the precipitate was removed by filtration, washed with cold water, and, where necessary, was recrystallized from a suitable solvent as, for example, from alcohol or acetic acid diluted with water (in both cases).

The characteristics of the rearrangement products are presented in Table 1.

LITERATURE CITED

1. O. Meth-Cohn, B. Tarnowski, and B. Narine, J. Chem. Soc., Perkin I, No. 5, 1531 (1981).
2. Ya. L. Gol'dfarb, M. M. Polonskaya, B. P. Fabrichnyi, and I. F. Shalavina, Dokl. Akad. Nauk SSSR, 126, 86 (1956).
3. L. N. Klemm and W. Hsin, J. Heterocycl. Chem., 12, 1183 (1975).
4. P. Claude and F. Outurquin, J. Heterocycl. Chem., 20, 113 (1983).
5. G. Ah-Kow, C. Paulmier, and P. Pastour, Bull. Soc. Chim. France, Part 2, 151 (1976).
6. D. Binder, G. Habison, and C. R. Noe, Synthesis, No. 4, 255 (1977).
7. I. L. Knunyants and B. P. Fabrichnyi, Reactions and Methods in the Investigation of Organic Compounds [in Russian], Vol. 3, Goskhimizdat, Moscow (1954), p. 139.
8. J. Cymerman-Craig and D. Willis, J. Chem. Soc., 1071 (1955).
9. O. Meth-Cohn and B. Narine, Synthesis, No. 2, 133 (1980).
10. J. Cymerman-Craig and A. R. Naik, J. Am. Chem. Soc., 84, 3410 (1962).
11. B. P. Fabrichnyi, I. F. Shalavina, and Ya. L. Gol'dfarb, Zh. Obshch. Khim., 31, 1244 (1961).
12. A. Buzas and J. Teste, Bull. Soc. Chim. France, No. 2, 359 (1960).
13. B. P. Fabrichnyi, S. M. Kostrova, G.P. Gromova, and Ya. L. Gol'dfarb, Khim. Geterotsikl. Soedin., No. 11, 1483 (1973).
14. M. P. Chabrier, B. Tchoubar, and S. Le Tellier-Dupre, Bull. Soc. Chim. France, 13, 332 (1946).
15. J. Engel, A. Kleemann, F. Stroman, and K. Thiemer, West German Offenlegungsschrift, No. 2,851,387; Chem. Abstr., 91, 74,460 (1979).

ELECTRONIC STRUCTURES AND SPECTRAL AND ACID–BASE PROPERTIES OF PYRROL-, THIOPHEN-, AND FURANANTHRONES

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The IR spectra, electronic absorption and luminescence spectra, solvatochromism, and basicities of compounds of the 6H-dibenz[cd,g]indol-6-one, 6H-anthra[9,1-bc]thiophen-6-one, and 6H-anthra[9,1-bc]furan-6-one groups were studied. The interrelationship between the indicated properties and such structural factors as the 1,10-anthraquinoid structure, the presence of a π-surplus heteroring, and the presence of substituents was examined.

Compounds with compositions that include an anthrone ring annelated with a heteroring in the peri positions and are arbitrarily called heterocyclic derivatives of anthrone occupy a prominent position in the chemistry of intermediates and dyes [1]. We have previously used spectral methods to study the electronic structures of anthrone derivatives with a six-membered heteroring in the case of their most important representatives, viz., pyridonanthrones (2-hydroxyazabenzanthrones) [2, 3]. The recently accomplished [4, 5] synthesis of the uninvestigated group of anthrone derivatives of the I type with five-membered pyrrole, thiophene, and furan rings, which have a formally 1,10-anthraquinoid distribution of bonds, makes it possible to examine their spectral properties as compared with the previously known 9,10-anthraquinoid isomers, viz., pyrrol- and thiophenanthrones of the II type.

