a solution of sodium carbonate, and the resulting precipitate was removed by filtration. The yellowish precipitate was purified by reprecipitation from DMF by the addition of water, after which it melted above 300°C with decomposition. UV spectrum, λ_{max} (log ε): 253 (4.24); 328 nm (4.54). Found: C 81.8; H 5.7; N 12.7%. $C_{23}H_{19}N_3$. Calculated: C 81.9; H 5.7; N 12.5%.

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SYNTHESIS AND ABSORPTION—FLUORESCENCE PROPERTIES OF 1,4-BIS(Δ^2-PYRAZOLIN-3-YL)- AND 1,4-BIS(3-PYRAZOLYL)BENZENES

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1,4-Bis(Δ^2-pyrazolin-3-yl)benzene derivatives were synthesized by the reaction of dibenzal-p-diacetylbenzene or 1,4-bis(β-dimethylaminopropionyl)benzene with various hydrazines. Some of these derivatives were converted to the corresponding 1,4-bis(3-pyrazolyl)benzene derivatives by oxidative dehydrogenation with sulfur. The absorption and fluorescence spectra of the synthesized compounds were measured, and the fluorescence quantum yields were determined.

Of the known organic luminophores, Δ^2-pyrazoline derivatives are widely used [1]. Of particular interest are 1,4-bis(Δ^2-pyrazolin-3-yl)benzenes (I), solutions of which not only luminesce intensely, but also are capable of generating laser emission [2]. The compounds of this type that are described in the literature generally contain aromatic substituents in the 1, 1', 5, and 5' positions. All of these compounds luminesce at 470-510 nm, whereas compounds that luminesce in the UV and blue-violet regions are of great interest today for laser technology. In this connection it seemed of interest to study the effect of substituents in the 1 and 5 positions of the pyrazoline rings on the luminescence spectra in order to obtain compounds of the I type that luminesce in the UV region. In addition, it was of interest to synthesize analogous dehydrogenated (aromatic) compounds, viz., 1,4-bis(3-pyrazolyl)benzenes (III, V), the luminescence properties of which have not been described in the literature.

Compounds Ia-c were obtained by reaction of dibenzal-p-diacetylbenzene (II) with substituted hydrazines [3]. In the case of the reaction of II with unsubstituted hydrazine in isopropyl alcohol we were unable to isolate any individual compound from the reaction mix-

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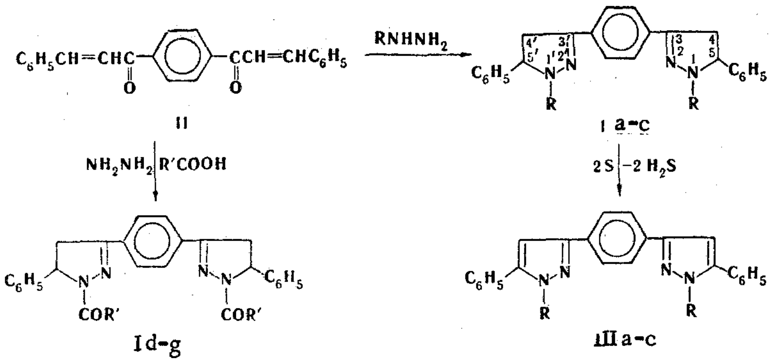
ture. The two bifunctional compounds — dichalcone II and the unsubstituted hydrazine — evidently form polymeric products in this case.

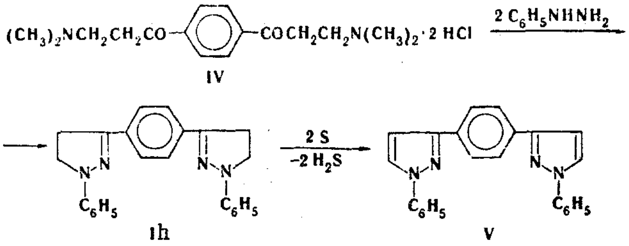
When aliphatic carboxylic acids were used as the solvent, 1,1'-diacyl derivatives Id-g were obtained in good yields from the unsubstituted hydrazine and dichalcone II.



I, III a R=C_6H_5; b R=p-$CH_3OC_6H_4$; c R=$C_6H_5CH_2$; I d R'=CH_3; e R'=C_2H_5; f R'=n-C_3H_7; g R'=i-C_3H_7

We attempted to obtain the same compounds by reaction of off-the-shelf acylhydrazines (R = COAlk) with dichalcone II; however, we were unable to isolate the expected products. The starting compounds were recovered when the components were refluxed in alcohols, whereas the acylhydrazine was acylated by the acid to give a diacylhydrazine when it was refluxed in acetic acid. It may be assumed that the more active unsubstituted hydrazine reacts initially with the dichalcone, after which the product is acylated by the carboxylic acid to give 1,1'-diacyl derivatives Id-g.

