SYNTHESIS AND SPECTRAL CHARACTERISTICS OF BIS- AND TRIS(Δ^2-PYRAZOLINYL) BENZENES

S. V. Tsukerman, É. V. Danil'chenko,
V. M. Nikitchenko, and V. F. Lavrushin

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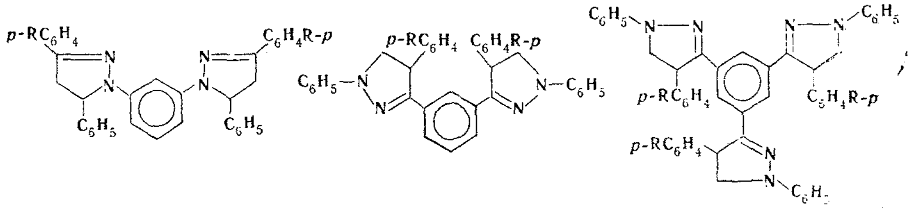
The electronic absorption and fluorescence spectra and the relative quantum yields of 1,3-bis(3-aryl-5-phenyl-Δ^2-pyrazolin-1-yl)- and bis- and tris(1-phenyl-5-aryl-Δ^2-pyrazolin-3-yl)benzenes were measured and are discussed.

Some compounds containing one or two Δ^2-pyrazoline rings have effective luminescence and therefore have found diverse applications [1-3]. In this respect, it seemed of interest to investigate compounds in which two Δ^2-pyrazoline rings in the 1 or 3 positions are connected by a 1,3-phenylene link and also substances with three pyrazoline chromophores in the 1, 3, and 5 positions of the benzene ring.

1,3-Bis(3-aryl-5-phenyl-Δ^2-pyrazolin-1-yl)benzene (Ia and Ib) were obtained by reaction of 1,3-dihydrazinobenzene with the appropriate chalcones and the isomeric bis(Δ^2-pyrazolin-3-yl)benzenes (IIa, b) were synthesized by the action of phenylhydrazine on the appropriate diketones [4]. In order to obtain compounds containing 3-pyrazoline rings (IIIa, b), 1,3,5-tris(cinnamoyl)benzene and its p-chloro-substituted analog were subjected to reaction with phenylhydrazine



I a-b II a-b III a-b

I-III a R = H; b R = Cl

Compounds I-III give the Knorr color reaction [5] and have intense fluorescence. Their IR spectra contain intense bands at 1500-1600 cm^{-1}, which are characteristic for pyrazoline rings [6], and absorption of an amino group at 3200-3600 cm^{-1} is absent.

It is known that the long-wave absorption in the spectrum of 1,3,5-triphenyl-Δ^2-pyrazoline (TPP) is due to charge transfer in the $C_6H_5\underset{|}{C}=N-\underset{|}{N}-C_6H_5$ chromophore grouping [7]. Conjugation is disrupted in Ia and IIa, and as a consequence of this, the maxima of their long-wave absorption and fluorescence bands (Table 1) are shifted hypsochromically, respectively, by 31 and 53 nm and 48 and 50 nm as compared with 1,4-bis(3,5-diphenyl-Δ^2-pyrazolin-1-yl)- and 1,4-bis(1,5-diphenyl-Δ^2-pyrazolin-3-yl)benzene [2].

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In addition, a small bathochromic effect of the absorption (13 and 12 nm) and fluorescence (14 and 3 nm) maxima is observed for Ia and IIa as compared with TPP from which it follows that a weak interaction between the two chromophores is nevertheless realized in this case. A somewhat greater interaction between the pyrazoline rings is observed for 1,3,5-tris(1,5-diphenyl-Δ^2-pyrazolin-3-yl)benzene (IIIa), in which the long-wave shifts are 8 and 7 nm as compared with I and 20 and 10 nm as compared with TPP. A similar phenomenon was noted by Kiprianov for the absorption of dyes with two identical chromophores in the meta positions of the benzene rings and by Lutskii for the interaction of the functional groups in m-substituted benzenes [9]. The bathochromic effect of the fluorescence (11 nm) and the considerable Stokesian shift for Ia as compared with IIa can be ascribed to the fact that joining of pyrazoline rings at the N_1 atom does not promote coplanarity, as a consequence of which the losses to emissionless conversion increase [2]. The introduction of a chlorine atom into the para position, i.e., transition from compounds *a* to b, as one should have expected [10], has almost no effect on the position of the absorption and fluorescence bands.