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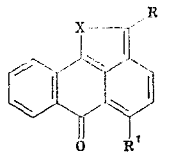
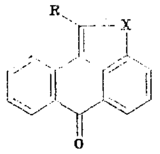


Ia-k



IIa-c

Ia,c IIa,b X=NMe; Ib,d $X=NC_6H_2Me_3$-2,4,6; Ie–g, IIc X=S; Ih–k X=O; Ia,b,c $R=R^1=H$; Ic,f,h–j, IIb $R=CO_2Me$; Id,g $R=NO_2$, k R=Ph; IIa,c R=H; Ic,d,f–h,k $R^1=H$, i $R^1=NHMe$, j $R^1=NMe_2$

In analyzing the electronic structures of heterocyclic derivatives of anthrone one should take into account the various variants of the π-electron interaction due to peri annelation of the heteroring and the anthrone ring. Depending on which structural factors one considers to be the determining ones, the heterocyclic derivatives of anthrone of the I type can be regarded as intramolecular donor–acceptor systems, heteroanalogs of benzophenalenone (benzanthrone), 1,10-anthraquinone-1-methides, or benzoylene derivatives of isoindole, benzo[c]thiophene, and benzo[c]furan. Consequently, the electron-donor character of the heteroring and the electron-acceptor character of the anthrone ring and the specific characteristics of the phenalenone, 1,10-anthraquinone, or indicated benzo[c]heterocycle systems came to the fore as regards the selected model. A combined analysis of the IR spectra and the electronic absorption and luminescence spectra, the solvatochromism, and the acid–base properties makes it possible to draw definite conclusions in this regard as applied to the ground and excited states.

N-Methyl- and N-mesitylpyrrolanthrones Ia,b (6H-dibenz[cd,g]indol-6-ones) and their 2-methoxycarbonyl and 2-nitroderivatives Ic,d, thiophenanthrone Ie (6H-anthra[9,1-bc]thiophen-6-one) and its 2-substituted derivatives If,g, 2-methoxycarbonylfurananthrones Ih–j, and 2-phenylfurananthrone Ik (6H-anthra[9,1-bc]furan-6-ones) served as the chief subjects of our investigation. For comparison, we used the isomeric N-methylpyrroloanthrones IIa,b (6H-naphth[1,2,3-cd]indol-6-ones), thiophenanthrone IIc (6H-anthra[1,9-bc]thiophen-6-one), and some other compounds.

According to the IR spectral data, the frequency of the stretching vibrations of the keto group is most informative. The decrease in the frequency of the vibrations of the C=O bond is an argument in favor of the similarity of pyrrolanthrones [6] and thiophenanthrone [7] of the II type to phenalenone. A characteristic sign of the latter is considered to be the polarization, which is due to the tendency to form a thermodynamically favorable phenalenium cation structure [8].

It is apparent from Table 1 that, just as in the case of pyrrolanthrone IIa and thiophenanthrone IIc, in the IR spectra of pyrrolanthrones Ia,b and thiophenanthrone Ie with an unsubstituted 2 position the frequency of the vibrations of the carbonyl group is shifted to 1645 cm^{-1} as compared with the "normal" value for anthrone and 9,10-anthraquinone. Phenalenone and 2,4,9-trichloro-1,10-anthraquinone have the same depressed ν_{CO} values. The introduction of a methoxycarbonyl group into the heteroring in the case of pyrrolanthrone does not change the frequencies of the vibrations of the C=O bond (Ia and Ic, Table 1), whereas in the case of thiophenanthrone it increases it greatly (Ie and If). 2-Methoxycarbonylfurananthrone Ih and 2-phenylfurananthrone Ik also have ν_{CO} values that are elevated up to the "normal" value. However, the introduction of a strong electron acceptor, viz., a nitro group,

TABLE 1. Frequency of the Stretching Vibrations of the C=O Bond in the IR Spectra (in $CHCl_3$) of Ia-k and IIa-c

Compound	ν_{CO}, cm^{-1}	Compound	ν_{CO}, cm^{-1}
Ia	1644	Ij	1660, 1705
Ib	1644	Ik	1670
Ic	1645, 1685	IIa	1645
Id	1664	IIb	1648, 1718
Ie	1645	IIc	1645 [7]
If	1675, 1740	Phenalenone	1643 [9]
Ig	1660	2,4,9-Trichloro-1,10-anthraquinone	1647 (inKBr) [10]
Ih	1662, 1705	Anthrone	1663 [11], 1670 (in CCl_4) [12]
Ii	1660, 1705	9,10-Anthraquinone	1677 [12]

TABLE 2. Electronic Absorption Spectra of Heterocyclic Derivatives of Anthrone (Ia-k and IIa-c)