We obtained 5- and 5'-unsubstituted bis(pyrazolinyl)benzene Ih by condensation of 1,4-bis(β-dimethylaminopropionyl)benzene hydrochloride (the double Mannich base of p-diacetylbenzene) (IV) with phenylhydrazine by refluxing in methanol.



The synthesis of this bispyrazoline, which is distinguished by the fact that the components are refluxed in 50% acetic acid in the presence of sodium acetate, has been described [4]. The melting point of Ih presented in [4] was 110-120°C (dec.), whereas the compound that we obtained melts sharply at 281-282°C. The fact that the compound that we obtained actually corresponds to structure Ih is confirmed by the results of elementary analysis, the spectral data presented in Table 2, and the mass spectrum, which contains a

TABLE 1. 1,4-Bis(Δ^2-pyrazolin-3-yl)benzene (I) and 1,4-Bis-(3-pyrazolyl)benzene (III, V) Derivatives

Compound	mp, °C	R_f	Found, % C	Found, % H	Found, % N	Empirical formula	Calc., % C	Calc., % H	Calc., % N	Yield, %
Ia	263—264	0,62	83,7	5,8	10,3	$C_{36}H_{30}N_4$	83,4	5,8	10,8	21
Ib	249—250	0,83	78,3	5,6	9,5	$C_{38}H_{34}N_4O_2$	78,9	5,9	9,7	16
Ic	74—75	0,85	83,7	6,4	9,8	$C_{38}H_{34}N_4$	83,5	6,3	10,3	63
Id	310—311	0,13	74,0	5,8	12,5	$C_{28}H_{26}N_4O_2$	74,6	5,8	12,4	52
Ie	225—226	0,35	75,4	6,2		$C_{30}H_{30}N_4O_2$	75,3	6,3		38
If	164	0,45	76,0	6,7		$C_{32}H_{34}N_4O_2$	75,9	6,8		80
Ig	201—202	0,58	76,3	7,0		$C_{32}H_{34}N_4O_2$	75,9	6,8		77
Ih	281—282	0,51	78,6	6,1		$C_{24}H_{22}N_4$	78,7	6,1		11
IIIa	260—261	0,75	84,1	5,2	10,9	$C_{36}H_{26}N_4$	84,0	5,1	10,9	48
IIIb	268—269	0,72	79,3	5,3		$C_{38}H_{30}N_4O_2$	79,4	5,3		21
IIIc	207—208	0,62	83,9	5,6	10,2	$C_{38}H_{30}N_4$	84,1	5,6	10,3	40
V	247—250	0,50	78,2	5,0		$C_{24}H_{18}N_4$	79,5	5,0		72

TABLE 2. Spectral-Luminescence Characteristics of 1,4-Bis(Δ^2-pyrazolin-3-yl)benzene (I) and 1,4-Bis(3-pyrazolyl)benzene (III, V) Derivatives

Compound	IR spectrum, cm^{-1}	Dioxane				Acetonitrile			
		absorption		emission		absorption		emission	
		λ_{max} (± 2 nm)	lg ε	λ_{max} (± 2 nm)	quantum yield	λ_{max} (± 2 nm)	lg ε	λ_{max} (± 2 nm)	quantum yield
Ia	1600, 1500, 1380, 880, 840, 750, 700	310 418	4,10 4,82	474 500	0,8	310 416	3,91 4,52	492	0,8
Ib	1608, 1500, 1380, 1240, 1040, 880, 840, 770, 710	329 430	4,11 4,72	503	0,8	330 425	4,02 4,57	530	0,4
Ic	1600, 1500, 1360, 840, 770, 710	320	4,52	422	0,2				
Id	1660, 1590, 1500, 1430, 1320, 850, 740	332 sh 344 358 sh	4,50 4,66 4,55	380 400 422 sh	0,6	326 sh 341 354	4,66 4,72 4,59	370 400 422 sh	0,7
Ie	1680, 1590, 1490, 1430, 1370	336 sh 347 363 sh	4,61 4,72 4,61	382 403 424 sh	0,5	329 sh 343 356 sh	4,49 4,60 4,48	384 sh 400	0,8
If	1670, 1590, 1500, 1430, 1360	334 sh 347 363 sh	4,68 4,75 4,62	389 403 424 sh	0,5	330 sh 343 356 sh	4,63 4,70 4,57	384 sh 400 422 sh	0,7
Ig	1670, 1600, 1500, 1430, 1360, 845, 770, 708	334 sh 348 363 sh	4,43 4,53 4,42	384 404 424 sh	0,5	330 sh 343 358 sh	4,72 4,81 4,61	384 400 422 sh	0,7
Ih		310 419	4,08 4,81	476 504 sh	0,6				
IIIa	1603, 1500, 860, 810, 770, 710	302	4,86	344 sh 358	0,7	300	4,70	344 sh 358	0,4
IIIb	1610, 1500, 1260, 1030, 840, 810, 770, 710	300	4,73	390	0,4	300	4,56	400	0,4
IIIc	1608, 1500, 860, 810, 770, 710	285	4,60	322 336 350	0,3	284	4,69	322 336 358	0,3
V		318	4,78	345 361 377 sh	0,8				

