LITERATURE CITED

1. A. P. Kriven'ko, T. G. Nikolaeva, A. A. Espenbetov, N. T. Komyagin, N. N. Sorokin, Yu. T. Struchkov, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 1, 71 (1985).
2. V. G. Kharchenko, A. P. Kriven'ko, O. V. Fedotova, and T. G. Nikolaeva, Khim. Geterotsikl. Soedin., No. 7, 944 (1982).
3. T. G. Nikolaeva, P. V. Reshetov, A. P. Kriven'ko, and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 10, 1370 (1983).
4. N. Barbulescu, F. Potmischil, and D. Römer, Rev. Rom. Chim., 15, 1601 (1970).
5. V. I. Vysotskii, Khim. Geterotsikl. Soedin., No. 9, 1236 (1970).
6. E. L. Eliel and F. W. Vierhapper, J. Org. Chem., 41, 199 (1976).
7. F. W. Vierhapper and E. L. Eliel, J. Org. Chem., 42, 51 (1977).
8. P. Vanhee, F. D. Pessemiev, M. Anteunis, and D. Tavernier, Rec. Trav. Chim., 98, 294 (1979).
9. C. Altona and M. Sundaralingam, Tetrahedron, 26, 925 (1970).
10. K. A. Nirmala and D. S. S. Gowda, Acta Cryst., B28, 839 (1982).
11. M. Cygler, Acta Cryst., B37, 1771 (1981).
12. L. E. Sutton (editor), Tables of Interatomic Distances and Configurations in Molecules and Ions, London (1968).
13. P. G. Gerr, A. I. Yanovskii, and Yu. T. Struchkov, Kristallografiya, No. 5, 1029 (1983).

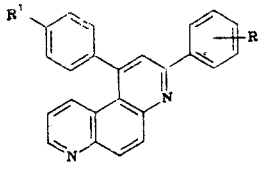
SPECTRAL-LUMINESCENCE CHARACTERISTICS OF 1,3-DIARYL-4,7-PHENANTHROLINES

N. S. Kozlov, K. N. Gusak,
V. A. Serzhanina, L. F. Gladchenko,
and N. A. Krot

UDC 547.836.543.426

The effect of the nature of the substituents and the solvent on the absorption and fluorescence spectra and the fluorescence quantum yields of 1,3-diaryl-4,7-phenanthrolines was studied. Electron-donor groups in the para position of the phenyl ring cause a bathochromic shift of the absorption and fluorescence spectra and an increase in the fluorescence quantum yields. A change in the polarity of the solvent leads to a significant shift of the fluorescence spectra of hydroxy and dialkylamino derivatives of 4,7-phenanthroline.

The spectral-luminescence properties of 4,7-phenanthroline derivatives have not been adequately studied. The fluorescence spectra of unsubstituted phenanthroline in the frozen state were described in [1-3], and the luminescence intensities of toluene solutions of unsubstituted 4,7-phenanthroline and three monoaryl-4,7-phenanthrolines were presented in only one communication [4]. Wiley and co-workers [4] state the fact of the decrease in the luminescence activity of these compounds as compared with a standard (p-terphenyl) without explaining the reasons for this phenomenon. No information regarding the spectral-luminescence properties of 1,3-disubstituted 4,7-phenanthrolines is available in the literature. In this connection the aim of the present research was to study the absorption and fluorescence spectra and the fluorescence quantum yields of 1,3-diaryl-4,7-phenanthrolines I-XX. The bases of the 4,7-phenanthroline series were obtained by the reaction of 6-(R-benzylideneamino)quinolines with acetophenone or its p-substituted derivatives (with acetone in the case of XX) in the presence of a proton catalyst, as previously described in [5].



I-XX

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk 220603. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1651-1654, December, 1987. Original article submitted July 25, 1986; revision submitted February 25, 1987.

0009-3122/87/2312-1329$12.50

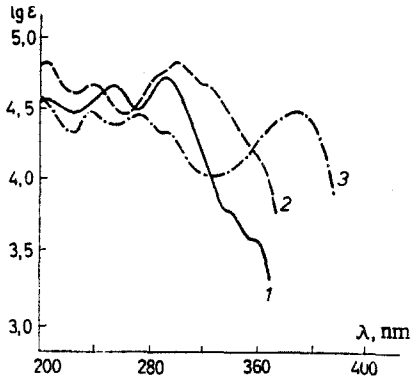


Fig. 1. Absorption spectra of solutions in alcohol: 1) 1,3-diphenyl-4,7-phenanthroline (I); 2) 1-phenyl-3-(p-nitrophenyl)-4,7-phenanthroline (XV); 3) 1-phenyl-3-(p-diethylaminophenyl)-4,7-phenanthroline (XII).

