5. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Interpretation of Mass Spectra in Organic Compounds, Holden-Day, San Francisco (1964).
6. Organic Chemistry [Russian translation], Vol. 2, Mir, Moscow (1979), p. 198.

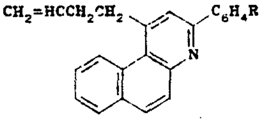
LUMINESCENCE SPECTRAL CHARACTERISTICS OF 1-(3-BUTENYL)-3-ARYLBENZO[f]QUINOLINES

V. A. Serzhanina, R. D. Sauts,
L. F. Gladchenko, and N. S. Kozlov

UDC 547.832.5:543.426:541.651

The effect of the nature of the substituents and the solvent on the absorption and fluorescence spectra and on the fluorescence quantum yield was studied in the series of 1-(3-butenyl)-3-arylbenzo[f]quinolines.

Earlier we investigated the spectral characteristics of a whole series of derivatives of benzo[f]quinoline and showed that many of them luminesce strongly in solutions [1, 2]. While continuing a study into the effect of structural factors on the luminescence spectral characteristics in the series of benzo[f]quinoline derivatives, we investigated the absorption and fluorescence spectra and the fluorescence quantum yields of 1-(3-butenyl)-3-arylbenzo[f]quinolines (I-V):



I-V

I R=H; II R=*p*-OCH$_3$; III R=*p*-F; IV R=*p*-Br; V R=*o*-OH

The bases (I-V) were obtained by the condensation of arylidene-2-naphthylamines with allylacetone in the presence of a protic catalyst [3]. The electronic absorption spectra of 1-(3-butenyl)-3-arylbenzo[f]quinolines have the form typical of the spectra of benzo[f]quinoline derivatives [1] and are characterized by three absorption bands: β (279-285 nm), p (294 nm), and α (345-370 nm) bands. The long-wave band has vibrational structure. The introduction of substituents R (Table 1) increases the intensity of all the absorption bands without having an appreciable effect on their positions. The exception is the hydroxyl group, which is at the ortho position of the phenyl ring and gives rise to a bathochromic shift of the α band with a simultaneous increase in its intensity.

The 1-(3-butenyl)-3-arylbenzo[f]quinolines luminesce strongly in solutions. The fluorescence spectra of the compounds show clearly defined vibrational structure (Table 1). They have mirror symmetry in the long-wave absorption band and lie in the UV region (λ_{max} ~370-400 nm). The Stokes shift of the fluorescence band amounts on the average to 30 nm. The substituents at the para position of the phenyl ring lead to a bathochromic shift of the fluorescence band in all the investigated solvents. The quantum yields of fluorescence for compounds (I-V) vary within wide limits (between 15 and 68%), and this is due to the different nature of the solvent. Thus, by changing the probability of singlet—triplet conversion, halogens reduce the quantum yield of fluorescence, and the quenching effect becomes stronger with increase in the atomic number of the halogen [4]. For instance, the quantum yield of luminescence for compound (IV) (R = Br) is half the quantum yield for fluorobenzo[f]quinoline (III). Such a decrease in the intensity can be explained by the increase in the weight of the radical and the associated loss of energy on the intramolecular vibrations. The fluo-

---

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1092-1094, August, 1987. Original article submitted April 25, 1986.

0009-3122/87/2308-0874$12.50

TABLE 1. Luminescence Spectral Characteristics of 1-(3-Butenyl)-3-arylbenzo[f]quinolines (I-V)