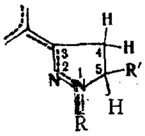
molecular-ion peak with m/e 366. In addition, this compound gives a qualitative Knorr reaction for a 1-arylpyrazoline — it gives a blue coloration under the influence of concentrated sulfuric acid in the presence of potassium dichromate. The conversion of Ih to the corresponding aromatic compound (V) also constitutes indirect evidence for the structure of Ih.

Bis(pyrazolyl)benzenes IIIa-c and V were obtained from the corresponding pyrazoline derivatives Ia-c, h by oxidative dehydrogenation with elementary sulfur [6]. The constants and yields of the compounds obtained are presented in Table 1.

The IR spectra (KBr pellets), the absorption spectra in the UV and visible regions, and the fluorescence spectra in two solvents were measured for the synthesized compounds.

The principal characteristic absorption bands in the IR spectra of bis(pyrazolinyl)-benzenes I (Table 2) are in agreement with the absorption bands of the analogous compounds [3]. In addition, the IR spectra of N-acyl derivatives of pyrazolines Id-g contain an intense band at 1680 cm^{-1}, which corresponds to the C=O stretching vibrations of N-acyl groups.

The electronic spectra of bis(pyrazolinyl)benzenes Ia-h contain two intense absorption bands at 310-430 nm. As in the case of other compounds of the pyrazoline series, substituents in the 5 and 5' positions have a weak effect on the character of the spectrum (e.g., Ia and Ih have very similar spectra, although the first compound has two phenyl groups in the 5 and 5' positions, while the second does not). Substituents in the 1 and 1' positions, on the other hand, have a strong effect on the position of the absorption maximum. This is evidently due to the fact that the substituent in the 5 position of the pyrazoline ring is not included in the overall π-conjugated system of the molecule, while the π electrons in the 1 position are conjugated with the p, π system of the heteroring and the aromatic ring in the 3 position.



The longest-wave absorption is therefore observed for p-anisyl derivative Ib (R = p-$CH_3OC_6H_4$), which has the logest conjugation chain, and the shortest-wave absorption is observed for benzyl derivative Ic (R = $CH_2C_6H_5$).

A pronounced shift of the absorption bands to the shortwave region occurs on passing from pyrazoline derivatives Ia-c, h to the corresponding pyrazole derivatives IIIa-c and V. The effect of the substituents in the 1 and 1' positions on the absorption spectra decreases appreciably for these compounds. Thus, in dioxane the long-wave absorption maxima of pyrazoline derivatives with p-anisyl (Ib) and benzyl (Ic) substituents in the 1 and 1' positions differ by 110 nm, whereas in the case of the corresponding pyrazole compounds IIIb and IIIc they differ by only 15 nm. A hypsochromic shift of the absorption maximum occurs when phenyl substituents are introduced in the 5 and 5' positions of the pyrazole derivatives (compare the absorption spectra of IIIa and V); this is not observed in the case of pyrazoline compounds Ia and Ih. This is associated with the fact that the π electrons of the phenyl substituents in the 1 and 5 positions of the pyrazole ring are conjugated with the π-electron system of the heteroring. However, because of the steric hindrance, they deviate somewhat from the plane of the molecule [7]. This leads to a decrease in the conjugation, probably particularly for the substituent in the 1 position, and to a shift of the absorption maximum for IIIa to the shortwave region as compared with V, in which the 1,1'-phenyl groups may be situated in the same plane with the heteroring.

However, as we have already stated, in the case of pyrazoline derivatives the substituents in the 5 and 5' positions are not conjugated with the pyrazole ring and may easily deviate from the plane of the heteroring without thereby interfering (sterically) with the conjugation of the heteroring with the substituents in the 1 and 1' positions.

All of the compounds obtained fluoresce intensely. 1,1'-Diaryl pyrazole derivatives Ia, b, h fluoresce at 474-503 nm, while all of the remaining compounds fluoresce at 320-420 nm. The fluorescence quantum yields (Table 2), which were found to be extremely high (0.3-0.8), were measured for each compound. The most intense fluorescence is observed in acetonitrile, while somewhat less intense fluorescence is observed in dioxane. Pyrazoline derivatives I fluoresced more intensely than the corresponding pyrazole derivatives III and V.

