CONDENSATION OF ETHYL ESTERS OF 6-PHENYL- AND 6-(p-METHOXYPHENYL)-2,4-DIOXOCYCLOHEXANE-1-CARBOXYLIC ACIDS WITH N-BENZYLIDENE-2-NAPHTHYLAMINES

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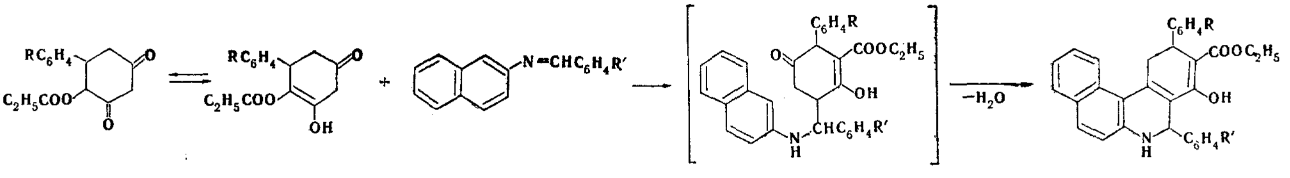
A number of ethyl esters of 2,5-diaryl-4-hydroxy-1,2,5,6-tetrahydrobenzo[a]phenanthridine-3-carboxylic acid were obtained by condensation of ethyl esters of 6-phenyl- and 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylic acids with N-benzylidene-2-naphthylamines, and their spectral characteristics were studied. It was established that the luminescence properties of these compounds and the character of their reaction with the solvent are determined by the proton-acceptor properties of the carbonyl and hydroxy groups.

Continuing our research on the effect of structural factors on the spectral-luminescence properties of dihydro derivatives of benzo[f]quinoline [1, 2] we synthesized ethyl esters of 2,5-diaryl-4-hydroxy-1,2,5,6-tetrahydrobenzo[a]phenanthridine-3-carboxylic acid (I-XV), which can be regarded as analogs of dihydro-substituted benzo[f]quinolines. Compounds I-XV were obtained by condensation of ethyl esters of 6-phenyl- or 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylic acids with N-benzylidene-2-naphthylamines.

It follows from the literature data [3, 4], as well as data from the IR and PMR spectra, that ethyl esters of 6-phenyl- and 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylic acids, which have a β-diketone structure, can undergo enolization. The IR spectrum of ethyl 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylate in KBr contain the following characteristic bands of stretching vibrations: 1610 (CO, C=C); 1730, 1250 ($COOC_2H_5$); 2500 ± 10, 3400 cm^{-1} (OH). Absorption at 3630 cm^{-1} appears in the spectrum of a solution in CCl_4. In all likelihood, the reaction of esters of cyclic β-keto enols with N-benzylidene-2-naphthylamines proceeds with the formation of the corresponding β-amino keto esters [5], which undergo cyclization to substituted tetrahydrophenanthridines with the splitting out of water.



I-XV

I-VII R=H; VIII-XV R=p-CH_3O; R′ see Table 1

The structures of I-XV (Table 1) were confirmed by the set of spectral data. The IR spectra in KBr contain absorption bands at 3300 (N−H), 1730 and 1250 ($COOC_2H_5$), and 3200 cm^{-1} (characteristic for the enol form [4]). The PMR spectrum of XII in $(CD_3)_2SO$ contains signals of an ethyl group (0.96, t; 3.90, q) and a CH_3O group (3.76, s) and a multiplet of aromatic protons (6.8-8.0 ppm). Maximally intense M^+ and $(M-1)^+$ ion peaks are observed in the mass spectra of I-XV. The agreement between the m/e values of the molecular-ion peaks and the molecular masses confirms the proposed structures for the synthesized compounds. The presence of an $(M-R'Ar)^+$ ion peak with m/e 396 in the mass spectra is characteristic for I-VIII. The fragmentation of the substituted tetrahydrophenanthridines under the influence of electron impact occurs via a general scheme that is similar to the scheme of the fragmentation of two-ring systems of the 1,2,3,4-tetrahydroquinoline, dipyridyl, quinoline, and 3-arylazoquinoline type [6-8].