The absorption spectra of the investigated compounds lie in the UV region and consist of three bands (in the Klahr classification): β (238-272 nm), p (283-318 nm), and α (324-340; 349-388 nm) bands. Their general form is characteristic for compounds with an angular structure (Fig. 1) [6]. As compared with the spectrum of phenanthrene [7], in the spectra of 4,7-phenanthrolines one observes smoothing out of the fine structure of the α band and a decrease in its intensity as a consequence of the accumulation of nitrogen atoms in the molecule. Substituents in the phenyl rings affect the position and intensity of the absorption bands (Table 1). Halogens (–I, +M) and a nitro group in the meta position, which is not in conjugation with the heteroring, have the smallest effect. Electron-donor alkylamino groups (XI-XIII) give rise to a significant bathochromic shift of the α band and a pronounced increase in its intensity; this is due to the possibility of absorption with charge transfer with participation of the electrons of these groups [8]. The presence of an electron-acceptor nitro group in the para position of the 3-phenyl ring gives rise to a significant increase in the intensities of all of the bands of the spectrum without changing their positions. The intensities of the absorption bands decrease when nitro groups (XVI) or a nitro group and a chlorine atom (XVII) are present in each of the phenyl rings, evidently because of the unconcerted character of the effect of the substituents on the conjugated heteroaromatic system.

The fluorescence spectra of most of the investigated compounds are made up of one rather broad structureless band. The Stokesian shift for I-IX is 21-94 nm. It is appreciably higher (144-180 nm) for 4,7-phenanthrolines with dialkylamino groups (XI-XIII). This fact constitutes evidence for intensification of the interaction of the 4,7-phenanthroline molecules with the medium in the excited state [9]. For 1,3-diphenyl-4,7-phenanthroline (I) and the halo derivatives (II-V) the position of the fluorescence maximum differs only slightly in all of the investigated solvents (Table 1). For IX (R = 4-OCH_3) λ_{max}^{fl} in benzene differs substantially from the λ_{max}^{fl} values of I-V and coincides with λ_{max}^{fl} for VI (R = 4-OH). Intensification of the electron-donor character of the 3-aryl substituent (XI-XIII) leads to a pronounced bathochromic shift of the fluorescence spectra in all of the investigated solvents; the transition from polar solvents (ethanol, DMSO) to a nonpolar solvent (benzene) gives rise to a significant short-wave shift of the fluorescence spectra ($\Delta\lambda$ = 103-115 nm) for the indicated compounds. This strong effect of the solvent on the flourescence spectrum can be caused only by the formation of a complex with the solvent in the excited state (an exciplex) or by the effects of an orientational interaction that are associated with changes in the dipole moment upon excitation of the molecule. We assume that the first assumption is most likely, since the greatest effect of a shift is observed in the presence of substituents that are capable of forming hydrogen bonds with the solvent of the $(Alk)_2N...H{-}OC_2H_5$ and similar types.

The nature of the substituents affects the energy characteristics of the investigated compounds. The fluorescence quantum yields of the compounds increase when electron-donor substituents are introduced into the para position of the phenyl ring (VI, IX,and XI-XIII) and decrease when a nitro group and a bromine atom are introduced. Fluorine and chlorine substituents in the para position do not have an appreciable effect on the quantum yields with respect to 1,3-diphenyl-4,7-phenanthroline. The presence in the phenyl rings of ortho substituents that decrease the conjugation in the molecule leads to a decrease in the fluorescence quantum yields. Thus VIII, which contains o-hydroxy and m-methoxy groups, does not luminesce at all, while the presence of these groups in the para position leads to an increase in the fluorescence quantum yields (VI and IX). As one should have expected, when a phenyl radical in the 1 position is replaced by a methyl group (XX), one observes a decrease

