value (γ -3 kcal/mole [1]). It should be noted that $-\Delta H>0$ for these compounds; however, K<1 in methanol. The reason for this is the decrease in the entropy of the system during the formation of the mesoionic form.

The coefficient of μ_{I}^{2} (0.005) is close to the value obtained for the electrostatic model of the solvent-dissolved substance interaction (~0.006 in methanol). The coefficient of μ_{II}^{2} is smaller than the value calculated from the electrostatic model. The latter is evidently associated with the fact that the calculation gives an elevated μ_{II} value. For example, in the case of the 8-hydroxy-N-methylquinolinium ion $\mu = 10.4$ D according to the calculation, whereas the experimentally measured value is ~6 D. It is interesting to note that in conformity with the electrostatic model of interaction in the solution the transition form, for example, methanol to octyl alcohol gives rise to an approximately one unit decrease in the pK_T value as a consequence of the change in ε . The latter is in satisfactory agreement with the experimentally observed change of approximately an order of magnitude in the concentration of the mesoionic form in this case.

LITERATURE CITED

- 1. Yu. A. Bankovskii, The Chemistry of Chelate Compounds of Mercaptoquinoline and Its Derivatives [in Russian], Zinatne, Riga (1978), p. 106.
- 2. A. R. Katritzky (editor), Physical Methods in the Chemistry of Heterocyclic Compounds, Academic Press (1963).
- 3. Z. P. Bruvers and I. V. Zuika, Khim. Geterotsikl. Soedin., No. 3, 387 (1980).

1, 3-DIPHENYL-2-AZAANTHRACENE AND 8-AZA-7-PHENYLBENZO [α] FLUORANTHENE

IN THE DIENE SYNTHESIS

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The diene condensation of 1,3-diphenyl-2-azaanthracene with maleic anhydride proceeds under more severe conditions than the analogous condensation with anthracene. On the basis of an analysis of the PMR data for the adduct obtained it was assumed that isomers of $\alpha, \alpha' - [9,10-dihydro-2-aza-1,3-diphenylanthrylene(9,10)]$ succinic anhydride with respect to the position of the anhydride bridge relative to the pyridine ring are formed in this condensation. 9,10-Dihydro-2-aza-1,3-diphenyl-9,10-(1'-cyanoethylene)anthracene was obtained in the condensation of the same azaanthracene with acrylonitrile. $\alpha, \alpha' - [5H-8-Aza-7-phenylbenzo[\alpha]$ fluoranthrylene(5,12b)] succinic anhydride is formed as a result of the similar condensation of 8-aza-7-phenylbenzo[α] fluoranthene with maleic anhydride, while isomeric (with respect to the position of the nitrile group in the ethylene bridge) 5H-8aza-7-phenyl-5,12b-(cyanoethylene)benzo[α] fluoranthenes were isolated in its condensation with the acrylonitrile. Data from the PMR and IR spectra were used to prove the structures of the adducts of the diene synthesis obtained.

We have previously synthesized heterocyclic nitrogen-containing analogs of anthracene and benzo[a]fluoranthene, viz., 1,3-diphenyl-2-aza-anthracene (I) and 8-aza-7-phenylbenzo[a]-fluoranthene (IV), by catalytic dehydrocyclization of 3-methyl-2,6-diphenyl-4-benzylpyridine [1].

In order to obtain information regarding the reactivities of these heterocyclic compounds and to synthesize new heterocycles we subjected these compounds to the diene synthesis with maleic anhydride, as well as with acrylonitrile. The reactions proceed unambiguous-

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ly with anthracene from the point of view of the structures of the resulting adducts. Isomeric adducts can be formed from azaanthracene and azabenzofluoranthene; isomers with different orientations (Z, E) of the anhydride bridge relative to the pyridine ring are formed in the case of condensation with maleic anhydride, while isomers with different orientations of the nitrile group in the ethylene bridge are formed in the case of condensation with acrylonitrile.

Azaanthracene I condenses with maleic anhydride under more severe conditions than anthracene [2]. The meso positions in azaanthracene are evidently somewhat deactivated as compared with anthracene; this is probably due to the effect of the nitrogen atom and the phenyl groups of the pyridine ring.