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TABLE 1. Ethyl 2,5-Diaryl-4-hydroxy-1,2,5,6-tetrahydrobenzo[a]phenanthridine-3-carboxylates (I-XV)

Compound	R′	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
I	H	247—248	81,2	5,4	2,5	$C_{32}H_{27}NO_3$	81,6	5,7	3,0	74
II	4-NO_2	250—251	74,0	5,0	5,5	$C_{32}H_{26}N_2O_5$	74,1	5,0	5,3	61
III	3-NO_2	245—246	74,0	5,1	5,4	$C_{32}H_{26}N_2O_5$	74,1	5,0	5,3	58
IV	4-CH_3O	202—203	78,7	5,8	2,8	$C_{33}H_{29}NO_4$	78,9	5,6	2,8	63
V	2-HO	251	78,3	5,2	2,7	$C_{32}H_{27}NO_5$	78,5	5,3	2.9	56
VI	4-Cl	254—255	75,6	5,0	2,7	$C_{32}H_{26}ClNO_3$	75,7	5,1	2,8	64
VII	4-Br	249—250	69,4	4,6	2,6	$C_{32}H_{26}BrNO_3$	69,6	4,7	2,5	63
VIII	H	289—290	78,7	5,6	2,5	$C_{33}H_{29}NO_4$	78,9	5,8	2,6	71
IX	4-NO_2	247—250	72,4	4,8	5,0	$C_{33}H_{28}N_2O_6$	72,4	4,9	5,1	59
X	3-NO_2	237	72,3	4,8	5,1	$C_{33}H_{28}N_2O_6$	72,4	4,9	5,1	57
XI	2-HO	167	76,4	5,4	2,9	$C_{33}H_{29}NO_5$	76,5	5,4	2,6	49
XII	4-Cl	211—212	73,8	5,0	2,5	$C_{33}H_{28}ClNO_4$	73,9	5,0	2,6	55
XIII	4-Br	212—213	68,0	4,6	2,3	$C_{33}H_{28}BrNO_4$	68,2	4,7	2,4	53
XIV	4-$(CH_3)_2N$	264—265	77,0	6,2	5,0	$C_{35}H_{34}N_2O_4$	77,1	6,2	5,1	51
XV	4-F	240—241	76,2	5,4	2,7	$C_{33}H_{28}FNO_4$*	76,2	5,3	2,7	58

*Found: F 3.6%. Calculated: F 3.6%.

The chemical structures of the synthesized compounds are similar to the chemical structures of the dihydro-substituted benzo[f]-quinolines, which were investigated in [1]. The spectral characteristics of the latter are due to hydrogenation of the C = N bond and the nature of the substituting groups in the molecule. The luminescence properties of dihydro-substituted benzo[f]quinolines that contain an ester groups are determined by the proton-acceptor properties of the carbonyl group of this grouping [1]. The indicated effects should also be displayed in the case of I-XV.

The three intense bands in the absorption spectra of the substituted tetrahydrophenanthridines (Table 2) correspond to transitions of the $\pi-\pi^*$ type (220-235, 270-300, and 330-375 nm). For most of the compounds the bands at 270-300 and 330-375 nm have a vibrational structure.

Most of the investigated compounds fluoresce intensely. The fluorescence quantum yield (η) varies over a wide range as a function of the structure of the compound and the character of the interaction with the solvent. The luminescence characteristics are determined primarily by the proton-acceptor properties of the carbonyl and hydroxy groups in the 3 and 4 positions. According to the data in [9], the formation of a charge-transfer complex in the excited state in protic solvents should lead to nonradiative deactivation. This is precisely what we observed for alcohol solutions of dihydro-substituted benzo[f]quinolines that contain one ester group [1]. However, I-XV have higher fluorescence quantum yields in ethanol, which is capable of forming hydrogen bonds with the carbonyl and hydroxy groups of the molecule, and fluoresce weakly in aprotic solvents (DMSO and benzene). The indicated fact can be due only to spatial stabilization of the molecule [10] due to the formation of intermolecular hydrogen bonds via the carbonyl and hydroxy groups.

