TABLE 2. Characteristics of the Substances Obtained

Compound	mp, °C	Found, %			Empirical formula	Calc., %		
		C	H	N		C	H	N
IX	108—110	86,2	8,4	6,4	$C_{18}H_{21}N$	86,1	8,4	6,6
X	82—82,5	86,9	8,3	4,8	$C_{22}H_{27}N$	86,5	8,8	4,6
XI	118—119	88,4	7,6	3,7	$C_{26}H_{27}N$	88,4	7,7	3,9
XII	140—141	81,6	7,6	3,7	$C_{28}H_{31}NO_2$	81,3	7,6	3,4
XV	70—70,5	79,4	8,1	—	$C_{17}H_{20}O_2$	79,7	7,9	—
XXV	145—146	82,7	6,1	3,8	$C_{27}H_{23}NO_2$	82,5	5,9	3,6

of the corresponding hydrogenated mixtures. 1,5-Diphenylpentane-1,5-diol (XV) crystallized on standing.

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2,3,3-TRIMETHYL-3H-PYRROLO[3,2-c]QUINOLINES AND POLYMETHINE DYES BASED ON THEM

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831.1'832.5.07:543.42

2,3,3-Trimethyl-3H-pyrrolo[3,2-c]quinoline and its 8-methoxy derivative were obtained from methyl isopropyl ketone 4-quinolylhydrazones. These bases form quaternary salts at the azine nitrogen atom, from which polymethine dyes were obtained. The changes in the absorption spectra of the dyes in solutions with various acidities were examined.

Luminescence and the generation of deeply colored form IA have been achieved in the case of dye I, which is a 3H-pyrrolo[2,3-b]pyridine derivative, by excitation of the more highly colored protic salt (IB) in connection with the loss by the latter of a proton in the excited state [1]. Such systems should be of promise as active laser media [2].

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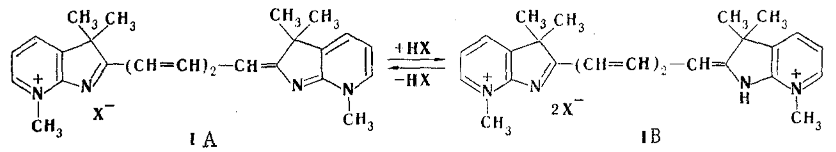
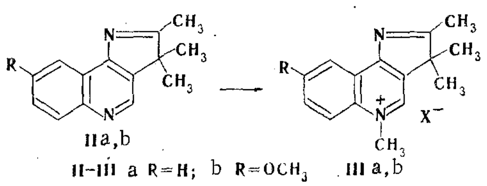


In order to investigate similarly constructed compounds we accomplished the synthesis of trimethylpyrroloquinolines IIa,b, the quaternary salts (IIIa, b) of which were used to obtain polymethine dyes.

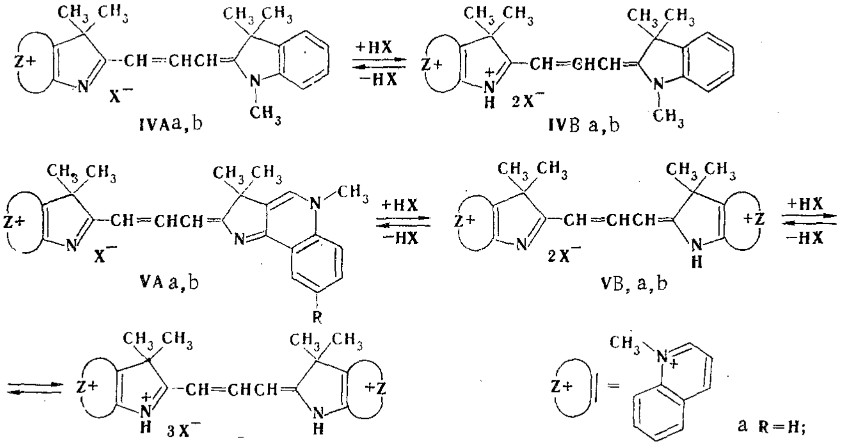


Bases IIa, b were obtained by Fischer indolization of methyl isopropyl ketone 4-quinolylhydrazones (VIa, b). As in the case of the similarly constructed pyrrolo[2,3-b]- and -[3,2-c]pyridines [3-5] and 1H-pyrrolo[3,2-c]quinolines [6], cyclization in acidic media was unlikely because of passivation of the quinoline ring. The conversion of quinolylhydrazone VIa to base IIa was therefore carried out by heating with a catalytic amount of zinc chloride, and its 6-methoxy derivative (VIb) was converted to base IIb in refluxing ethylene glycol.