The fluorescence quantum yields (Y_{fl}) of dyes Ia-b and IIa are close to Y_{fl} for TPP. The accumulation of pyrazoline rings (transition from IIa to IIIa) is accompanied by a decrease in Y_{fl} by a factor of almost two. The presence of chlorine atoms in IIb and IIIb causes an increase in Y_{fl} as compared with the corresponding unsubstituted derivatives.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds (2 mg per 200 mg) were recorded with a UR-20 spectrometer at 600-3800 cm^{-1}. The UV spectra of $2\text{-}4 \cdot 10^{-4}$ M solutions of the compounds in dioxane were recorded with an SF-4A spectrophotometer. The fluorescence spectra and quantum yields were determined with an apparatus consisting of an SF-4 monochromator and an FÉU-37 photoelectric adapter with allowance for a correction for the spectral sensitivity of the apparatus, which was calibrated with an incandescent lamp with a known color temperature. The luminescence was excited with beams (λ 365 nm) isolated from the spectrum of a DRSh-500 mercury-quartz lamp with a UFS-2 light filter. The relative quantum yields were determined by the method in [11]. The quantum yield of TPP was taken as unity.

The purity of the compounds was checked by liquid chromatography in columns over aluminum oxide.

1,3-Bis(cinnamoyl)benzene. This compound, with mp 144° was obtained in 72% yield by the method in [12]. UV spectrum, λ_{max}, nm (log ε):238 (4.34) and 308 (4.34).

1,3-Bis(4-chlorocinnamoyl)benzene. A 1.6-g (0.01 mole) sample of 1,3-diacetylbenzene and 2.8 g (0.02 mole) of 4-chlorobenzaldehyde were dissolved by heating in 50 ml of alcohol, and 5 ml of 20% NaOH was added dropwise with stirring. After 24 h, the precipitated crystals were removed by filtration, washed with water and alcohol, and recrystallized from isopropyl alcohol—acetic acid (1:5) to give 2.0 g (50%) of a product with mp 225°. Found: C 70.7; H 4.0; Cl 17.5%. $C_{24}H_{16}Cl_2O_2$. Calculated: C 70.8; H 3.9; Cl 17.4%. UV spectrum λ_{max}, nm (log ε): 240 (4.25) and 318 (4.23).

1,3-Bis(1,5-diphenyl-Δ^2-pyrazolin-3-yl)benzene (IIa). A 3.38-g (0.01 mole) sample of 1,3-bis(cinnamoyl)benzene was dissolved by heating in a small amount of acetic acid, and 2.16 g (0.02 mole) of freshly distilled phenylhydrazine was added. The mixture was then refluxed for 3 h. The precipitate that formed when the mixture was cooled was removed by filtration and washed with alcohol until the phenylhydrazine had been removed. The product was purified by chromatography in benzene solution over aluminum oxide and was recrystallized from benzene—isopropyl alcohol (1:15) to give 2.3 g (45%) of IIa with mp 208°. Found: C 83.5; H 6.1; N 10.9%. $C_{36}H_{30}N_4$. Calculated C 83.4; H 5.8; N 10.8%.

