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DIPYRAZOLINYL-SUBSTITUTED 1,4-DISTYRYLBENZENES

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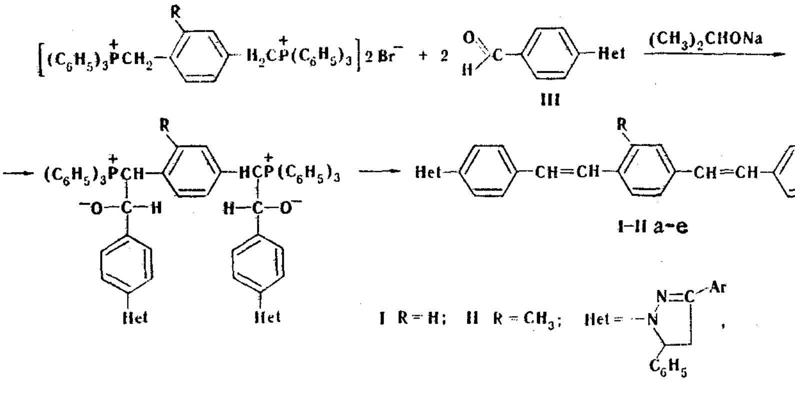
UDC 547.538.778.2

A number of dipyrazolinyl-substituted 1,4-distyryl- and 1,4-distyryl-2-methylbenzenes — new luminophores that have intense yellow-green luminescence — were obtained by the Wittig reaction by refluxing 1-(4-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines and aromatic bisphosphonium salts in isopropyl alcohol in the presence of sodium isopropoxide. The low reactivities of the aldehydes used and the predominant formation of trans isomers in the Wittig reaction are noted. Data from the IR and electronic absorption spectra and the fluorescence spectra of the synthesized compounds are presented.

The introduction of a 3-aryl-2-pyrazolin-1-yl residue into 1,2-diarylethylenes or their heterocyclic-substituted derivatives makes it possible to obtain effective organic luminophores that have longer-wavelength luminescence than their structural fragments [1, 2]. In order to search for new luminophores with yellow-green luminescence it seemed expedient to synthesize a number of dipyrazolinyl-substituted derivatives of 1,4-distyrylbenzene (Ia-e).

It is known that a substantial deficiency of luminophores with molecules with linear structures that limits the possibilities of their practical application is their low solubility in organic media [3]. This deficiency can be eliminated to a certain extent in a number of 1,4-distyrylbenzenes by the incorporation of methyl groups in the central benzene ring [4]. In this connection, we synthesized II in addition to luminophores I.

Luminophores I and II were synthesized by the Wittig reaction starting from the corresponding phosphonium salts and 1-(4-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines (III) via the scheme



See Table 1 for the Ar values.

Attempts to carry out the reaction under traditional conditions [5], i.e., in methanol at room temperature and with the use of sodium methoxide for the conversion of the phosphonium salt to the corresponding intermediate phosphorane [6], showed that aldehydes III do not

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TABLE 1. Characteristics of 1,4-Distyrylbenzene Derivatives Ia-e and IIa-e

Compound	Ar	mp, °C	λ_{max}, nm (in toluene)		IR spectra in KBr, cm^{-1}		N found, %	Empirical formula	N calc., %	Yield, %
			absorption	fluorescence	γ_{CH}	$\nu_{C=N}$				
Ia	C_6H_5	289	430	480, 510	965	1608	7,7	$C_{52}H_{42}N_4$	7,8	22
Ib	$4\text{-}CH_3C_6H_4$	291—293	430	485, 505	962	1600	7,3	$C_{54}H_{46}N_4$	7,5	20
Ic	$4\text{-}CH_3OC_6H_4$	274—276	428	480, 505	955	1602	7,4	$C_{54}H_{46}N_4O_2$	7,2	25
Id	$4\text{-}ClC_6H_4$	277—279	432	485, 510	960	1605	7,4	$C_{54}H_{40}N_4Cl_2$	7,1	20
Ie	$—CH{=}CHC_6H_5$	298—300	445	505	954	1602	7,2	$C_{56}H_{46}N_4$	7,2	28
IIa	C_6H_5	220—222	430	480, 510	960	1600	7,5	$C_{53}H_{44}N_4$	7,6	25
IIb	$4\text{-}CH_3C_6H_4$	206—208	430	485, 515	960	1605	7,6	$C_{55}H_{48}N_4$	7,3	20
IIc	$4\text{-}CH_3OC_6H_4$	203—205	430	485, 515	950	1606	7,0	$C_{55}H_{48}N_4O_2$	7,0	25
IId	$4\text{-}ClC_6H_4$	204—206	428	485, 515	957	1606	7,1	$C_{53}H_{42}N_4Cl_2$	7,0	20
IIe	$—CH{=}CHC_6H_5$	222—224	445	505	950	1602	7,1	$C_{57}H_{48}N_4$	7,1	28

react with the disphosphonium salts used. Since electron-donor substituents in aromatic aldehydes have an unfavorable effect on the rate of the Wittig reaction [7], the data obtained confirm the previous conclusion [8, 9] regarding the strong electron-donor effect of the 3,5-diphenyl-2-pyrazolin-1-yl residue.