It is apparent from Table 2 that the p-OCH_3 and p-Cl substituents in the phenyl rings of the molecule have virtually no effect on the luminescence properties. This can evidently be explained by the fact that the phenyl rings are not included in the overall conjugation chain. An o-hydroxy group sharply reduces the fluorescence yield (V and XI). The presence of a nitro group leads to complete quenching of fluorescence (II, III, IX, and X).

For all of the synthesized compounds the position of the fluorescence spectrum depends on the nature of the solvent. The transition from benzene to ethanol leads to a considerable bathochromic shift of the fluorescence ($\Delta\lambda_{fl}$ = 53 nm); the absorption spectra are shifted ~10 nm. The additional shift of the fluorescence spectra as compared with the absorption spectrum ($\Delta\lambda_{add}$ = 43 nm) constitutes evidence for the additional effect of the solvent on the excited tetrahydrophenanthridine molecule.

Two mechanisms for this phenomenon are known: the formation of a complex with the solvent in the excited state [11], and a change in the orientation interactions in the excited state associated with an increase in the dipole moment of the fluorescing molecule [12]. According to [11], the formation of a complex with the solvent in the excited state leads to a bathochromic shift of the fluorescence spectrum. As a consequence of this, the fluorescence spectra of the investigated compounds in ethanol, which enters into the formation of a hydrogen bond with the carbonyl and hydroxy groups in the 3 and 4 positions, lie in a longer-wave region than in the more polar DMSO. The shift of the maximum in the fluorescence spectrum is ~45 nm, whereas the

TABLE 2. Spectral-Luminescence Characteristics of I-XV

Compound	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-4}$) in ethanol	Luminescence, λ_{max}, nm (η, %)		
		ethanol	DMSO	benzene
I	233, 271, 282, 293, 343, 373 (4,63; 4,05; 4,22; 4,29; 3,22; 3,99)	457 (42)	413 (38,5)	404 (15.5)
II	232, 288, 370 (4,51; 4,29; 3,84)	— (0)	— (0)	— (0)
III	232, 281, 294 (4,65; 4,23; 4,34)	— (0)	— (0)	— (0)
IV	230, 283, 294, 343, 373 (4,68; 4,30; 4,31; 3,94; 4,06)	457 (40)	413 (34)	404 (9,6)
V	233, 271, 284, 295, 377 (4,66; 4,27: 4,38; 4,42; 4,09)	458 (2)	413 (1,2)	405 (1,2)
VI	234, 281, 293, 342, 373 (4,67; 4,23; 4,31; 3,93; 3,99)	457 (42,5)	413 (40)	404 (12,8)
VII	226, 274, 328 (4,68; 4,54; 4,20)	457 (26)	413 (14,7)	404 (3,8)
VIII	232, 271, 288, 293, 342, 373 (4,65; 4,10; 4,23; 4,30; 4,03; 4,09)	457 (39,4)	414 (23,0)	402 (13,2)
IX	230, 283, 294, 370 (4,61; 4,37; 4,33; 3,92)	— (0)	— (0)	— (0)
X	233, 271, 281, 293, 341, 373 (4,70; 4,25; 4,31; 4,28; 3,95; 4,01)	— (0) 455 (28)	— (0) 415 (23)	— (0) 400 (1,8)
XI	227, 285 (4,55; 4,29)			
XII	226, 273, 281, 294, 330, 357 (4,73; 4,52; 4,50; 4,32; 4,18; 4,13)	457 (33)	413 (13)	405 (5,6)
XIII	232, 282, 294, 344, 374 (4,75; 4,40; 4,34; 3,97; 4,02)	457 (11,9)	414 (5,5)	405 (2,1)
XIV	232, 282, 292, 343, 371 (4,65; 4,23; 4,23; 4,09; 4,16)	457 (2.7)	415 (2)	410 (0,7)
XV	230, 277, 291, 344, 374 (4,50; 4,26: 4,22; 3,45; 3,52)	457 (41,4)	412 (21)	404 (9,5)

absorption maximum is not shifted at all. In aprotic solvents with different polarities (DMSO and benzene) the fluorescence maxima of the investigated compounds are shifted 10 nm relative to one another (Table 2) vis-a-vis $\Delta\lambda_{abs} = 10$ nm. The absence of a difference in the shifts of the absorption and fluorescence spectra as the polarity of the solvent changes constitutes evidence that the dipole moments of the investigated molecules do not change during excitation.