Compound	λ_{max}, nm		λ_{max}, nm (lg ε) (ethanol)
	hexane	benzene	
Ia	520, 510, 484, 455 sh	534, 505 sh	552 (4,10)
Ib	520, 484, 455 sh	531, 505 sh	550 (4,12)
Ic	486, 456, 435 sh	500, 473	495 (4,27)
Id	493, 460, 435	495, 465, 440 sh	494 (4,48), 465 (4,23), 440 sh (3,80)
Ie	496, 486, 467, 463 sh	486	492 (4,02)
If	492, 485, 466 sh	494, 472 sh	488 (3,36)
Ig	Not dissolved	520, 490	515 (4,38), 490 sh (4,25)
Ih	502, 468, 440 sh	510, 480	494 (4,28), 463 sh (4,15)
Ii	557, 543 sh, 520, 488 sh	563, 523, 492 sh	552 (4,38), 514 (4,25), 486 sh (3,90)
Ij	548, 538, 509, 480 sh	546, 517	541 (4,20), 510 (4,18), 475 sh (3,86)
Ik	576, 539, 500 sh	588, 555 sh	588 (3,94)
IIa	419, 396	430, 412	430 (4,04)
IIb	425, 405	434, 418	434 (4,18)
IIc	381, 365	389, 375 sh	390 (4,06)

leads to an increase in the frequency of the vibrations of the carbonyl group both in the case of thiophenanthrone (Ig) and in the case of pyrrolanthrone (Id). A similar pattern is observed in the pyrrolanthrone series of the II type. When a strong electron-acceptor substituent — a nitro or diazonium group — is introduced into the heteroring of N-methylpyrrolanthrone IIa, the ν_{CO} frequency increases from 1645 cm^{-1} to 1660 cm^{-1} [6], although the change is insignificant when a methoxycarbonyl group is introduced (IIb, Table 1).

Consequently, in the ground state of heterocyclic derivatives of anthrone of the I and II type there is a shift of the electron density toward the keto group that is suppressed when an electron-acceptor substituent is introduced into the heteroring, and this occurs more readily, the lower the degree of π-surplus character of the heteroring. Hence it may be concluded that polarization in the ground state is due mainly to the electron-donor effect of the annelated heteroring rather than to the "phenalenone-like" or 1,10-anthraquinoid structure.

The character of the effect of an amino group in the peri position on the ν_{CO} frequency of compounds of the I type proved to be unexpected. As a rule, when there is an amino group that has a hydrogen atom and is located in the peri position relative to the carbonyl group, one observes the formation of an intramolecular hydrogen bond (IHB) and, as a consequence, a decrease in the ν_{CO} frequency in the IR spectrum. The introduction into the 5 position of furananthrone of a methylamino (Ii, Table 1), cyclohexylamino, or phenylamino group [4] has virtually no effect on the ν_{CO} value, and this serves as a sign of the absence of an IHB. However, a band of vibrations of an isolated N–H bond does not appear in the IR spectra. This contradiction requires additional study. Galushko and Dokunikhin [13, 14], who observed a similar pattern in the IR spectra of 5-aminoisoxazolanthrones, proposed the presence of a strong IHB. We consider more likely the assumption of its absence, which is confirmed by data on the basicities of 5-aminofurananthrones (see below). The reason for the disadvantageousness of an IHB may be the increase in the distance between the peri-oriented atoms as a result of distortion of the angles in the case of annelation of a five-membered ring, similar to the increase in the distance between the peri positions in acenaphthene [15] or 5H-benz[cd]indol-5-one [16].

The existence in the ground state of polarization due to the electron-donor character of the heteroring poses a problem regarding the role of intramolecular charge transfer on passing to the excited state. The color of most organic dyes, including anthraquinone dyes, is determined by the so-called charge-transfer band — an electron transition in which electrons of the donor are shifted in the direction of the acceptor part of the molecule. The excited state in this case is characterized by usually greater polarity than the ground state, and the compounds display positive solvatochromism. Tying up of the electrons of the donor, which excludes charge transfer, leads to the disappearance of the band.

