2. Ya. A. Strods, I. É. Lielbriedis, and O. Ya. Neiland, Khim. Geterotsikl. Soedin., No. 7, 977 (1977).
3. N. S. Kozlov, V. D. Pak, and Z. Z. Nugumanov, Khim. Geterotsikl. Soedin., No. 2, 194 (1970).
4. I. É. Lielbriedis and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSSR, Ser. Khim., No. 2, 193 (1969).
5. J. Hedge, C. Kruse, and H. Snyder, J. Org. Chem., 26, No. 9, 3616 (1961).
6. P. Schuster, O. Polanski, and F. Wessely, Monatsh., 95, No. 1, 53 (1964).
7. E. Horning and M. Horning, J. Org. Chem., 11, 95 (1964).

ACIDITIES OF ANTHRAQUINONE AND ITS HYDROXY DERIVATIVES*

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The acidities of anthraquinone and its 1- and 6-hydroxy derivatives were studied. It is shown that the anthrone ring in the anthrapyridone molecule displays a strong electron-acceptor effect that stabilizes the anion during the development in the pyridone ring of a negative charge as a result of ionization; as a consequence of this, anthrapyridone and 1-hydroxyanthrapyridone are considerably stronger acids than 2-pyridone and 3-hydroxy-2-pyridone, respectively.

It has been previously shown on the basis of quantum-chemical calculations of the π charges on the atoms and the bond orders that anthrapyridone, which is the basis of a valuable series of dyes, to a certain extent retains the properties of pyridone and anthraquinone [2, 3]. This conclusion is to some extent confirmed by the IR spectra of anthrapyridone and its derivatives [2], according to which the overall intensity of the bands of the CO groups of anthrapyridone in the IR spectra is close to the arithmatic sum of the intensities of the CO groups of 2-pyridone and anthrone; this may constitute evidence for the similarity in the amide and ketone CO groups and the anthrapyridone CO groups of the corresponding model compounds.

To ascertain the degree of probability of the redistribution of the electron density between the 2-pyridone and anthrone rings in the anthrapyridone molecule as compared with model compounds in the ground state, we studied the acidities of anthrapyridone and its 1- and 6-hydroxy derivatives and some model compounds (Table 1). The ionization constants corresponding to the detachment of a proton were measured spectrophotometrically in solutions in aqueous ethanol (1:1).

It has been established [2, 3] that anthrapyridone exists in the lactam form. The 2-pyridone $\rightleftharpoons$ 2-hydroxypyridine tautomeric equilibrium is also shifted to favor the lactam form [4]. A comparison of the NH acidities of anthrapyridone (I) and 2-pyridone (II) therefore gives information regarding the character of the effect of a condensed anthrone fragment on the heteroring in the anthrapyridone molecule. It follows from the pK_a values presented in Table 1 that the anthrone fragment has a substantial electron-acceptor effect on the pyridone ring in anthrapyridone, as a result of which the acidity of anthrapyridone is 2.66 pK_a units higher than the acidity of 2-pyridone. The ionization of anthrapyridone I is accompanied by a bathochromic shift of the long-wave absorption band, which in the nonionized form is expressed in the form of a shoulder (Fig. 1).

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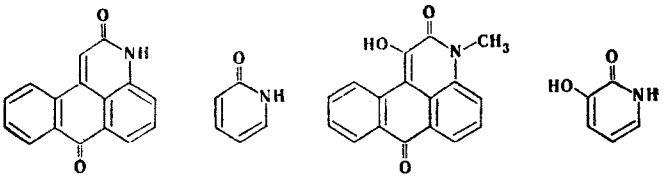
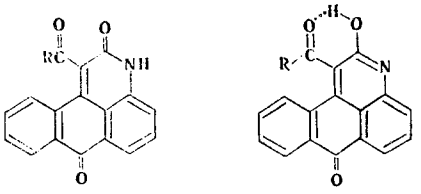


I II III IV

A comparison of the acidity of 1-hydroxy-N-methylanthrapyridone (III) and 3-hydroxy-2-pyridone (IV) leads to a similar conclusion. Annelation of the anthrone ring increases the acidity of the hydroxy group in the heteroring 2.52 pK_a units. 1-Hydroxyanthrapyridone III is such a strong acid that it exists completely in the dissociated state in alcohol solution. Evidence for this is provided by the absence of changes in the electronic spectrum when sodium hydroxide is added to an alcohol solution of III and by the pronounced hypsochromic shift when mineral acids are added (Fig. 2).

