarin 1 and the impairment of lasing parameters. However, in alcohol only 4-carboxy-7-diethylamino-coumarin (IX) among the photoproducts (VII)–(IX) absorbs appreciably in the region corresponding to lasing by coumarin 1.[116] The aldehyde (VIII) likewise makes a significant contribution to the photoinitiated increase in the optical density of the active medium in the long-wavelength region, but subsequent interaction of compound (VIII) with the solvent leads to the formation of the hemiacetal (X), which does not absorb the luminescence radiation, is responsible for the dark relaxation of the optical density in the lasing region (Fig. 2), and determines the lasing energy in irradiated alcoholic solutions of coumarins.[116]

In order to seek ways of increasing the photostability of lasing media based on 4-methylcoumarins, the mechanism of the photochemical oxidation of these compounds was investigated by several groups of workers.[59,117–120] In air-saturated ethanol, the quantum yield of the photochemical reaction is 5×10^{-4}, is independent of the dye concentration, and in the range $10^{-4}-10^{-2}$ M the reaction constitutes the principal photodegradation pathway.[117] The efficiency of the photochemical oxidation of the methyl group increases with enhancement of the electron-donating properties of the substituent in the 7-position. The process is sensitised by triplet sensitisers and is almost independent of the energy of the absorbed quantum in the wavelength range 254–365 nm. The oxidation

reaction proceeds via a free-radical mechanism and is initiated by the bimolecular reaction between the excited coumarin and oxygen:[117]



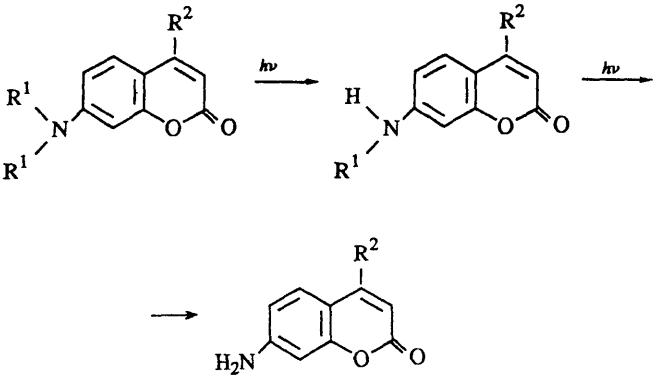
where



The study of the photochemical processes occurring in solutions of coumarins containing a methyl-group in the 4-position revealed the following pathways leading to the expansion of the stock of available active lasing media: removal of oxygen from the solution by bubbling the latter with an inert gas;[121,122] the use of coumarins not containing a CH_3 group[123] or containing the non-oxidisable CF_3 group in the 4-position'[124] inhibition of the radical oxidation reactions by photostabilisers;[125] adsorption of 4-carboxy-7-diethylaminocoumarin on the Al_2O_3 filter in the laser pumping system.[115]

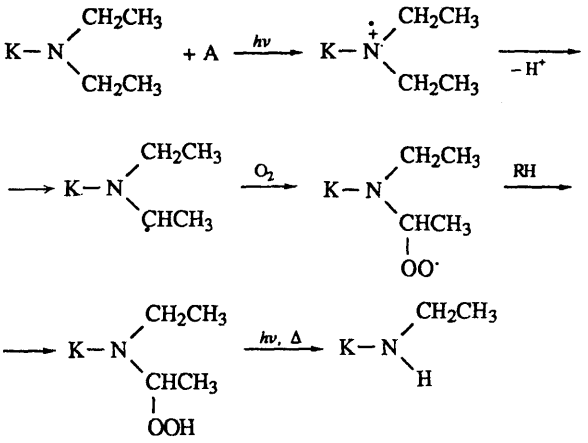
(c) Photochemical reactions of alkylamino-groups