Structures IIa,b for the bases obtained were confirmed by the PMR spectra.

Although pyrroloquinolines II have two basic centers, monoquaternary salts (IIIa, b) are formed in the case of quaternization with dimethyl sulfate or methyl iodide. In this case alkylation takes place at the azine nitrogen atom; this was determined unambiguously from the absorption spectra of the polymethine dyes obtained from these salts.

Salts IIIa, b react readily with 1,3,3-trimethyl-2-formylmethyleneindole in refluxing acetic anhydride to give unsymmetrical carbocyanines (IVa, b), but they are virtually inert under the standard conditions of the synthesis of symmetrical carbocyanines with ethyl orthoformate. Dyes Va, b, were obtained only when the orthoester was replaced by the more active diethoxymethyl acetate



The rather deep color of neutral methanol solutions of symmetrical dyes VA (Fig. 1, curves 1 and 4), which are formed without the admixture of other dyes, provides a basis to assume the presence in their molecules of a long conjugation chain, which is possible only in the case of quaternization of the pyridine ring nitrogen atom. If this were not so, a shorter conjugation chain should be formed in the case of alkylation of the pyrrolenine nitrogen atom, and one might have expected absorption maxima at 550-600 nm, as in the case of substituted indocarbocyanines [7].

The correctness of the determination of the site of alkylation is also confirmed by the change in the color of dyes V and IV in solutions with various acidities. The presence in their molecules of two (symmetrical dyes V) or one (unsymmetrical dyes IV) nitrogen atom with free electron pairs that do not participate in conjugation suggests the possibility of the

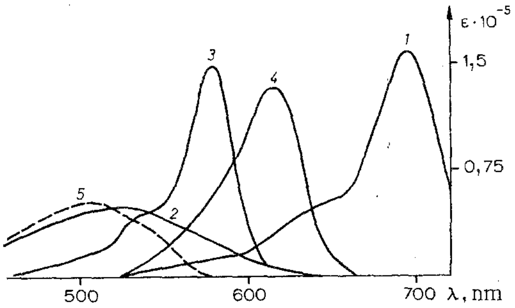
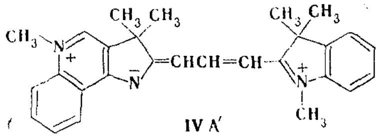


Fig. 1. Absorption spectra of dyes Va (1-3) and IVa (4, 5): 1) and 4) in methanol; 2) in a 5% solution of acetic acid in methanol; 3) and 5) in a 5% solution of HCl in methanol.

addition of protons to these centers without disruption of the conjugation chain. A broad absorption band that is shifted to the short-wave region is observed for a 5% methanol solution of acetic acid in the case of dye Va (Fig. 1). This corresponds to the formation of form VBa with an unsymmetrical distribution of the electron density in the chromophore that passes from the nitrogen atom of the quinoline part of one ring to the nitrogen atom of the pyrrolenine part of the second ring. Contraction of the absorption band and deepening of the color, although not to the extent observed in the neutral solution, are again observed in more acidic solutions (a 5% methanol solution of HCl) (Fig. 1). This is in complete agreement with the formation of form VCa with a symmetrical distribution of the electron density in the chromophore bounded by the pyrrolenine rings of both rings.

In contrast to symmetrical dyes VA, dyes IVA add a proton only in methanol solutions of hydrochloric acid with the formation of form IVB (Fig. 1, curve 5). In the case of a neutral solution the maxima of unsymmetrical dyes IVA are close to the arithmetic mean of the maxima of the corresponding symmetrical dyes (VA and indocarbocyanine). The absence of a deviation constitutes evidence for the close electron-donor characters of the rings that form these dyes [8, 9]. The rather narrow absorption band of dye IVAa (Fig. 1, curve 4) is in agreement with symmetry of the electron density in its molecule.

The 4-quinoline ring in the dyes is a better electron donor than the indolenine ring [8], and the corresponding unsymmetrical dye with the same length of the chromophore as in dye IV should have appreciable deviation. The decrease in the electron-donor character in the case of transformation of the 4-quinoline ring to the pyrroloquinoline ring of dyes IV is due to the greater electronegativity of the sp^2-hybridized nitrogen atom as compared with the methylidyne group. This means that structure IVA' should be taken into account in addition to the two boundary structures with a positive charge on one of the terminal heterorings in the description of the distribution of the electron density in the molecules of dyes IVA.



IV A'

The addition of a proton in acidic solution to the nitrogen atom of the pyrroloquinoline system increases its electronegativity. The indolenine ring is therefore a better electron donor in form B of dyes IV. The great asymmetry of the electron density of the chromophore, which is manifested in the great deviation (49 nm) and the broad absorption band of dye IVa in acidic solution, is a consequence of this (Fig. 1).