The heterocyclic derivatives of anthrone (I) are characterized by intense absorption in the near-UV region at about 300 nm and in the visible region at about 500 nm, which is responsible for their color. Data on the positions of the maxima in the visible region in vari-

TABLE 3. Spectral-Luminescence Characteristics of Heterocyclic Derivatives of Anthrone (Ia,c,e,f,h,i and IIa-c)

Compound	Toluene			Ethanol[a]	
	λ_{max}, nm		η	luminescence λ_{max}, nm	η
	absorption	luminescence			
Ia	530	580	0,14	630	0,17
Ic	495	530	0,59	587	0,59
Ie	485	565	0,53	604	0,40
If	490	528	0,12	565	0,40
Ih	505	538	0,46	593	0,26
Ii	555, 515	610, 570	0,80	600, 565	0,77
IIa[b]	430	480	0,50		
IIb	435	485	0,32		
IIc	390	Absent	—	457	0,12

a) See the absorption λ_{max} in Table 2.

b) According to the data in [6], in $CHCl_3$.

ous solvents are presented in Table 2. Of Ia-h, only pyrrolanthrones Ia,b with an unsubstituted 2 position have clearly expressed solvatochromism. However, they absorb in the longest-wave region.

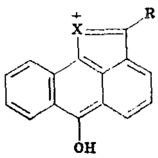
The introduction of an electron-acceptor substituent into the pyrrole ring (Ia and Ic,d in Table 2) leads to a hypsochromic effect and a loss of solvatochromism, which constitutes evidence for the absence of charge transfer on passing to the excited state. A decrease in the polarity of the excited state occurs under the influence of not only a nitro group but also a methoxycarbonyl group which, according to the IR spectral data, does not affect the polarity of the ground state. The hypsochromic shift that takes place simultaneously with the decrease in solvatochromism shows that charge transfer makes a definite contribution to the lowering of the energy level of the excited state of pyrrolanthrones Ia,b. However, the retention of the long-wave band in the spectra of 2-substituted pyrrolanthrones Ic,d, thiophenanthrones Ie-g, and furananthrone Ih, during passage of which to the excited state, charge transfer does not occur, judging from the absence of solvatochromism, constitutes evidence that it does not play a decisive role. It may be assumed that the color of heterocyclic derivatives of anthrone of the I type is associated with their 1,10-anthraquinoid structure and, as for 1,10-anthraquinone derivatives (λ_{max} ~ 470 nm), is due to a π,π^* transition [1, 17].

An increase in the π system through the introduction of an aryl residue into the heteroring or conjugation with the unshared pair of electrons of an amino group in the anthrone ring leads to a long-wave shift with deepening of the color. Thus replacement of the methoxycarbonyl group in the 2 position of furananthrone by a phenyl group gives rise to a 70-nm bathochromic shift (Ih and Ik, Table 2), and the introduction of an amino group into the 5 position of furananthrone leads to a 50- to 60-nm shift (Ih and Ii, j).

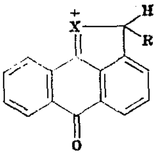
Heterocyclic derivatives of anthrone of the I type display yellow-orange luminescence in solutions. As in the absorption spectra, in the luminescence spectra (Table 3) one observes a short-wave shift and a decrease in the effect of the solvent when an electron-acceptor substituent is introduced into the heteroring, but the sensitivity of the luminescence spectrum to a change in the structure is higher in a number of cases. For example, the presence of a 2-methoxycarbonyl group in thiophenanthrone (Ie and If), which has little effect on the position of the maximum in the absorption spectrum (Table 2), leads to a short-wave shift (about 40 nm) of the maximum in the luminescence spectrum (Table 3). Passing from toluene to ethanol for thiophenanthrone Ie and 2-methoxycarbonyl derivatives Ic,f,h causes little change in the positions of the absorption maxima, whereas in the luminescence spectra it gives rise to a 40- to 55-nm long-wave shift (Tables 2 and 3), as a consequence of which the Stokesian shift increases from 35 nm to about 100 nm on passing from toluene to ethanol. The quantum yield and the very capacity for luminescence depend on the character of the substitution. The introduction of a methoxycarbonyl group into the 2 position of pyrrolanthrone (Ia and Ic, Table 3) increases the quantum yield to 0.6, whereas the introduction of a methylamino group (Ih and Ii) or a cyclohexylamino group [4] into the 5 position of furananthrone increases the quantum yield to 0.8; the introduction of a dimethylamino group (Ij) or a phenylamino group [4] leads to disappearance of luminescence.