The most numerous group of coumarin phosphors contain an amino- or alkylamino-group in the 7-position. 7-Alkylaminocoumarins are dealkylated under the influence of radiation, the dealkylation products being formed with a greater or small probability virtually under any photolytic conditions. They were first isolated and identified by Winters, et al.[115] after irradiating coumarin 1 in ethanol. In the latest studies,[59,101] it has been shown that the process is common to all 7-alkylamino-coumarins:

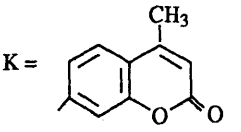


$R^1 = CH_3,\ C_2H_5;\quad R^2 = CH_3,\ CH_2OH,\ CF_3.$

7-Alkylaminocoumarins are dealkylated in accordance with the same mechanism as other tertiary and secondary amines—via α-aminoalkyl radicals, which are formed when electron acceptors abstract a hydrogen atom or an electron and a proton according to the following most probable scheme:



where



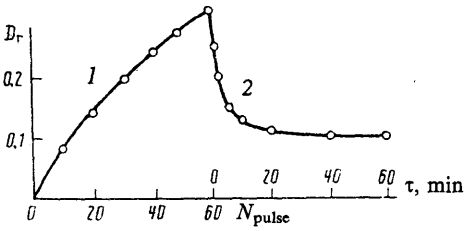


Figure 2. Variation of the optical density of an ethanol solution of coumarin 1 ($c = 10^{-3}$ M, $L = 5$ cm) in the lasing region at a wavelength of 460 nm during irradiation by light pulses (N_{pulse}) from an IFP=2000 lamp at a frequency of 0.3 Hz (curve *1*) and during the subsequent dark process (curve *2*).[116]

Various oxidants, for example aromatic nitro-compounds,[126] the solvent,[111] another coumarin molecule in an excited state,[49,127,128] and singlet oxygen,[58,59,62] can also function as electron (hydrogen atom) acceptors.

The role of the photochemical oxidation by singlet oxygen, which is extremely common in organic photochemistry, in the photodegradation of coumarins has been investigated in fair detail. It has been established[59,62] that the interaction of 7-alkylaminocoumarins with $^1O_2$ leads to the oxidative photo-*N*-dealkylation and does not usually involve the 3,4-bond in the pyrone fragment. With the exception of the 4-hydroxy-derivative,[103] coumarins without amino-groups do not react on treatment with $^1O_2$.

On direct photolysis in a number of solvents, the photo-*N*-dealkylation proceeds according to the self-sensitised photochemical oxidation mechanism, which consists in the initial activation of oxygen by the transfer to the latter of the excitation energy from the triplet level of coumarin and the formation of singlet oxygen, which oxidises the dye in the electronic ground state:

$$K \rightsquigarrow {}^3K^*,$$

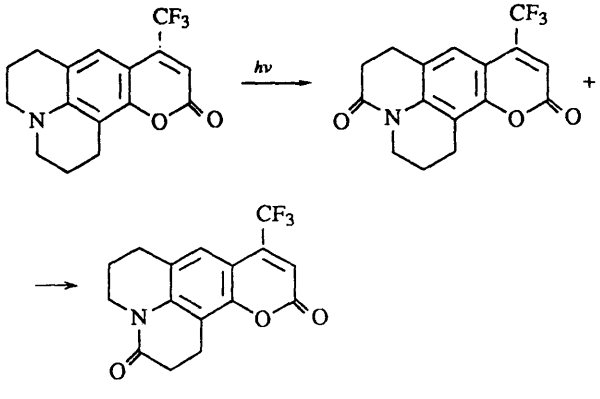
$${}^3K^* + {}^3O_2 \rightarrow K + {}^1O_2,$$

$$K + {}^1O_2 \rightarrow N\text{-dealkylation products}.$$

For example, in benzene the photo-*N*-dealkylation of coumarin 1 (the main photochemical reaction) via the mechanism of the self-sensitised photochemical oxidation by singlet oxygen proceeds to an extent greater than 70% for a $^1O_2$ generation quantum yield of ~ 0.1 and an overall rate constant for the physical and chemical quenching of singlet oxygen by coumarin of 10^6 litre mol^{-1} s^{-1}.[62] The formation of the clathrate complex between coumarin 1 and β-cyclodextrin increases the stability of the dye as regards the action of $^1O_2$ in aqueous solutions by an order of magnitude.[128]