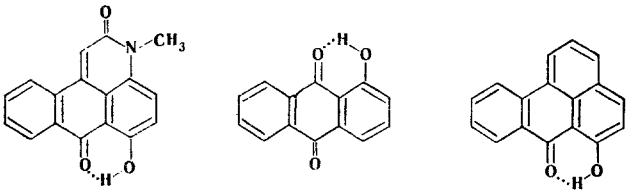


Va, VIa Vb, VIb

V R = CH_3; VI R = C_6H_5

It is interesting that the introduction of an electron-acceptor substituent such as an acetyl or benzoyl group in the 1 position of anthrapyridone not only does not increase its NH acidity but even reduces it ∿0.7 pK_a units. It may be assumed that, in contrast to anthrapyridone (I) itself, 1-acyl derivatives V and VI do not exist in the lactam form (Va and VIa) but rather in the lactim form (Vb and VIb), stabilized by an intramolecular hydrogen bond, which is also responsible for the reduced acidity.

To evaluate the effect of the pyridone ring on the anthrone portion of the molecule in anthrapyridone we studied the acidity of 6-hydroxyanthrapyridone VII. It is apparent from the pK_a values that VII is a weaker acid than 1-hydroxyanthraquinone (VIII) (pK_a = 1.34), whereas its acidity is virtually equal to the acidity of 6-hydroxybenzanthrone (IX). An examination of the effect of annelation of the 2-pyridone ring as compared with the benzene ring in simpler cases indicates its somewhat greater electron-acceptor character. Thus 6-hydroxy-2-quinolone (X) has an acidity that is 0.73 pK_a units higher than the acidity of 2-naphthol (XI) [5].



VII VIII IX

From an examination of the pK_a values it may be concluded that the electronic effect of the pyridine ring in 6-hydroxyanthrapyridone is equivalent to the effect of the peri-condensed benzene ring in 6-hydroxybenzanthrone but, with respect to its acceptor character, is inferior to the effect of the second CO group in 1-hydroxyanthraquinone. Thus peri annelation of the α-pyridone and anthrone rings is manifested in the relatively reduced acceptor effect of the α-pyridone ring. Depending on the structure, the change in the state of the acid–base equilibrium is the overall result of the effect of structural factors in the neutral molecule of the acid and is the conjugate anion. The electron-acceptor interaction is manifested to a greater degree with respect to the negatively charged center in the anion than with respect to the neutral NH group or OH group in the acid, stabilizing the anion molecule by charge delocalization. It may therefore be assumed that the noted increase in the acidities of the anthrapyridone and its derivatives as compared with the model compounds is due mainly to stabilization of the anion. The redistribution of the electron density in the ground state of nonionized molecules is insignificant. This is also con-

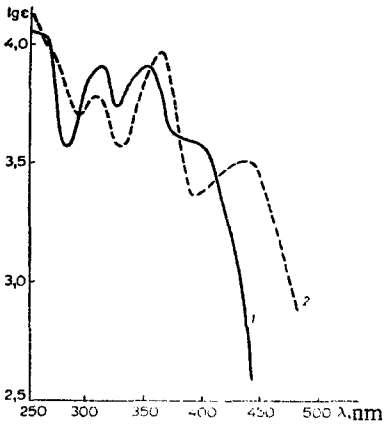


Fig. 1

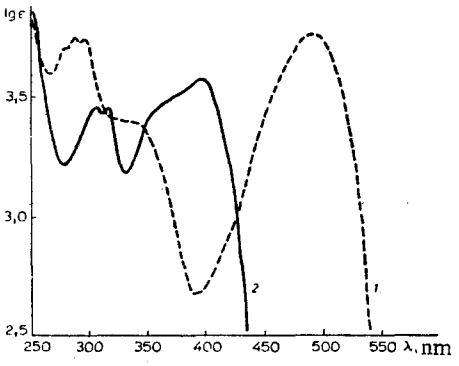


Fig. 2

Fig. 1. Electronic spectra of anthrapyridone (I): 1) in 50% aqueous ethanol; 2) in a 0.05 N solution of NaOH in 50% aqueous ethanol.

Fig. 2. Electronic spectra of 1-hydroxy-N-methylanthrapyridone: 1) in 50% aqueous ethanol; 2) in a 0.05 N solution of HCl in 50% aqueous ethanol.

TABLE 1. Acidity Constants (pK_a) (in 50% ethanol)

Compound	Name	Analytical λ, nm (log ε)	pK_a
I	Anthrapyridone	362 (4,20)	9,50
II	2-Pyridone	235 (3,23)	11,16
III	1-Hydroxy-N-methylanthrapyridone	490 (4,28)	6,43
IV	3-Hydroxy-2-pyridone	315 (3,96)	9,95
V	1-Acetylanthrapyridone	445 (4,40)	10,18
VI	1-Benzoylanthrapyridone	451 (4,07)	10,23
VII	6-Hydroxy-N-methylanthrapyridone	512 (4,00)	11,21
VIII	1-Hydroxyanthraquinone	310 (3,68)	9,87
IX	6-Hydroxybenzanthrone	451 (4,24)	11,18
X	6-Hydroxy-2-quinolone	385 (3,67)	10,6 (9,31)*
XI	2-Naphthol	348 (3,60)	11,33 (9,67)*

*In water.

firmed by the calculation of the π-electron densities in the anthrapyridone and 2-pyridone molecules by the self-consistent-field (SCF) MO method [2].