 $\alpha, \alpha' - [9, 10-Dihydro-2-aza-1, 3-diphenylanthrylene(9, 10)]$ succinic anhydride (II) is formed from anthracene I and maleic anhydride only at 250°C (in 40% yield). It was isolated in the form of high-melting colorless crystals. 9,10-Dihydro-2-aza-1,3-diphenyl-9,10-(1'-cyanoethylene)anthracene (III) was obtained in 75% yield in the condensation of azaanthracene I with acrylonitrile.



According to the chromatographic data, adduct II is an individual substance. However, on the basis of the characteristics of the PMR spectra it may be assumed that it is a mixture of isomers (Z, E) in a ratio of 2:1. The signals of the 9-H and 10-H protons of the predominant isomer are found at δ 5.35 and 5.24 ppm, while the signals of the bridge 1'-H and 2'-H protons are found at 3.90 ppm. The signals of the 9-H and 10-H protons and the bridge protons of the isomer that is formed in smaller amounts are found at 5.3, 5.02, and 3.65 ppm, respectively. A doublet of a 9-H proton (J = 2.5 Hz) is observed in the PMR spectra of III at 4.93 ppm, while a triplet of a 10-H proton (J = 2.5 Hz) is found at 4.42 ppm. The correctness of the assignment of the signals in the spectrum of this adduct was confirmed by double resonance. Simplification of the multiplet of the 1'-H proton at 2.7-3.0 ppm is observed when the signal of the 9-H proton is irradiated, while the multiplet of the 2'-H proton at 1.8-2.5 ppm is simplified when the signal of the 10-H proton is irradiated. The weak-field shift of the signal of the 9-H proton in adducts II and III is evidently due to the shielding effect of the phenyl group attached to C₁.

 $\alpha, \alpha' - [5H-8-Aza-7-phenylbenzo[\alpha]fluoranthylene(5,12b)]$ succinic anhydride (V) is obtained as colorless high-melting crystals when benzo[α]azafluoranthene IV is heated for a long time with maleic anhydride in benzene. The data from the PMR spectrum confirm its structure; a doublet of a 5-H proton ($J_{5,1}' = 3.0 \text{ Hz}$) is located at 5.51 ppm, a doublet of doublets of a l'-H proton ($J_{1',5} = 3.0 \text{ Hz}, J_{1',2'} = 10.0 \text{ Hz}$) is found at 4.43 ppm, and a doublet of a 2'-H proton is located at 3.82 ppm,



An adduct of benzo [a]azafluoroanthene IV with acrylonitrile was obtained in the form of a mixture of isomers with respect to the orientation of the cyano group in the ethylene bridge. 5H-8-Aza-7-phenyl-5,l2b-(2'-cyanoethylene)benzo[a]fluoranthene (VIa) (mp 208-209°C)and <math>5H-8-aza-7-phenyl-5,l2b-(1'-cyanoethylene)benzo[a]fluoranthene (VIb) (mp 202-203°C) wereisolated from it by means of column chromatography. The conclusion regarding the structuresof these isomers was made on the basis of the multiplicity of the signal of the 5-H proton intheir PMR spectra. In the spectrum of isomer VIa the signal of this proton is a triplet with $<math>\delta$ 4.52 ppm (J = 3.0 Hz), whereas it is a broad doublet in the spectrum of VIb. The PMR spectrum of isomer VIa is similar to the spectrum of III obtained under double-resonance conditions with irradiation of the 9-H proton.

The yield of isomer VIa increases when the time is increased in the condensation of benzo[a]azafluoranthene IV with acrylonitrile, whereas the yield of isomer VIb decreases correspondingly. This is evidently due to the reversibility of the reaction [3] and the different thermodynamic stabilities of VIa and VIb.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CDCl₃ and CF₃COOH were recorded with Hitachi-Perkin-Elmer (90 MHz) and Varian XL-100 (100 MHz) spectrometers with tetramethylsilane as the internal standard. The IR spectra were recorded with a UR-20 spectrometer. Activity II neutral aluminum oxide was used for thin-layer and column chromatography of III and VI, while Silufol UV-254 silica gel was used for II and V.