On passing from dilute to concentrated ($c > 10^{-2}$ M) solutions, the mechanism of the photo-*N*-dealkylation changes to a bimolecular mechanism, which includes the abstraction of an electron (hydrogen atom) by an excited coumarin molecule from an unexcited one ($k = 10^7$ litre mol^{-1} s^{-1} in ethanol[128]). In this connection, one should note that in alcoholic solutions at low concentrations the main photochemical reaction of 7-dialkylamino-4-methylcoumarins is the photochemical oxidation of the methyl group, whereas at high concentrations the bimolecular photo-*N*-dealkylation predominates.

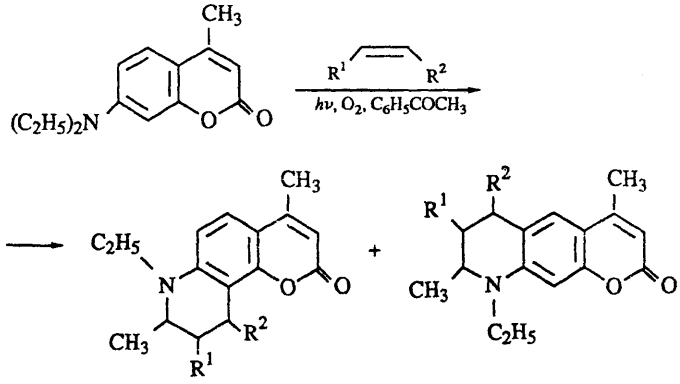
The formation of amides in the photochemical oxidation of alkylaminocoumarins has been reported in a number of communications.[59,101] Thus two isomeric amides are formed on irradiation of coumarin 153 in air-saturated acetonitrile:[102]



Evidently amides are formed as products of photo-*N*-dealkylation on oxidation of the intermediate α-aminoalkyl radicals by oxygen.

In deoxygenated solutions, the radicals undergo other dark reactions — they recombine with solvent molecules[129] and give rise to oligomers.[49,101] The role of radicals in the photodegradation of deoxygenated solutions has been confirmed by the inhibition of the reaction by divalent sulphur compounds.[127]

The heterocyclisation of alkylamino-groups in the 6- and 8-position in the coumarin ring is of interest. On photoirradiation in the presence of olefins containing more than one electron-accepting substituents, 7-aminocoumarins do not give rise to adducts resulting from the [2 + 2]cycloaddition to the 3,4-bond, but in the presence of acetophenone, a triplet sensitiser, they afford heterocyclisation products in a quantum yield of 0.01:[130]



The mechanism of the photochemical reaction proposed by Kirpichenok, et al.[130] involves the participation of acetophenone in the T_1 state as the oxidant in the formation of the α-aminoalkyl radical and the addition of the latter to the olefin.

It follows from the data presented in this Section of the review that the photochemical reactions involving the alkylamino-group are initiated by the formation of α-aminoalkyl radicals, the different dark reactions of which determine the nature of the final product.

- - - o0o - - -

The results considered show that during the last decade our knowledge about the photochemical reactions of coumarin derivatives has greatly expanded. Various photochemical reactions of compounds of this class have been investigated, but the available information about certain aspects of the photolysis, for example, about the irreversible photodegradation of the chromophore, is inadequate. Nevertheless, on the basis of the known values it is possible in many instances to predict the behaviour of coumarin derivatives on photoirradiation. The results described determine to a large extent the course of future studies, which will have to be carried out in the search for effective ways of increasing the photostability of the organic phosphors in this important class.