The isomeric anthrone derivatives of the II type are much more highly colored than the corresponding derivatives of the I type. In their absorption and luminescence spectra the maxima are shifted 100-150 nm to the shorter-wave region (Tables 2 and 3). In contrast to the spectrum of pyrrolanthrone Ia, the absorption spectrum of the isomeric pyrrolanthrone IIa is not sensitive to the proton-donor character of the solvent (no shift is observed on passing from benzene to ethanol and acetic acid), and the introduction of a methoxycarbonyl group (IIa and IIb) leads to a bathochromic rather than a hypsochromic shift (Table 2). From this it may be concluded that charge transfer during excitation does not play a role in the formation of the electronic spectrum in this case.

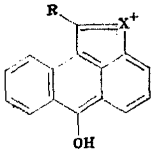
Cations that are more deeply colored than the bases are formed by the action of strong acids in pyrrol-, thiophen-, and furananthrones Ia-h. After protonation, N-methylpyrrolanthrone Ia and, at a slower pace, thiophenanthrone Ie, are converted to 2,2'-dehydro dimers [5]; the protonated forms of the remaining compounds are stable. The significant bathochromic shift upon protonation (Table 4) indicates the addition of a proton to the carbonyl oxygen atom to give cation III, inasmuch as, in the case of addition of the proton to the α-carbon atom of the heteroring (IV), as in isoindole [18], one should have expected a similarity to the spectrum of protonated 9,10-anthraquinone, i.e., a hypsochromic effect. Similarly, the isomeric pyrrol- and thiophenanthrones of the II type are protonated at the oxygen atom to give more deeply colored cations V.



III



IV



V

Whereas bases I and II differ with respect to the position of the heteroatom and the distribution of the bonds, conjugate acids III and V differ only with respect to the position of the heteroatom. Proceeding from the lower thermodynamic stability of 1,10-anthraquinone as compared with 9,10-anthraquinone [1] or, in a different way of examining the structure, the o-quinoid isoindole and benzo[c]thiophene as compared with indole and benzo[b]thiophene, one might have expected a large gain in energy on passing to the protonated form of derivatives of the I type. Another reason for the increased basicities of I may be the more favorable conditions for charge delocalization in cation III, in which the electron-donor hydroxy group and the cationic center are attached to the same central ring, whereas in cation V they are attached to different rings.

To compare the basicities of the heterocyclic derivatives of anthrone of the I and II type we determined the constants of the acid–base equilibria in acetic acid by spectrophotometry. Data for three pairs of compounds are presented in Table 4: pyrrolanthrones Ib and IIa ($\Delta pK_a = 0.46$), methoxycarbonylpyrrolanthrones Ic and IIb ($\Delta pK_a = 1.1$), and thiophenanthrones Ie and IIc ($\Delta pK_a \approx 0.5$). In the first pair nonidentical substituents attached to the nitrogen atom do not introduce substantial distortions into the ΔpK_a value, since the mesityl residue in pyrrolanthrone Ib, because of steric hindrance, deviates from conjugation, and the methyl group in pyrrolanthrone IIa has no effect, and its replacement by a hydrogen atom does not change the pK_a value. In the second pair the excessive increase in the ΔpK_a value is probably a consequence of the great proximity of the methoxycarbonyl group to the protonation center in pyrrolanthrone IIb. Thus the difference in the basicities of isomers I and II, which is due to the difference in the distribution of the bonds, does not exceed one pK unit. Taking into account what we stated above regarding the better conditions for charge delocalization in the V cations, almost nothing remains for the fraction of the gain in energy due to rearrangement of the 1,10-anthraquinoid structure of bases I upon protonation. A comparison of the acid–base equilibria does not show that 1,10-anthraquinoid pyrrol- and thiophenanthrones of the I type, which are benzoylene derivatives of isoindole and benzo[c]thiophene, are energically substantially less favorable than the 9,10-anthraquinoid isomers of the II type, which are benzoylene derivatives of indole and benzo[b]thiophene. The additional stabilization energy is possibly provided by the greater uniformity of the bonds in I as compared with 1,10-anthraquinone and the corresponding benzo[c]heterocycles. In contrast to furananthrones [4], pyrrol- and thiophenanthrones [5] do not undergo the Diels–Alder reaction; this serves as an indirect indication of the uniformity of the bonds.