TABLE 1. Spectral Characteristics of Bis- and Tris(Δ^2-pyrazolinyl)-benzenes

Compound	Absorption	Fluorescence		Stokesian shift, $\Delta\nu$, cm^{-1}
	λ_{max}, nm (log ε)	λ_{max}, nm	Y_{fl}	
Ia	238 (4,36), 292 (4,10), 369 (4,51)	460	0,97	5360
Ib	242 (4,50), 294 (4,11), 374 (4,55)	464	0,92	5190
IIa	246 (4,25), 310 (3,95), 368 (4,45)	449	1,08	4900
IIb	244 (4,40), 314 (3,98), 367 (4,44)	452	1,65	5130
IIIa	234 (4,52), 270 (4,27), 376 (4,69)	456	0,45	4670
IIIb	232 (4,56), 286 (4,22), 377 (4,64)	458	0,58	4720
TPP	242 (4,18), 315 (3,89), 356 (4,30)	446	1,00	5670

1,3-Bis[1-phenyl-5-(4-chlorophenyl)-Δ^2-pyrazolin-3-yl-benzene) (IIb). This compound was obtained by the preceding method to give 2.95 g (57%) of a product with mp 252°. Found: Cl 11.9; N 9.7%. $C_{36}H_{28}Cl_2N_4$. Calculated: Cl 12.1; N 9.5%.

1,3,5-Tris(cinnamoyl)benzene.* A 2.04-g (0.01 mole) sample of 1,3,5-triacetylbenzene and 3.18 g (0.03 mole) of benzaldehyde were dissolved by heating in 800 ml of alcohol, 25 ml of 25% alcoholic KOH was added gradually, and the mixture was refluxed for 4 h. The resulting precipitate was filtrated, refluxed with acetic acid three times, each time with a new portion (200 ml) of acetic acid, and removed by filtration without cooling. This procedure gave a light-yellow solid that was almost insoluble in organic solvents (acetic acid, dimethylformamide, dimethyl sulfoxide, etc.) and formed a green-yellow coloration (halochromism) with concentrated H_2SO_4. The yield of product with mp 330° was 3.3 g (70%). Found: C 84.7; H 5.3%. $C_{33}H_{24}O_3$. Calculated: C 84.6; H 5.2%. UV spectrum, λ_{max}, nm: 234 and 315 (the spectrum was measured qualitatively because of the low solubility of the compound).

1,3,5-Tris(4-chlorocinnamoyl)benzene. This compound was obtained by the preceding method from 1,3,5-triacetylbenzene and 4-chlorobenzaldehyde. The yield of product with mp 356° was 3.7 (65%). Found: C 69.5; H 3.9; Cl 18.7%. $C_{33}H_{21}Cl_3O_3$. Calculated: C 69.3; H 3.7; Cl 18.6%.

1,3,5-Tris(1,5-diphenyl-Δ^2-pyrazolin-3-yl)benzene (IIIa). A 4.68-g (0.01 mole) sample of 1,3,5-tris(cinnamoyl)benzene was added to a solution of 2.0 g of potassium hydroxide in 100 ml of phenylhydrazine, and the mixture was refluxed for 6 h. The mixture was then cooled and poured with stirring into 400 ml of ethanol. The resulting precipitate was removed by filtration, washed with hot alcohol, dried, and dissolved in the minimum amount of benzene. The benzene solution was subjected to chromatographic purification over aluminum oxide. After the solvent had been removed, the residue was recrystallized from benzene to give 4.8 g (65%) of IIIa with mp 181°. Found: C 82.7; H 5.7; N 11.4%. $C_{51}H_{42}N_6$. Calculated: C 82.9; H 5.7; N 11.4%.

1,3,5-Tris[1-phenyl-5-(4-chlorophenyl)-Δ^2-pyrazolin-3-yl]benzene (IIIb). This compound was obtained by the method used to prepare IIIa. Workup gave 5.4 g (65%) of a product with mp 227° (from benzene). Found: Cl 12.7; N 10.1%. $C_{51}H_{39}Cl_3N_6$. Calculated: Cl 12.6; N 10.0%.

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*According to our data (IR spectra and chemical properties) the substance described in [13] as 1,3,5-tris(cinnamoyl)benzene (1,3,5-trichalcone) should in fact be considered to be the product of primarily aldol condensation of 1,3,5-triacetylbenzene with benzaldehyde.

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