References

1. H Gold *Chemistry of Synthetic Dyes* (Edited by K Venkataraman) (Translated into Russian), Khimiya, Leningrad, 1977, Vol. 6, p. 329
2. K H Drexhage *Dye Lasers* (Edited by F P Schaefer) (Translated into Russian), Mir, Moscow, 1976, p. 172
3. R S Davidson, M M Hilchenbuch *Photochem. Photobiol.*, 1990, **52** 431
4. R V Bensasson, E J Land, T G Truscott *Flash Photolysis and Pulse Radiolysis in Biology and Medicine* (Translated into Russian), Mir, Moscow, 1987, p. 332
5. V A Barachevskii, G I Lashkov, V A Tsekhomskii *Fotokhromizm i Ego Primenenie* (Photochromism and Its Applications), Khimiya, Moscow, 1977, p. 54
6. I I Grandberg, L K Denisov, O A Popova *Khim. Geterotsikl. Soedin.*, 1987, 147

7. A R Reddy, D V Prasad, M Darbarwar *J. Photochem.*, 1986, **32** 69
8. A N Fletcher, D E Bliss *Optics Commun.*, 1983, **47** 57
9. I I Tkach, T A Mikhailova, A V Reznichesnko, et al. *Khim. Geterotsikl. Soedin.*, 1990, 321
10. N Yu Vasil'eva, I V Sokolova, A M Degtyarenko, A V Kropachev *Izv. Vyssh. Uchebn. Zaved. Zaved. Fiz.*, 1990, 123
11. M M Asimov, V N Gavrilenko, L Kozma, et al. *Zh. Prikl. Spektrosk.*, 1990, **53** 201
12. O A Ponomarev, Yu F Pedash *Zh. Fiz. Khim.*, 1989, **63**(2) 546 [English translation in *Russ. J. Phys. Chem.*, 1989(2)]
13. W Rettig, A Klock *Can. J. Chem.*, 1985, **63** 1649
14. R V Subba Rao, M Krishnamurthy, S K Dogra *J. Photochem.*, 1986, **34** 55
15. A Mangini, R Passerini *Gazz. Chim. Ital.*, 1957, **87** 243
16. U Brackmann *Lambdachrome Lazer Dyes, Lambda Physik. Gmbh*, Gottingen, D-3400, 1986
17. C E Weelock *J. Am. Chem. Soc.*, 1959, **81** 1348
18. M S A Abdel-Mottaleb, B A El-Sayed, M M Abo-Aly, M Y El-Kady *J. Photochem. Photobiol. A*, 1989, **46** 379
19. G Jones (II), W R Jackson, C Choi *J. Phys. Chem.*, 1985, **89** 294
20. O A Ponomarev, E R Vasina, V G Mitina, A A Sukhorukov *Zh. Fiz. Khim.*, 1990, **64**(4) 974 [English translation in *Russ. J. Phys. Chem.*, 1990(4)]
21. L K Denisov, L M Mel'nikova, M A Kirpichnok, I I Grandberg *Zh. Prikl. Spektrosk.*, 1991, **54** 135
22. T Moriya *Bull. Chem. Soc. Jpn.*, 1988, **61** 1873
23. L I Loboda, I V Sokolova, E A Postol, et al. *Zh. Fiz. Khim.*, 1984, **58**(10) 2462 [English translation in *Russ. J. Phys. Chem.*, 1984(10)]