EXPERIMENTAL

The PMR spectra of the compounds were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The electronic spectra were recorded with an SF-10 spectrophorometer.

4-(3-Methyl-2-butylidenehydrazino)quinoline (VIa) and Its 6-Methoxy Derivative (VIb). These compounds were obtained by heating a mixture of the corresponding quinolylhydrazines [10] and 50% excess methyl isopropyl ketone at 100°C for 3 h. The water and excess ketone were removed by vacuum distillation with benzene, and the hydrazones were used without purification for the cyclization.

2,3,3-Trimethyl-3H-pyrrolo[3,2-c]quinoline (IIa). A mixture of 2.3 g (1 mmole) of VIa and 40 mg of anhydrous zinc chloride was heated at 200°C (in the bath) for 3 h, and the melt was triturated with 10% sodium hydroxide solution. The precipitate was washed with water, dissolved in benzene, and chromatographed on aluminum oxide. Sublimation in vacuo gave 1.1 g (48%) of a product with mp 116°C (from hexane). PMR spectrum (CCl_4): 8.69 (1H, s, 4-H), 7.18-8.45 (4H, m, aromatic), 2.27 (3H, s, 2-CH_3), and 1.30 ppm [6H, s, 3,3-$(CH_3)_2$]. Found: C 79.8; H 6.6; N 13.3%. $C_{14}H_{14}N_2$. Calculated: C 80.0; H 6.6; N 13.3%.

8-Methoxy-2,3,3-trimethyl-3H-pyrrolo[3,2-c]quinoline (IIb). This compound was obtained by refluxing a solution of 2.6 g (1 mmole) of VIb in 12 ml of ethylene glycol for 3 h. The reaction mixture was diluted with water, and the precipitate was separated and chromatographed in benzene on aluminum oxide. Recrystallization from aqueous methanol gave 0.8 g (33%) of a product with mp 97°C (from heptane). PMR spectrum (CCl_4): 8.44 (1H, s, 4-H), 7.78 (1H, d, J = 9.2 Hz, 6-H), 7.50 (1H, d, J = 3.0 Hz, 9-H), 7.05-7.24 (1H, m, 7-H), 3.89 (3H, s, CH_3O), 2.23 (3H, s, 2-CH_3), and 1.30 ppm [6H, s, 3.3-$(CH_3)_2$]. Found:C 74.8; H 6.6; N 11.5%. $C_{15}H_{16}N_2O$. Calculated: C 75.0; H 6.7; N 11.7%.

2,3,3,5-Tetramethyl-3H-pyrrolo[3,2-c]quinolinium Bromide (IIIa, X = Br) and Its 8-Methoxy Derivatives (IIIv, X = Br). A mixture of 1 mmole of IIa, b and 2 ml (20 mmole) of dimethyl sulfate was maintained at room temperature for 24 h, after which it was diluted with ether, and the precipitated salt was removed by filtration and washed with ether. The yields of salts IIIa, b in the form of methylsulfates were close to quantitative. For analysis, the anion was exchanged for bromide in aqueous solution. Salt IIIa decomposed at 272°C (from water). Found: Br 25.9; N 9.1%. $C_{15}H_{17}BrN_2$. Calculated: Br 26.2; N 9.2%. Salt IIIb decomposed above 300°C (from water). Found: Br 23.1; N 8.2%. $C_{16}H_{19}BrN_2O$. Calculated: Br 23.3; N 8.4%.

2-[3-(1,3-Dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)propen-1-yl]-3,3,5-trimethyl-3H-pyrrolo[3,2-c]quinolinium Perchlorate (IVAa, X = ClO_4) and Its 8-Methoxy Derivative (IVAb, X = ClO_4). These compounds were obtained by refluxing a mixture of 1 mmole of salt IIIa or IIIb in the form of the methylsulfates, 4 mmole of 1,3,3-trimethyl-2-formylmethyleneindoline, and 5 ml of acetic anhydride for 3 min. After dilution of the reaction mixture with ether, the dye crystals were removed by filtration, washed with ether, dissolved in boiling methanol, and precipitated with sodium perchlorate. This procedure gave 315 mg (62%) of dye IVAa, which decomposed at 230°C (from methanol). UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-4}$): in methanol, 618 nm (13.2); in a 5% solution of HCl in methanol, 516 nm (5.1). Found: Cl 7.1; N 8.4%. $C_{28}H_{30}ClN_3O_4$. Calculated: Cl 7.0; N 8.3%. This procedure was also used to obtain 365 mg (68%) of dye IVAb, which decomposed at 281°C (from methanol). UV spectrum λ_{max} ($\varepsilon \cdot 10^{-4}$): in methanol, 620 (15.4); in a 5% solution of HCl in methanol, 522 nm (6.7). Found: Cl 6.5; N 7.7%. $C_{29}H_{22}ClN_3O_5$. Calculated: Cl 6.6; N 7.8%.