 $\alpha, \alpha^*-[9,10-\text{Dihydro-2-aza-1},3-\text{diphenylanthrylene}(9,10)]$ succinic Anhydride (II). A mixture of 0.3 g (0.9 mmole) of azaanthracene I and 1.05 g (1.08 mmole) of maleic anhydride was heated at 250-255°C for 20 min. The reaction products were refluxed in 30 ml of a mixture of heptane with ethyl acetate (1:2 by volume), and the hot solution was filtered and cooled to give 0.15 g (40%) of adduct II with mp 271-272°C [from ethyl acetate-heptane (1:3)] and Rf 0.89 [ethyl acetate-heptane (3:1)]. IR spectrum (in mineral oil), v: 1870 and 1810 cm⁻¹ (CO). Found: C 81.2; H 4.4; N 3.0%; M⁺ 429. C_{2.9}H_{1.9}NO₃. Calculated: C 81.1; H 4.4; N 3.3%; M 429.

<u>9,10-Dihydro-2-aza-1,3-diphenyl-9,10-(1'-cyanoethylene)anthracene (III).</u> A mixture of 1 g (3 mmole) of azaanthracene I and 2.12 g (40 mmole) of acrylonitrile was heated in a sealed ampul at 170-180°C for 4 h. It was then cooled and poured into 30 ml of a mixture of ethyl acetate with heptane (1:2 by volume). The resulting precipitate was removed by filtration to give 0.87 g (75%) of adduct III with mp 169-170°C [from ethyl acetate-heptane (2:1)] and R_{f} 0.36 [ethyl acetate-hexane (1:4)]. PMR spectrum, δ : 2.7-3.0 (1H, m, 1'-H) and 1.8-2.5 ppm (2H, m, CH₂). IR spectrum (in KBr), v: 2246 cm⁻¹ (CN). Found: C 87.4; H 5.2; N 7.2%; M⁺ 384. C_{2e}H₂₀N₂. Calculated: C 87.6; H 5.2; N 7.3%; M 384.

 $\frac{\alpha, \alpha'-[5H-8-Aza-7-phenylbenzo[a]fluoranthylene(5,12b)] succinic Anhydride (V). A solution of 0.3 g (0.9 mmole) of azabenzo[a]fluoranthene IV and 0.45 g (4.5 mmole) of maleic anhydride in 15 ml of benzene was refluxed for 18 h, after which it was cooled, and the resulting precipitate was removed by filtration to give 0.15 g (44%) of adduct V with mp 227-228°C [from ethyl acetate-heptane (2:1)] and R_f 0.88 [ethyl acetate-heptane (3:1)]. IR spectrum (in mineral oil), v: 1850 (shoulder) and 1790 cm⁻¹ (CO). Found: C 81.5; H 3.9; N 3.2%; M⁺ 427. C₂₉HL₂NO₃. Calculated: C 81.5; H 4.0; N 3.3%; M 427.$

 $\frac{5H-8-Aza-7-phenyl-5,12b-(2'-cyanoethylene)benzo[a]fluoranthene (VIa) and 5H-8-Aza-7-phenyl-5,12b-(1'-cyanoethylene)benzo[a]fluoranthene (VIb). A) A mixture of 1 g (3 mmole) of azabenzo[a]fluoranthene IV and 2.12 g (40 mmole) of acrylonitrile was heated in a sealed ampul at 185-190°C for 4 h, after which it was cooled and treated with 30 ml of a mixture of ethyl acetate with heptane (1:2 by volume). The resulting precipitate was separated to give 0.62 g of VIa with mp 208-209°C [from ethyl acetate-heptane (1:1)] and Rf 0.46 [ethyl acetate-heptane (1:2)]. PMR spectrum, & 3.21 (1H, q, CHCN) and 2.2-2.8 ppm (2H, m, CH₂). IR spectrum (in KBr), v: 2246 cm⁻¹ (CN). Found: C 88.0; H 4.7; N 7.3%; M⁺ 382. C₂₀H₁₀N₂. Calculated: C 87.9; H 4.7; N 7.3%; M 382. The residue (0.35 g, mp 192-195°C) obtained from the mother liquor after separation of VIa was chromatographed with a column [h = 20 cm, d = 2 cm, elution with heptane-ethyl (10:1)]. The initial substance isolated was 0.23 g (20%) of adduct VIb with mp 202-203°C (with the same mixture of ethyl acetate and heptane) and Rf 0.59 [ethyl acetate-heptane (1:2)]. PMR spectrum, &: 1.8-2.6 ppm (4H, m CHCN and CH₂). IR spectrum (in KBr), v: 2248 cm⁻¹ (CN). Found: C 87.9; H 4.7; N 7.3%; M⁺ 382. C₂₀H₁₀N₂.$