24. R T Kuznetsova, I V Sokolova, R M Fofonova, et al. *Zh. Fiz. Khim.*, 1989, **63**(3) 747 [English translation in *Russ. J. Phys. Chem.*, 1989(3)]
25. E M Goryaeva, A M Gorelik, V F Donyagina, et al. *Zh. Prikl. Spektrosk.*, 1990, **52** 306
26. J A Barltrop, J D Coyle *Excited States in Organic Chemistry* (Translated into Russian), Mir, Moscow, 1978, p. 115
27. G Jones (II), W Jackson, A Halpern *Chem. Phys. Lett.*, 1980, **72** 391
28. I V Sokolova, N Yu Vasil'eva, L I Loboda, et al. *Izv. Vyssh. Uchebn. Zaved. Fiz.*, 1986, 79
29. M S A Abdel-Mottaleb, M S Antomous, M M Abo-Aly, et al. *J. Photochem. Photobiol. A*, 1989, **59** 259
30. G Chu, F Yangbo *J. Chem. Soc., Faraday Trans. 1*, 1987, **83** 2533
31. A Nag, T Chakrabarty, K Bhattacharyya *J. Phys. Chem.*, 1990, **94** 4203
32. J A Van Gompel, G B Schuster *J. Phys. Chem.*, 1989, **92** 1292
33. R W Yip, Y X Wen *J. Photochem. Photobiol. A*, 1990, **54** 263
34. K N Knox, E J Land, T G Truscott *J. Photochem. Photobiol., B*, 1988, **1** 315
35. T A Shakhverdov, V N Kalinin, V L Ermolaev *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1990, **54** 460
36. R F Kubin, A N Fletcher *Chem. Phys. Lett.*, 1983, **99** 49
37. T Moriya *Bull. Chem. Soc. Jpn.*, 1984, **57** 1723
38. T Moriya *Bull. Chem. Soc. Jpn.*, 1986, **59** 961
39. T Moriya *Bull. Chem. Soc. Jpn.*, 1987, **60** 3855
40. T Moriya *Bull. Chem. Soc. Jpn.*, 1988, **61** 753
41. G Jones, S Griffin, C Choi, W Bergmark *J. Org. Chem.*, 1984, **49** 2705
42. T G Pavlopoulos *Spectrochim. Acta*, 1986, **42** 47
43. B R Henry, R V Hunt *J. Mol. Spectrosc.*, 1971, **39** 466
44. P Crozet *Chem. Phys. Lett.*, 1974, **25** 114
45. E J Land, T G Truscott *Photochem. Photobiol.*, 1979, **29** 861
46. W W Mantulin, P-S Song *J. Am. Chem. Soc.*, 1973, **95** 5122
47. N K Ray, V K Ahuja *Photochem. Photobiol.*, 1973, **17** 347
48. K I Priyadarsini, D B Naik, P N Moorthy *Chem. Phys. Lett.*, 1989, **157** 525
49. G Jones, W Bergmark *J. Photochem.*, 1984, **26** 179
50. T G Pavlopoulos, D J Golich *J. Appl. Phys.*, 1988, **64** 521
51. K I Priyadarsini, D B Naik, P N Moorthy *J. Photochem. Photobiol. A*, 1990, **54** 251
52. K I Piyadarsini, D B Naik, P N Moorthy *J. Photochem. Photobiol. A*, 1989, **46** 239