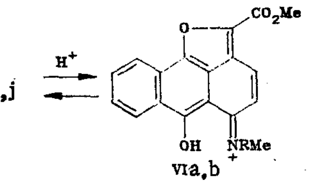
TABLE 4. Basicities and Electronic Spectra of Heterocyclic Derivatives of Anthrone (Ib,c,e,h,i,j and IIa-c) in Acetic Acid

Compound	λ_{max}, nm (lg ε)		pK_a
	base	conjugate acid	
Ib	555 (3,92)	635 sh (3,70), 601 (3,73)	$-0{,}22\pm0{,}05^a$
Ic	500 (4,17)	635 (4,02)	$-1{,}40\pm0{,}05$
Ie	500 (3,97)	637 (4,00)	$-3{,}1\pm0{,}2$
Ih	500 (4,13), 470 sh (4,00)	632 (3,90)	$-4{,}5\pm0{,}2$
Ii	557 (4,23), 516 (4,13)	520 (3,92), 500 (3,91)	$0{,}42\pm0{,}05^a$
Ij	552 (4,14), 520 (4,12)	500 (3,92)	$0{,}67\pm0{,}05^a$
IIa	444 (4,02)	539 (4,04), 513 (4,03)	$-1{,}30\pm0{,}05$
			$-0{,}68\pm0{,}05^a$
IIb	442 (4,07)	543 (4,12)	$-2{,}5\pm0{,}1$
IIc	390 (4,00)	493 (4,12)	$-3{,}5\pm0{,}1$

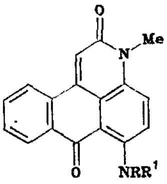
a) in 90% acetic acid.

Replacement of the heteroatom on passing from pyrrolanthrone to thiophen- and furananthrone gives rise to a decrease in the basicity of ~3 pK units (Ib and Ie, Ic and Ih; Table 4), introduction of a methoxycarbonyl group into the heteroring leads to a decrease of ~1 pK unit (Ib and Ic, IIa and IIb), and the introduction of an amino group into the 5 position of furananthrone increases the basicity by ~5 pK units (Ih and Ii,j).

One's attention is directed to the similarity in behavior with respect to acids of 5-methylamino- (Ii) and 5-dimethylaminofurananthrone (Ij). When they are protonated, the long-wave absorption band is shifted hypsochromically, and the band at 400 nm, which is absent in the spectrum of furananthrone Ih, is retained. The spectra of the protonated forms are similar to one another and do not coincide with the spectrum of 2-methoxycarbonylfurananthrone Ih, suggesting, as it were, that the proton is bonded to the amino group. Consequently, in both cases, i.e., Ii and Ij, the proton is attached to the carbonyl oxygen atom, and the structure is described by hydroxyimmonium structure VI.



VIa,b



VII a,b

VI a R=H; b R=Me; VII a $RR^1=C_5H_{10}$; b $R=R^1=H$

The basicities of amino-substituted Ii and Ij differ by only 0.25 pK unit (Table 4). At the same time, in the series of 9,10-anthraquinone compounds with a tertiary amino group in the peri position relative to the carbonyl group the basicities exceed by several orders of magnitude the basicities of compounds with a primary or secondary amino group, and they frequently have a different protonation center. Thus, 6-piperidinopyridonanthrone VIIa with pK_a = 5.03 (in 50% ethanol) is protonated directly at the amino nitrogen atom, whereas 6-aminopyridonanthrone VIIb with pK_a = 0.76 (in 90% acetic acid) is initially protonated at the oxygen atom of the heteroring and then at the oxygen atom of the carbonyl group [2]. The special properties of compounds with a tertiary amino group are due chiefly to the gain in energy as a consequence of the formation of an intramolecular hydrogen bond (IHB) upon protonation [19]. The lack of exaltation of the basicity of 5-dimethylamino-substituted Ij compels one to assume that an IHB is absent in its protonated form VIb. In conjunction with the IR spectral data regarding the absence of an IHB in 5-methylamino-substituted Ii (see above), this indicates the disadvantageousness of an IHB in 5-aminofurananthrones.

It follows from the analysis presented above that polarization of the molecules of heterocyclic anthrone derivatives of the I type in the ground and excited states is due to the presence of a π-surplus heteroring and does not have a substantial effect on the nature of the electronic transition. The 1,10-anthraquinoid structure does not have an appreciable effect in the ground state of pyrrol- and thiophenanthrones but does play a decisive role in the formation of the electronic spectra.