2-[3-(3,5-Dihydro-3,3,5-trimethyl-2H-pyrrolo[3,2-c]quinolin-2-ylidene)propen-1-yl]-3,3,5-trimethylpyrrolo[3,2-c]quinolinium Methylsulfate (VAa, X = CH_3SO_4) and Its 8,8'-Dimethoxy Derivative (VAb, X = CH_3SO_4). A 2-mmole sample of triethylamine was added to a refluxing mixture of 1 mmole of salt IIIa or IIIb in the form of methylsulfates, 2 mmole of diethoxymethyl acetate, and 5 ml of acetic anhydride, and the mixture was refluxed for 5 min. It was then cooled, and the dye crystals were removed by filtration. This procecure gave 160 mg (56%) of dye VAa, which decomposed at 236°C (from ethanol). UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-4}$): in methanol, 696 (15.8); in a 5% solution of acetic acid in methanol, 530 (5.0); in a 5% solution of HCl in methanol, 583 nm (14.9). Found: N 9.9; S 5.6%. $C_{32}H_{34}N_4O_4S$. Calculated: N 9.8; S 56.%. This procedure gave 195 mg (62) of dye VAb, which decomposed at 301°C (from methanol). UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-4}$): in methanol. 704 (17.0); in a 5% solution of acetic acid in methanol, 534 (4.8); in a 5% solution of HCl in methanol, 595 nm (14.3). Found: N 9.0; S 5.0%. $C_{34}H_{38}N_4O_6S$. Calculated: N 8.9; S 5.1%.

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HYDROHALOGENATION OF 1- AND 2-VINYLINDAZOLES

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The electronic absorption spectra of 1-vinyl- and 2-vinylindazoles and their protonated forms were analyzed. The spectra were subjected to quantum-chemical calculation within the Pariser—Parr—Pople (PPP) π-electron approximation, and the thermodynamic parameters of the reaction of indazoles with phenol (K_{as} and ΔH) were calculated. It is shown that 1-vinylindazole adds hydrogen halides to the nitrogen atom or the double bond of the vinyl group, depending on the reaction temperature. The formation of hydrohalides is characteristic for 2-vinylindazole.

We have previously accomplished the synthesis of 1- and 2-vinylindazoles (I, II) by the reaction of acetylene with indazole in the presence of catalysts [1]. The present research is devoted to a study of the addition of hydrogen chloride and bromide to vinylindazoles and their protonation by means of UV spectroscopy.

The spectra were analyzed in comparison with the results of quantum-chemical calculations within the Pariser—Parr—Pople (PPP) approximation. The experimental and calculated values of the energies, the intensities of the electron transitions, and the positions of the maxima of the absorption bands in the UV spectra are presented in Table 1. The satisfactory agreement between the calculated and experimental values for the selected system of semiempirical parameters was demonstrated in [2].

The spectrum of indazole (III) is characterized by three absorption regions. A long-wave band with a resolved vibrational structure (the distance between its components is ~700 cm^{-1}) that is characteristic for aromatic compounds corresponds to the first electron transition (E_{calc} = 4.49 eV). The second band at 253 nm is also due to one electron transition (E_{calc} = 5.22 eV); its vibrational structure is smoothed out, and the distance between the individual maxima is ~1000 cm^{-1}. The short-wave band at 203 nm is determined by two electron transitions — 5.88 and 5.78 eV. The spectrum of the 1-ethyl derivative (IV) is similar to the spectrum of indazole itself. This constitutes evidence for the existence of indazole III in the 1-H form and is in agreement with previous studies [3]. Replacement of the ethyl group in the 1 position of the ring by a vinyl group leads to a decrease in the calculated values of the energies of the electron transitions. This shows up experimentally in the bathochromic shift of the long-wave band from 294 nm to 308 nm with an increase in its extinction.

It follows from an analysis of the configuration interactions and the coefficients of population of the molecular orbitals (MO) that the nature of the first four electron transitions in vinylindazole I remains unchanged as compared with 1-H-indazole. The high value of the extinction coefficient (ε) of the band at 247 nm can be explained by the contribution of a third electron transition to it in addition to the second. The energy of the third electron transition decreased from 5.78 eV to 5.37 eV. The band at 209 nm is due to one electron

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