Thus, the additional shift of the fluorescence spectra of the investigated compounds is due only to the formation of a complex with the solvent in the excited state.

EXPERIMENTAL

The IR spectra of KBr pellets and CCl_4 solutions (10%) of the compounds at 400-3600 cm^{-1} were recorded with a UR-20 spectrometer. The PMR spectrum of a 10% solution of XII in $(CD_3)_2SO$ was recorded with a JNM-PS-100 spectrometer with tetramethylsilane as the internal standard. The mass spectra were obtained with a Varian MAT-311 spectrometer under the following conditions: The cathode emission current was 1000 μA, and the ionizing-electron energy was 70 eV. The samples were introduced directly into the ion source of the mass spectrometer, and the temperature of the ion source was 200°C. The absorption spectra of the solutions were recorded with Unicam SP-8000 and Specord UV-vis spectrophotometers. The fluorescence spectra and 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 dry ethanol, DMSO, and benzene. The fluorescence quantum yields were measured by a relative method; a solution of 3-amino-N-methylphthalimide in ethanol was used as the standard.

The ethyl esters of 6-phenyl- and 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylic acids were obtained by the methods in [13, 14].

Ethyl 2-(R-Phenyl)-5-(R'-phenyl)-4-hydroxy-1,2,5,6-tetrahydrobenzo[a]phenanthridine-3-carboxylates (I-XV). A mixture of 0.01 mole of N-benzylidene-2-naphthylamine and 0.01 mole of ethyl 6-phenyl- or 6-(p-methoxyphenyl)-2,4-dioxocyclohexane-1-carboxylate in 15.20 ml of alcohol was refluxed for 5-10 min, after which it was cooled, and the crystalline precipitate was removed by filtration and recrystallized from alcohol–dimethylformamide (1:1).

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SYNTHESIS AND CHEMICAL PROPERTIES OF 1-ETHYL-3-ARYL-2-IMIDAZOLIDINONES WITH A HYDROXYUREA FRAGMENT IN THE 4 POSITION

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Treatment of 2-ethylamino-2-methylpropanol oxime with aryl isocyanates leads to 4-[N-(arylcarbamoyl)hydroxyamino[-1-ethyl-3-aryl-5,5-dimenthyl-2-imidazolidionones, which are acylated by acid chlorides and methyl isocyanate to give the corresponding O-acyl derivatives and are converted to 2-(2-oxo-1-ethyl-3-aryl-5,5-dimethyl-4-imidazolidinyl)-4-aryl-1,2,4-oxadiazolidine-3,5-diones by the action of methyl chlorocarbonate.

Continuing our investigation of the cyclization of acylated derivatives of α-substituted oximes, we have established that treatment of 2-ethylamino-2-methylpropanal oxime (I) [1] with aryl isocyanates does not lead to N-arylcarbamoyl derivatives, as in the case of 2-hydroxyamino-2-methylpropanal oxime [2], or to their cyclization products, viz., 4-hydroxyamino-2-imidazolindinones [3,4], but rather to products of carbamoylation of the latter, i.e., to 4-[(N-arylcarbamoyl)hydroxyamino[-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (II). In addition, the reaction mixture contains starting I. When an isocyanate is also added, the reaction goes to completion, and only II are formed.

The intermediates are probably N-carbamoyl derivatives of I, which readily undergo intramolecular cyclization to give 4-hydroxyamino-1-ethyl-3-aryl-5,5-dimethyl-2-imidazolidinones (III) (hydroxyamino derivative IIId was isolated), which undergoes carbamoylation to give II.

Treatment of I all at once with a twofold excess of phenyl isocyanate gives 4-[O-(phenylcarbamoyl)hydroxyamino]-1-ethyl-3-phenyl-5,5-dimethyl-2-imidazolidinone (IV), which is probably the product of intra-

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