EXPERIMENTAL

The IR spectra were measured with a UR-20 spectrometer. The electronic spectra were recorded with Specord UV-vis and Perkin–Elmer 552 spectrophotometers. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FEU-18 optical emission detector, and an M-95 microammeter. The photoluminescence was excited with a DRSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated by means of a DMR-4 monochromator; the quantum yields (η) were determined by the method of equal absorption.

The spectrophotometric determination of the ionization constants was carried out in 100% and 90% acetic acid with the addition of H_2SO_4 by the method in [2]. The series of spectral curves had distinct isobestic points. The H_0 values, which correspond to half protonation, were taken as the pK_a values. The maximum in the spectrum of the base served as the analytical wavelength in the case of Ic,e,h-j, the long-wave maximum in the spectrum of the conjugate acid served this purpose in the case of IIa-c (Table 4), and the maximum at 420 nm served this purpose for Ib.

The synthesis of pyrrol- and thiophenanthrones Ia-g was described in [5], and the synthesis of furananthrones Ih-j was described in [4]. 2-Phenylanthrone Ik was synthesized by the method in [20], and thiophenanthrone IIc was synthesized by the method in [21]. The synthesis of pyrrolanthrones IIa,b was presented in [22], the authors of which kindly provided us with the compounds.

LITERATURE CITED

1. M. V. Gorelik, The Chemistry of Anthraquinones and Their Derivatives [in Russian], Khimiya, Moscow (1983).
2. T. A.Mikhailova, B. E. Zaitsev, and M. V. Gorelik, Zh. Org. Khim., 15, 1516 (1979).
3. T. A. Mikhailova, B. E. Zaitsev, G. V. Sheban, and M. V. Gorelik, Khim. Geterotsikl. Soedin., No. 6, 803 (1981).
4. M. V. Gorelik and R. A. Alimova, Zh. Org. Khim., 20, 818 (1984).
5. M. V. Gorelik and R. A. Alimova, Zh. Org. Khim., 20, 1553 (1984).
6. E. G. Sadovykh, Master's Dissertation, Scientific-Research Institute of Organic Intermediates and Dyes, Moscow (1981).
7. R. Neidlein and H. Seel, Arch. Pharm. (Weincheim), 311, 324 (1978).
8. S. Hünig and E. Wolff, Chimia, 22, 33 (1968).
9. V. D. Orlov, S. L. Solodar', Yu. N. Surov, L. M. Vinogradov, and S. E. Chistova, Zh. Org. Khim., 18, 615 (1982).
10. M. V. Gorelik, S. P. Titova, and V. A. Trdatyan, Zh. Org. Khim., 15, 157 (1979).
11. B. E. Zaitsev, T. A. Mikhailova, G. N. Rodionova, and M. V. Kazankov, Zh. Fiz. Khim., 47, 1095 (1973).
12. B. E. Zaitsev and N. A. Trankvil'nitskaya, Zh. Prikl. Spektrosk., 18, 449 (1973).
13. A. M. Galushko and N. S. Dokunikhin, Zh. Org. Khim., 15, 575 (1979).
14. A. M. Galushko and N. S. Dokunikhin, Zh. Org. Khim., 18, 1539 (1982).
15. H. W. W. Erlich, Acta Cryst., 10, 699 (1957).
16. M. B. Laing, R. A. Sparks, and K. N. Trueblood, Acta Cryst., B, 28, 1980 (1972).
17. L. P. Brivina, N. S. Strokach, D. N. Shigorin, and M. V. Gorelik, Zh. Fiz. Khim., 54, 349 (1980).
18. F. S. Babichev, V. A. Kovtunenko, and A. K. Tyltin, Usp. Khim., 50, 2073 (1981).
19. M. V. Gorelik, B. A. Korolev, and Hang Ir Kwong, Zh. Org. Khim., 12, 2589 (1976).
20. R. Scholl and J. Donat, Ber., 66, 514 (1933).
21. L. Gattermann, Ann., 393, 113 (1912).
22. M. V. Kazankov and E. G. Sadovykh, Khim. Geterotsikl. Soedin., No. 6, 785 (1978).