53. R V Bensasson, O Chalvet, E J Land, J C Ronfard-Haret *Photochem. Photobiol.*, 1984, **39** 287
54. R Costalat, J Blais, J-P Ballini, et al. *Photochem. Photobiol.*, 1990, **51** 255
55. E Quenten, P Adriaens *Photochem. Photobiol.*, 1986, **43** 485
56. N J De Mol, G M Beijersbergen van Henegouwen *Photochem. Photobiol.*, 1979, **30** 331
57. N Singh, J A Vadasz *Photochem. Photobiol.*, 1978, **28** 539
58. O V Zin'kovskaya, N A Kuznetsova, O L Kaliya *Zh. Prikl. Spektrosk.*, 1984, **41** 626
59. R J Trebra, T H Koch *J. Photochem.*, 1986, **35** 33
60. W Poppe, L J Grossweiner *Photochem. Photobiol.*, 1975, **22** 217
61. S Yu Egorov, A A Krasnovskii, Jr., V L Sukhorukov, A Ya Potapenko *Biofizika*, 1986, **31** 154
62. O V Zin'kovskaya, N A Kuznetsova, A V Reznichenko *Khim. Vys. Energ.*, 1987, **21** 352
63. K I Priyadarsini, D B Naik, P N Moorthy *Chem. Phys. Lett.*, 1988, **148** 572
64. T Moriya *Bull. Chem. Soc. Jpn.*, 1983, **56** 6
65. L M Rubeko, A I Akimov, L K Denisov, B M Uzhinov *Zh. Prikl. Spektrosk.*, 1981, **35** 436
66. L D Derkacheva, A I Krymova, V A Petukhov, N S Platonov *Opt. Spektrosk.*, 1982, **53** 73
67. O S Wolfbeis *Z. Phys. Chem. (Munich)*, 1981, **125** 15
68. H H Morrison, H Curtis, T McDowell *J. Am. Chem. Soc.*, 1966, **88** 5415
69. R Hoffman, P Wells, H Morrison *J. Org. Chem.*, 1971, **36** 102
70. K Muthuramu, V Ramamurthy *J. Org. Chem.*, 1982, **47** 3976
71. F Lewis, D Howard, J Oxman *J. Am. Chem. Soc.*, 1973, **105** 3344
72. K Muthuramu, V Ramamurthy *Indian J. Chem., Sect. B*, 1984, **23** 502
73. D V Rao, H Ulrich, F A Stuber, A A R Sayigh *Chem. Ber.*, 1973, **106** 388
74. N Ramnath, V Ramamurthy *J. Org. Chem.*, 1984, **49** 2807
75. H Umemoto, T Kitao *Kogyo Kagaku Zasshi*, 1970, **73** 2200
76. J Gervais, F C De Schryver *Photochem. Photobiol.*, 1975, **21** 71
77. A Moysan, A Cazaussus, F Gaboriau, et al. *Photochem. Photobiol.*, 1988, **47** 327
78. S C Shim, S S Lee, S J Choi *Photochem. Photobiol.*, 1990, **51** 1
79. J P Y Kao, S T Isaacs, J E Hearst *Photochem. Photobiol.*, 1990, **51** 273
80. J Meng, D Fu, X Yao, et al. *Tetrahedron*, 1989, **45** 6979
81. K Gnanaguru, N Ramasubbu, K Venkatesan, V Ramamurthy *J. Photochem.*, 1984, **27** 355
82. K Gnanaguru, N Ramasubbu, K Venkatesan, V Ramamurthy *J. Org. Chem.*, 1985, **50** 2337