Calculated: C 88.0; H 4.7; N 7.3%; M 382. The next substance isolated was 0.05 g of adduct VIa (for an overall yield of 58%).

B) A total of 0.53 g (42%) of adduct VIa and 0.39 g (33%) of adduct VIb were obtained from 1 g (3 mmole) of IV and 2.12 g (40 mmole) acrylonitrile after heating in a sealed ampul at $185-195^{\circ}$ C for 1 h.

LITERATURE CITED

 N. S. Prostakov, Mario Torres, A. V. Varlamov, and G. A. Vasil'ev, Khim. Geterotsikl. Soedin., No. 5, 648 (1979).

2. E. Clar, Chem. Ber., <u>64</u>, 1682 (1931).

3. W. E. Bachmann and M. C. Kloetzel, J. Am. Chem. Soc., 60, 481 (1938).

ELECTRONIC ABSORPTION SPECTRA AND STRUCTURES OF THE CONJŪGATE ACIDS OF 5-HYDROXY- AND 5-AMINOANTHRAQUINONEPYRIDINES

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The structures of 5-hydroxy and 5-amino derivatives of naphtho[2,3-h]quinoline-7,12-dione (anthraquinonepyridine) and their conjugate acids were investigated by experimental and computational [Pariser-Parr-Pople (PPP)] methods. The hydroxy derivative exists in the keto form, while the cation of the hydroxy form is formed during protonation; the amino derivative exists in the amino form but is converted to a cation with an imino structure upon protonation. In both cases the addition of a proton is accompanied by rearrangement of the π -electon structure of the molecules. The assignment of the S_{π,π^*} transitions in the electronic spectra of the bases and their conjugate acids is given on the basis of a quantum-chemical calculation.

Anthraquinonepyridine (naphtho[2,3-h]quinoline-7,12-dione) compounds that contain a substituent in the 5 position with a hydrogen atom that has proton lability are capable of tautomerism due to transfer of the proton to the heteroring nitrogen atom. This sort of tautomerism has been demonstrated for 5-hydroxy-substituted compounds (I) [1] and has been proposed for 5-amino-substituted compounds (II) [2]. In the present research we made an attempt to estimate the relative stabilities of the possible tautomers and their conjugate acids on the basis of quantum-chemical calculations and compared the calculated electronic spectra with the experimental spectra.

Stabilities of the Tautomers

It is apparent from Table 1 that of the three tautomeric forms of I and II, according to the heats of atomization ΔH , the most stable form for I is Ib, while structure IIa is the most stable form for II. It follows from an analysis of the energies of the σ and π bonds that the π -bond energy is responsible for the greatest stability of one of the three forms. In fact, the σ -bond energy for all forms of I and II remains virtually unchanged, while the π -bond energy undergoes considerable changes; E_{π} has the greatest value for form Ib in the case of the 5-hydroxy derivative, while E_{π} has the greatest value for form IIa in the case of the 5-amino derivative. A second stabilizing factor of the corresponding tautomer in solutions and in the condensed state is the solvation energy. It follows from the calculation that the coefficient of solvation (M_{SOlv}) of form Ib in the case of the hydroxy derivative is greater by a factor of approximately two than in the case of the remaining forms. For the stable tautomer of the 5-amino derivative, on the other hand, the coefficient of solvation is smaller by a factor of approximately two than for the next energically advantageous tautomer.

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