TABLE 1. Spectral-Luminescence Characteristics of 1,3-Diaryl-4,7-phenanthrolines

Compound*	R	Absorption spectra, λ_{max}, nm (log ε)	Fluorescence, λ_{max}, nm (η, %)		
			benzene	ethanol	DMSO
I	H	225 (4,62); 255 (4,70); 291 (4,78); 337 (3,79); 354 (3,40)	385 (15)	385 (18)	400 (18)
II	4-F	225 (4,76); 255 (4,49); 293 (4,90); 340 (3,92); 357 (3,62)	385 (16)	385 (18)	387 (23)
III	2-F	223 (4,44); 250 (4,55); 289 (4,63); 336 (3,62); 353 (3,15)	378; 388 (12)	380 (9)	385 (8)
IV	4-Cl	227 (4,22); 258 (4,35); 294 (4,53); 312 (4,28); 354 (3,12)	385 (20)	385 (21)	386 (18)
V	4-Br	227 (4,22); 259 (4,47); 294 (4,65); 337 (3,76); 349 (3,66)	386 (9)	386 (11)	400 (11)
VI	4-OH	231 (4,42); 238 (4,38); 318 (4,32); 360 (3,84)	398 (21)	435 (5)	458 (6)
VII	2-OH	228 (4,50); 260 (4,53); 292 (4,57); 337 (4,24); 361 (4,12)	390 (0,02)	390 (0,01)	425 (2)
VIII	2-OH—3-OCH_3	230 (4,45); 264 (4,28); 299 (4,48); 353 (3,89)	Does not fluoresce		
IX	4-OCH_3	231 (4,52); 268 (4,39); 283 (4,48); 324 (4,41); 362 (3,76)	398 (37)	406 (45)	408 (34)
X	2,4-$(OCH_3)_2$	230 (4,48); 287 (4,34); 312 (4,27); 357 (3,91)	Does not fluoresce		
XI	4-$N(CH_3)_2$	237 (4,47); 266 (4,50); 290 (4,31); 375 (4,00)	460 (45)	555 (9)	575 (24)
XII	4-$N(C_2H_5)_2$	236 (4,52); 272 (4,49); 294 (4,34); 388 (4,50)	462 (52)	550 (12)	565 (41)
XIII	4-$N(C_2H_4Cl)_2$	237 (4,53); 267 (4,46); 294 (4,34); 361 (4,48)	440 (53)	505 (37)	552 (60)
XIV	3-NO_2	250 (4,37); 288 (4,43); 337 (3,97); 357 (3,70)	Does not fluoresce		
XV	4-NO_2	240 (4,71); 299 (4,86); 358 (4,18)	373; 389; 410 (5)	Does not fluoresce	
XVI	4-NO_2	246 (3,72); 297 (4,16)	374; 390; 410 (5)	Does not fluoresce	
XVII	4-Cl	246 (4,01); 272 (4,34); 329 (4,12)	Does not fluoresce		
XVIII	4-Cl	246 (4,63); 259 (4,64); 296 (4,78); 318 (4,48); 338 (3,90); 355 (3,60)	380 (12)	382 (14)	388 (11)
XIX	4-Br	227 (4,68); 261 (4,67); 296 (4,84); 339 (3,90); 360 (3,60)	380 (7)	382 (6)	388 (7)
XX**	4-Br	234 (4,08); 256 (4,15); 294 (4,34); 312 (4,23);	365; 384 (3)	364; 380 (6)	384 (2)

*I-XV R^1 = H, XVI, XVII R^1 = p-NO_2, XVIII, XIX R^1 = p-Cl.
**A CH_3 group in place of $R^1C_6H_4$ in the 1 position.

in the fluorescence quantum yield; this is caused by a decrease in the conjugation chain in the molecule of the compound. We also observed a similar phenomenon in series of benzo[f]-quinolines [10]. In comparing the fluorescence quantum yields of 1,3-diaryl-4,7-phenanthrolines with the quantum yields of the mononitrogen analogs — 1,3-diarylbenzo[f]quinolines [11] — one should note the decrease in luminescence when a second nitrogen atom is introduced into the heterocyclic system [12]. Nevertheless, in the series of synthesized 4,7-phenanthrolines there are compounds that can be classified as compounds that luminesce well. The quantum yields of such compounds (45-60%) are commensurable with the quantum yield (60%) of the standard — 3-amino-N-methylphthalimide.

EXPERIMENTAL

The UV spectra of 10^{-4} M solutions of the compounds in alcohol were recorded with a Specord UV-VIS spectrophotometer; the layer thickness was 0.199 cm. The fluorescence spectra and the absolute fluorescence quantum yields were measured with a Fica-55 absolute spectrofluorimeter. Excitation of the luminescence was realized at the long-wave absorption band. The solvents were anhydrous ethanol, DMSO, and benzene. A solution of 3-amino-N-methylphthalimide in ethanol was used as the standard.

1,3-Diaryl-4,7-phenanthrolines I-XVII. These compounds were obtained by the method in [5].