83. L A Holt, I H Leaver, B Milligan *Textile Research J.*, 1976, **46** 539
84. J W Hanifin, E Cohen *Tetrahedron Lett.*, 1966, 1419
85. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1988, 1169
86. M A Kirpichenok, L M Mel'nikova, D S Yufit, et al. *Khim. Geterosikl. Soedin.*, 1988, 1176
87. M A Kirpichenok, D S Yufit, L M Mel'nikova, et al. *Khim. Geterosikl. Soedin.*, 1990, 1022
88. M A Kirpichenok, D S Yufit, L M Mel'nikova, et al. *Khim. Geterosikl. Soedin.*, 1990, 1319
89. R G Hunt, C J Potter, S T Reid, M L Roantree *Tetrahedron Lett.*, 1975, 2327
90. K-H Pfoertner *Helv. Chim. Acta*, 1976, **59** 834
91. Yu Yu Stoilov, S P Bazhulin *Kvantovaya Elektronika*, 1986, **13** 633
92. B D Ratiner, T Otsuki *Chem. Lett.*, 1989, 1035
93. J Cadet, P Vigny, W R Midden *J. Photochem. Photobiol. B*, 1990, **6** 197
94. S Caffieri, A W M Lefeber, F Dall'Acqua, G M J Beijersbergen van Henegouwen *J. Photochem. Photobiol., B*, 1990, **7** 347
95. S Caffieri, A Daga, D Vedaldi, F Dall'Acqua *J. Photochem. Photobiol., B*, 1988, **2** 515
96. F Dall'Acqua, P Martelli *J. Photochem. Photobiol., B*, 1991, **8** 235
97. G Rigatti *Photochem. Photobiol.*, 1967, **6** 711
98. L Musajo, F Bordin, R Bevilacqua *Photochem. Photobiol.*, 1967, **6** 927
99. J E Hearst *Chem. Res. Toxicol.*, 1989, **2** 69
100. R Bevilacqua, F Bordin *Photochem. Photobiol.*, 1973, **17** 191
101. G Jones (II), W R Bergmark, W R Jackson *Optics Commun.*, 1984, **50** 320
102. T P Zhestkova, G G Ryabchikova, A K Pikaev *Zh. Prikl. Spektrosk.*, 1980, **33** 934
103. S S Chibber, R P Sharma *Indian J. Chem., Sect., B*, 1979, **18** 538
104. O A Ponomarev, O E Bondarenko, V G Mitina, L A Sleta *Khim. Fiz.*, 1990, **9** 477
105. C D Gutsche, B A M Oude-Alink *J. Am. Chem. Soc.*, 1968, **90** 5855
106. S C Chim, S J Choi *Photochem. Photobiol.*, 1990, **52** 669
107. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1989, 460
108. M A Kirpichenok, L M Mel'nikova, L K Denisov, I I Grandberg *Khim. Geterosikl. Soedin.*, 1990, 1028
109. N A Gordeeva, M A Kirpichenok, A I Chernyshev, et al. *Khim. Geterosikl. Soedin.*, 1990, 1172
110. N A Gordeeva, M A Kirpichenok, V S Yufit, et al. *Khim. Geterosikl. Soedin.*, 1990, 1033
111. N S Patalakha, M A Kirpichenok, N A Gordeeva, I I Grandberg *Izv. Timiryazev Sel'skokhoz. Akad.*, 1989, 157
112. J T Kunjappu, K N Rao *J. Photochem.*, 1987, **39** 135
113. J T Kunjappu *J. Photochem. Photobiol., A*, 1991, **56** 365
114. I Petkov, A Bojilova, P Markov *Monatsh. Chem.*, 1990, **121** 85
115. B H Winters, H I Mandelberg, W B Mohr *Appl. Phys. Lett.*, 1974, **25** 723
116. O V Zin'kovskaya, N A Kuznetsova, O L Kaliya, E A Luk'yanets *The Chemical Nature of the Dark Relaxation Processes in Lasting Media Based on Coumarin 47*, Minsk, 1986, 13 pp.—Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 29.1.86, No. 293-86
117. E A Kalmykova, N A Kuznetsova, O L Kaliya *Zh. Obshch. Khim.*, 1990, **60** 946
118. K I Priyadarsini, J T Kunjappu, P N Moorthy *Indian J. Chem., Sect. A*, 1987, **26** 899
119. E I Akimova, M I Snegov *Opt. Spektrosk.*, 1987, **63** 71
120. L Z Vinogradov, A A Krasheninnikov, V P Klindukhov, et al. *Zh. Prikl. Spektrosk.*, 1989, **50** 401
121. US P. 4479223, 1984
122. US P. 4562580, 1985
123. US P. 4051062, 1977
124. US P. 3891563, 1975
125. US P. 4428859, 1984
126. D Dopp, J Heufer *J. Photochem.*, 1986, **32** 243
127. R J Trebra, T H Koch *Appl. Phys. Lett.*, 1983, **42** 129
128. E A Kalmykova, N A Kuznetsova, O L Kaliya, M A Tavrizova *Zh. Obshch. Khim.*, 1991, **61** 1003
129. R J Trebra, T H Koch *J. Photochem. Photobiol., A*, 1987, **41** 111
130. M A Kirpichenok, L M Mel'nikova, L K Denisov, et al. *Khim. Geterotsikl. Soedin.*, 1989, 30

Received 25th June 1991