Compound	Absorption, λ_{max}, nm (lg ε) (ethanol)	Luminescence					
		ethanol		benzene		DMSO	
		λ_{max}, nm	η, %	λ_{max}, nm	η, %	λ_{max}, nm	η, %
I	280 (4,59); 294 (4,37); 346 (3,67); 361 (3,67)	372; 388	51	369; 386	41	374; 391	51
II	285 (4,64); 294 (4,58); 348 (3,95); 365 (3,98)	379; 393	68	373; 390	49	380; 396	57
III	279 (4,67); 294 (4,47); 345 (3,85), 362 (3,88)	373; 387	45	369; 385	39	375; 391	37
IV	282 (4,74); 294 (4,58); 346 (3,90); 363 (3,93)	376; 390	21	372; 388	15	378; 395	19
V	282 (4,63); 294 (4,50); 353 (4,16); 370 (4,22)	Does not fluoresce					

rescence disappears when an ortho-hydroxy group is introduced into the phenyl ring. Here the conjugation between the benzoquinoline ring and the substituent is evidently destroyed. Luminescence quenching by a substituent at the ortho position, which is contrary to Parker's rule about the activating effect of ortho and para substituents [5], has been described in the literature [6, 7]. In the case of compound (V), additional fluorescence quenching is observed in DMSO on account of the formation of a complex of the $-O-H \ldots O=S(CH_3)_2$ type.

In its effect on the fluorescence spectrum and the magnitude of its quantum yield the butenyl substituent is analogous with alkyl substituents, as seen from comparison of the spectral characteristics of 1-(3-butenyl)-3-(p-methoxyphenyl)benzo[f]quinoline and the model compounds 1-methyl-3-(p-methoxyphenyl)benzo[f]quinoline [$\lambda_{max\,fl}$ (ethanol), 374, 392 nm; η 66%] and 1-ethyl-3-(p-methoxyphenyl)benzo[f]quinoline ($\lambda_{max\,fl}$ (ethanol), 377, 393 nm, η 66%] [1]. Like the introduction of alkyl substituents, the introduction of the butenyl group into the model compound 3-(p-methoxyphenyl)benzo[f]quinoline [$\lambda_{max\,fl}$ (ethanol): 376, 393, 418 nm; η 71%] leads to the disappearance of the long-wave band in the region of 418 nm and to an insignificant decrease in the quantum yield of fluorescence.

Analysis of the data given in Table 1 shows that changes in the polarity and nature of the solvent does not have an appreciable effect on the spectral position of the fluorescence bands. This indicates that in the excited state of the benzoquinoline system the symmetry of the electron cloud and, accordingly, the dipole moment of the molecule do not change. The presence of fairly strong luminescence in a proton-donating solvent (ethanol) can be explained, as in the case of quinoline [8], by the formation of a hydrogen bond between the nitrogen atom and the solvent. This reduces the effect of the nonbonded electrons of the nitrogen atoms on the π-electron cloud of the whole benzoquinoline molecule and thereby reduces the spin—orbital interaction and, consequently, the probability of interconversion. Solutions in proton-accepting solvents (DMSO, benzene) have lower quantum yields of luminescence, and in the more viscous DMSO, which hinders rotation of the terminal substituents, the quantum yields of fluorescence are as a rule higher than those in benzene solutions [9], where vibrational spin—orbital interaction between the lowest $s_{\pi\pi^*}$ and the highest $s_{n\pi^*}$ states with subsequent conversion to the triplet level is more likely [4].

EXPERIMENTAL

The synthesis of compounds (I-V) was described in [3]. The absorption spectra of the solutions of benzo[f]quinolines (I-V) were recorded on a Specord UV-vis spectrophotometer. The fluorescence spectra were obtained on a Fica-55 absolute spectrofluorimeter. Excitation of the fluorescence was realized at a wavelength of 350 nm lying in the region of the long-wave absorption band. The absolute quantum yields of fluorescence were calculated by a relative method. The standard was a solution of 3-amino-N-methylphthalimide in absolute ethanol. Ethanol, DMSO, and benzene purified by standard procedures were used as solvents.

LITERATURE CITED

1. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. V. Vorob'eva, O. D. Zhikhareva, G. S. Shmanai, and R. D. Sauts, Khim. Geterotsikl. Soedin., 1977, No. 9, 1237.