1,3-Disubstituted 4,7-Phenanthrolines XVIII-XX. A mixture of 5 mmoles of 6-(R-benzylideneamino)quinoline, 5 mmole of p-chloroacetophenone (or 50 mmole of acetone for XX), 0.5

ml (5 mmole) of concentrated HCl, and 30 ml of butanol (or ethanol for XX) was refluxed for 2 h, after which the resulting precipitate (after evaporation of the solvent in the case of XX) was triturated in 30 ml of 25% ammonium hydroxide, washed successively with water and ethanol, and crystallized from ethanol–benzene (4:1).

Compound XVIII. This compound, with mp 234-235°C, was obtained in 28% yield. Found: C 71.3; H 4.0; Cl 17.4; N 6.6%. $C_{24}H_{24}Cl_{12}N_2$. Calculated: C 71.8; H 3.5; Cl 17.7; N 7.0%.

Compound XIX. This compound, with mp 237-238°C, was obtained in 21% yield. Found: C 64.6; H 3.0; Br + Cl 25.8; N 6.6%. $C_{24}H_{14}BrClN_2$. Calculated: C 64.6; H 3.1; Br + Cl 25.9; N 6.3%.

Compound XX. This compound, with mp 183-184°C, was obtained in 12% yield. Found: C 65.2; H 3.7; Br 22.6; N 7.9%. $C_{19}H_{13}BrN_2$. Calculated: C 65.3; H 3.8; Br 22.9; N 8.0%.

LITERATURE CITED

1. H.-H. Perkampus, A. Knop, and J. V. Knop., Z. Naturforsch., 23a, 840 (1968).
2. R. Schaaf and H.-H. Perkampus, Tetrahedron, 37, 341 (1981).
3. V. D. Shatrov, V. S. Kuznetsov, O. M. Andreev, et al., Zh. Prikl. Spektrosk., 29, 51 (1978).
4. R. H. Wiley, C. H. Garboe, and F. N. Hayes, J. Org. Chem., 23, 268 (1958).
5. N. S. Kozlov, K. N. Gusak, V. A. Serzhanina, and N. A. Krot, Khim. Geterotsikl. Soedin., No. 10, 1398 (1985).
6. R. N. Nurmukhametov, Absorption and Luminescence of Aromatic Compounds [in Russian], Khimiya, Moscow (1971), p. 216.
7. C. Brown and B. J. Sikkel, J. Chem. Soc., Perkin Trans. 1, No. 12, 3007 (1982).
8. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. S. Shmanai, I. P. Stremok, G. P. Korotyshova, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 4, 511 (1978).
9. 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., No. 9, 1237 (1977).
10. N. S. Kozlov, O. D. Zhikhareva, and L. F. Gladchenko, Vestsi AN BSSR, Ser. Khim., Navuk, No. 5, 72 (1979).
11. N. S. Kozlov, L. V. Korobchenko, G. S. Shmanai, and M. P. Tsvirko, Khim. Geterotsikl. Soedin., No. 1, 116 (1976).
12. B. M. Krasovitskii and B. M. Bolotin, Organic Luminophores [in Russian], Khimiya, Moscow (1984), p. 334.

SELECTIVE O- AND N_3-ALKYLATION OF 2-ALKYLTHIO-4-HYDROXYPYRIMIDINES BY HALOACETATES

P. I. Vainilavichyus and V. Yu. Syadyaryavichyute

UDC 547.854.07:543.422:541.124

The effect of a number of factors on the regioselectivity of alkylation of 2-alkylthio-4-hydroxypyrimidines by methyl bromoacetate has been studied. In non-polar and low-polarity solvents N_3-alkylation predominated whereas O-alkylation occurred in aprotic dipolar solvents. Preparative methods for the synthesis of O- and N_3-carbomethoxymethyl 2-alkylthio-4-hydroxypyrimidines have been developed.

We have previously shown [1] that the sodium salts of 2-methylthio-4-hydroxypyrimidines (Ia, b) form a mixture of O- and N_3-alkylation products (IIa, b; IIIa, b) in methanol.

With a view to developing a preparative method for O- and N_3-carbalkoxymethyl 2-alkylthio-4-hydroxypyrimidines (II, III) we have studied the effects of a number of factors on the regioselectivity of alkylation of 4-hydroxypyrimidines I using methyl chloro- and bromoacetates

V. Kapsukas State University, Vilnyus, 232734.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1655-1658, December, 1987. Original article submitted July 7, 1986.

0009-3122/87/2312-1332$12.50