EXPERIMENTAL

Chromatography was carried out on Silufol UV-254 plates and in a thin layer of L 100/250μ silica gel. The chromatograms were developed with UV light or iodine vapors. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with a Hitachi EPS-3T spectrophotometer; the fluorescence spectra were recorded with the same spectrophotometer with the aid of a G-3 fluorescence adapter, which is a small wide-aperture monochromator with a 120-W xenon lamp. The fluorescence was excited with light with a wavelength close to the maximum of the long-wave absorption band of the compound (usually 300 or 365 nm). 2-Aminopyridine (10^{-5} M) in 0.1 N sulfuric acid solution (emission maximum 360 nm, fluorescence quantum yield 0.6 [8]) and quinine bisulfate (10^{-5} M) in 0.1 N sulfuric acid (emission maximum 461 nm, fluorescence quantum yield 0.55 [9]) were used as the standards for the determination of the quantum yields. The quantum yields were calculated by the standard method [9]. The accuracy in the determination was ±30%. The fluorescence spectra were corrected with allowance for the spectral sensitivity of the apparatus determined by means of a tungsten lamp with a known color temperature by the method in [9].

N-Substituted 1,4-Bis(5-phenyl-Δ^2-pyrazolin-3-yl)benzenes (Ia-c). A solution of 0.01 mole of dibenzal-p-diacetylbenzene (II) and 0.05 mole of the corresponding hydrazine in 100 ml of glacial acetic acid was refluxed for 7 h, after which it was cooled, and the precipitate was removed by filtration, washed with glacial acetic acid and water until the wash water was neutral, and dried over $CaCl_2$. The substance was purified by recrystallization from benzene (Ia, b) or by chromatography in a thin layer of silica gel in a benzene–ether system (4:1). The purity of the compounds obtained was monitored by chromatography on Silufol UV-254 in a benzene–ether system (4:1). The constants are presented in Tables 1 and 2.

1,4-Bis(1-acyl-5-phenyl-Δ^2-pyrazolin-3-yl)benzenes (Id-g). A solution of 2 g (6 mmole) of dibenzal-p-diacetylbenzene (II) and 2.8 g (55 mmole) of hydrazine hydrate in 100 ml of the corresponding carboxylic acid was refluxed for 6 h, after which Id was isolated by evaporation of the acid with a rotary evaporator up to half the original volume. The resulting precipitate was removed by filtration and recrystallized from glacial acetic acid. In the remaining cases the reaction mixture was evaporated to dryness, and the residue was dissolved in 100 ml of chloroform. The solution was washed successively with 10% aqueous sodium carbonate solution and water until the wash water was neutral and dried over magnesium sulfate, and the chloroform was evaporated. The product was purified by column chromatography with a 1.5 by 40 cm column filled with silica gel (L 100/250μ) by elution with benzene–ether (1:1) and subsequent recrystallization from benzene (Ie) and cyclohexane (If and Ig). The purity of the compounds obtained was monitored by chromatography in a benzene–ether system (1:3).

1,4-Bis(1-phenyl-Δ^2-pyrazolin-3-yl)benzene (Ih). A solution of 1.75 g (5 mmole) of 1,4-bis(β-dimethylaminopropionyl)benzene hydrochloride (IV) [4] in 20 ml of methanol was added dropwise with stirring at 40-50°C in 30 min to a solution of 1.1 g (10 mmole) of phenylhydrazine in 20 ml of methanol containing 1 ml of 40% NaOH solution, and the mixture was refluxed for 1 h. It was then cooled, and the yellow precipitate was removed by filtration and washed successively with methanol, water, and methanol. The dry precipitate was dissolved in a small amount of benzene, and the solution was filtered through a layer of silica gel. The benzene was evaporated, and the residue was recrystallized from benzene and chromatographed on Silufol UV-254 in a benzene–hexane system (3:1).

1,4-Bis(3-pyrazolyl)benzene Derivatives (IIIa-c, V). A mixture of 0.01 mole of the 1,4-bis(Δ^2-pyrazolin-3-yl)benzene (Ia–c, h) and 0.02 mole of sulfur was heated in a stream of nitrogen at 180-260°C for 4-7 h until hydrogen sulfide evolution ceased. The product was purified by recrystallization from benzene (IIIa) or acetic acid (V) [5] or by TLC on silica gel in benzene–ether systems (6:1 for IIIb and 10:1 for IIIc). The purity of the compounds obtained was monitored by chromatography on Silufol UV-254 in a benzene–ether system (6:1).

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