2. N. S. Kozlov, L. F. Gladchenko, R. D. Sauts, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., 1978, No. 12, 1646.
3. N. S. Kozlov, R. D. Sauts, and V. A. Serzhanina, Khim. Geterotsikl. Soedin., 1986, No. 11, 1519.
4. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Moscow (1984), p. 334.
5. S. Parker, Photoluminescence of Solutions [Russian translation], Mir, Moscow (1972), p. 510.
6. B. M. Krasovitskii and B. M. Bolotin, Khim. Geterotsikl. Soedin., 1974, No. 11, 1443.
7. H. S. Kozlov, V. A. Serzhanina, G. V. Vorob'eva, R. D. Sauts, and L. F. Gladchenko, Dokl. Akad. Nauk BSSR, 22, 910 (1978).
8. V. L. Ermolaev and I. P. Kotlyar, Opt. Spektr., 9, 353 (1960).
9. N. S. Kozlov, L. F. Gladchenko, F. A. Serzhanina, G. S. Shmanai, I. P. Stremok, G. P. Korotyshova, and R. D. Sauts, Khim. Geterotsikl. Soedin., 1978, No. 4, 511.

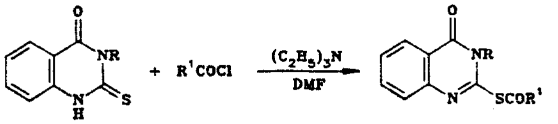
ACYLATION OF 2-THIOXOQUINAZOL-4-ONES:
FORMATION OF 2-ACYLTHIOQUINAZOL-4-ONES

L. M. Yun, S. Yangibaev, V. Ya. Alekseeva,
K. A. V'yunov, and Kh. M. Shakhidoyatov

UDC 547.856.1:544.951

The acylation of 2-thioxoquinazol-4-ones by various acylating agents was studied. The main products are 2-benzoylthioquinazol-4-ones. Minor amounts of the $N_{(3)}$-acylation products are formed.

The aim of the present work was to investigate the acylation of 2-thioxoquinazol-4-ones (I, II) and to seek conditions for selective reaction. The reactions of (I, II) with benzoyl, para-nitrobenzoyl, and ortho-methoxybenzoyl chlorides were realized in an organic solvent and were monitored by TLC. Triethylamine was used as hydrogen chloride acceptor. The choice of solvent is restricted. The triethylammonium salt (I, II) is poorly soluble in low-polarity solvents, and acylation under heterogeneous conditions leads to the formation of a mixture of products from acylation at the $N_{(3)}$ nitrogen atom and at the sulfur atom. The acylation of (I, II) takes place most selectively in DMFA, which dissolves the salts (I, II) well.



I, II

IIIa-d, IVa-c

I, III R=H; II, IV R=CH_3; III, IVa $R^1=C_6H_5$, b $R^1=p\text{-}NO_2C_6H_4$, c $R^1=m\text{-}NO_2C_6H_4$, $R^1=o\text{-}CH_3OC_6H_4$

In addition to the 2-benzoylthioquinazol-4-ones (IIIa-d, IVa-c), according to TLC, the reaction mixture contains the products from acylation of (I) at the $N_{(3)}$ atom, but their content does not exceed 3-5%. These substances (they did not separate from the solution) are separated from the isomeric compounds (IIIa-d, IVa-c) during recrystallization. The $N_{(3)}$- and S-acylated thioxoquinazolones were identified by comparison of their mobilities during TLC. Compounds (II-IV) have similar R_f values (Table 1), which are always 0.20 lower than for the corresponding $N_{(3)}$ isomers. During the acylation of (Ia) with benzoyl chloride, in addition to the isolated isomer (IIIc), the product from acylation at the $N_{(3)}$ atom, identified

---

Institute of Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Lensovet Technological Institute, Leningrad. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1095-1097, August, 1987. Original article submitted March 6, 1986; revision submitted January 12, 1987.