EXPERIMENTAL

The electronic spectra of the compounds were measured at 20°C with an SF-4A spectrophotometer. In the determination of the pK_a values weighed samples (0.5 mg-mole) of the investigated compounds were dissolved in 100 ml of 96% ethanol, 5 ml of the starting solution was mixed with an equal volume of an aqueous solution (0.01 and 0.05 N) of acid, alkali, or buffer solution, after which the optical densities of the solutions were measured at the selected analytical wavelength (Table 1). Solutions containing a mixture of monosubstituted sodium phosphate and disubstituted potassium phosphate were used as buffer solutions. The pH values of the working solutions were measured with a pH-340 potentiometer with glass and silver chloride electrodes. The pK_a values were calculated from the formula

$$pK_a = pH + \lg \frac{\alpha_{ion} - \alpha_{buff}}{\alpha_{buff} - \alpha_{non}}.$$

The pH range was selected within ±0.5 unit from the approximate pK_a values determined beforehand in such a way that the pH values of the prepared solutions differed from one another by ∿0.2 unit. The measurements were made for seven to eight solutions, and the pK_a value was calculated on the basis of each measurement; the arithmetic means were found, and the scatter between the maximum and minimum pK_a values obtained in individual determinations did not exceed 0.06 unit.

LITERATURE CITED

1. B. E. Zaitsev, T. A. Mikhailova, and M. V. Kazankov, Khim. Geterotsikl. Soedin., No. 10, 1357 (1974).
2. B. E. Zaitsev, T. A. Mikhailova, G. N. Rodionova, and M. V. Kazankov, Zh. Fiz. Khim., 47, 1095 (1973).
3. B. E. Zaitsev and T. A. Mikhailova, Khim. Geterotsikl. Soedin., No. 6, 812 (1974).
4. I. Elquero, C. Martin, A. R. Katritzky, and P. Linda, The Tautomerism of Heterocycles, Supplement 1, Advances in Heterocyclic Chemistry (1976).
5. A. J. Gordon and R. A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, Wiley-Interscience (1973).

ELECTROPHILIC SUBSTITUTION IN THE 1-PHENYL-2-ACYLPYRAZOLIDINE SERIES

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Bromination, nitration, and sulfonation reactions in the acylphenylpyrazolidine series were investigated. 1-(p-Bromophenyl)-2-acylpyrazolidines are formed in good yields in the bromination of these compounds over a wide range of temperatures in various solvents. Removal of the acyl group takes place simultaneously with sulfonation in the para position of the phenyl ring in the sulfonation of phenylacylpyrazolidines with concentrated sulfuric acid at room temperature; the p-sulfophenylpyrazolidines formed in this case exist in the form of betain structures. The nitration of acylphenylpyrazolidines with concentrated nitric acid (sp. gr. 1.52) leads to 1-(2,4-dinitrophenyl)-2-acylpyrazolidines. However, the nitration of these compounds with dilute nitric acid (sp. gr. 1.35) is accompanied by pronounced resinification; both 2,4-dinitrophenyl and p-nitrophenyl-2-acylpyrazolidines, as well as dimers of the latter, were detected among the reaction products.

Five-membered cyclic arylhydrazines — 1-arylpyrazolidines — are key compounds in the synthesis of pyrimidoindole derivatives [1]. Reduction [2, 3] with lithium aluminum hydride (LAH) of the corresponding readily available aryl-3-pyrazolidones or aryl-5-pyrazolidones serves as the principal method for their synthesis. However, compounds containing groups that are sensitive to the action of LAH in the phenyl ring cannot be obtained by this method. The electrophilic substitution reactions in cyclic arylhydrazine derivatives have not been adequately studied [4]. In our research we investigated the electrophilic substitution reactions (bromination, sulfonation, and nitration) of 1-phenyl-2-acylpyrazolidines (I). The action of bromine in various solvents (CCl_4, $CHCl_3$, and CH_3COOH) on these pyrazolidines (I) over a wide range of temperatures (from −10 to +20°C) leads to 1-(p-bromophenyl)-2-acylpyrazolidines (II) in 60-80% yields. Substitution in the para position is confirmed by the PMR spectra of these compounds, which contain two doublets of an A_2B_2 system in the aromatic proton region, and by the IR spectra, in which an absorption band of p-substituted phenyl ring appears at 840 cm^{-1}. In contrast to 1-phenyl-3-pyrazolidone, the bromination of which is accompanied by simultaneous oxidation of the five-membered ring to the corresponding pyrazolone [5], products of oxidation of the pyrazolidine ring were not detected in the case of bromination of I. Moreover, isomers that are possible in the bromination reaction also were not found, i.e., the process is regiospecific.

The nitration of I proceeds less unambiguously. Thus nitration with dilute nitric acid (sp. gr. 1.35) in acetic anhydride at −10 to −30°C leads to a mixture of mononitro derivatives IVa-d in low yield containing their dimerization products (V). Nitration with concen-

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