We found that the reaction could be carried out by prolonged refluxing of the reagents in isopropyl alcohol with the use of sodium isopropoxide as a stronger base than sodium methoxide. In connection with the instability of the phosphoranes and the low reactivities of the aldehydes, the sodium isopropoxide was added to the reaction mixture in portions vis-à-vis a 1.5-fold excess of the phosphonium salt with respect to the aldehyde. However, even under these conditions we were unable to obtain high yields of I and II. Modification of the reaction conditions made it possible to obtain I and II, which contain strong electron-donor substituents, in higher yields than in the preparation of 4',4''-bis(dimethylamino)-1,4-distyrylbenzene under the usual conditions (10% yield [10]).

In contrast to the synthesis of diaryl derivative 1,4-distyrylbenzene, which leads to the formation of a mixture of isomers [11], trans,trans isomers are primarily obtained in the synthesis of I and II. A comparison of the spectral luminescence properties (the IR and UV absorption spectra and the fluorescence spectra) of Ic and Id, which were subjected to isomerization [10] and were not isomerized, showed that they are identical. The trans configuration of the molecules of all of the synthesized compounds is confirmed by the presence in their IR spectra of a band of out-of-plane CH deformation vibrations of the trans-ethylene group (γ_{CH}) at 950-965 cm^{-1}. The predominant formation of trans isomers was also noted in the preparation of the corresponding pyrazolinyl-substituted derivatives of stilbene [12]. The characteristics of the synthesized compounds are given in Table 1.

In addition to the γ_{CH} band in the IR spectra that we mentioned above, the very intense band corresponding to the stretching vibrations of the C=N bonds of the pyrazoline rings ($\nu_{C=N}$) at 1600-1608 cm^{-1} (Table 1) is of great value for the identification of the compounds obtained. In this same region one usually observes the absorption of the stretching vibrations of C=C bonds ($\nu_{C=C}$) [13], which in the case of the compounds obtained is evidently of low intensity and is overlapped by $\nu_{C=N}$ absorption in view of symmetrical structure of the compounds and weak polarization of the ethylene groups. The characteristic (for 1-aryl-2-pyrazolines) band at 1516-1522 cm^{-1}, which corresponds to the stretching vibrations of a phenyl ring bonded to a nitrogen atom [14], is the most intense band in the IR spectra of all I and II.

As we assumed, the pyrazolinyl-substituted I and II that we synthesized absorb and fluoresce (Table 1) in a longer-wavelength region of the spectrum than unsubstituted 1,4-distyrylbenzenes and 1,4-distyryl-2-methylbenzenes (for the latter compounds the absorption λ_{max} is 355 nm, and the fluorescence λ_{max} is 420 nm; these values are identical in toluene [4]).

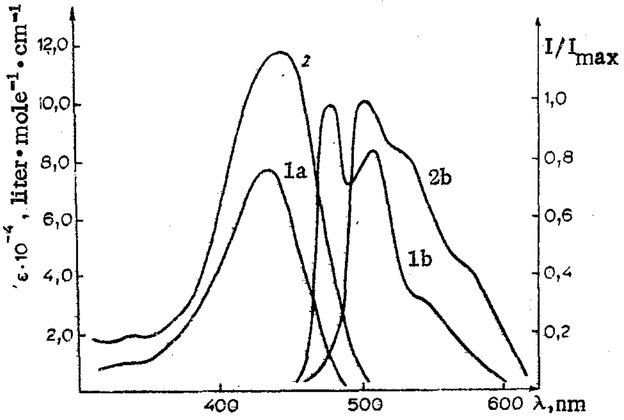

Fig. 1. Absorption (a) and fluorescence (b) spectra in toluene: 1) 4',4"-bis(3,5-diphenyl-2-pyrazolin-1-yl)-1,4-distyrylbenzene; 2) 4',4"-bis(3-styryl-5-phenyl-2-pyrazolin-1-yl)-1,4-distyryl-2-methylbenzene.

The bathochromic effect in the absorption spectra that is induced by the incorporation of 3,5-diphenyl-2-pyrazolin-1-yl groupings as 4',4" substituents in the 1,4-distyrylbenzene molecule appreciably exceeds the effect observed in the case of incorporation of dimethylamino groups (the absorption λ_{max} for 4',4"-bis(dimethylamino)-1,4-distyrylbenzene in dimethylformamide is 405 nm [15]). A similar regularity has been noted for various pyrazolinyl-substituted arylethylenes [2].

In contrast to the structureless absorption curves, the fluorescence spectra of I and II in toluene have, as a rule, a distinctly expressed vibrational structure (Fig. 1); this is characteristic for 1,4-distyrylbenzene derivatives [15]. The introduction of substituents in the phenyl ring in the 3 position of the pyrazoline rings has virtually no effect on the position of the absorption and fluorescence bands. However, an increase in the length of the conjugation chain of the 3-aryl groupings by replacement of the phenyl groups by styryl groups (Ie and IIe) is accompanied by appreciable bathochromic and bathofluoric effects. The introduction of a methyl group in the central benzene ring does not affect the spectral-luminescence characteristics of the luminophores. However, in this case the solubilities of the methyl-containing II in toluene are approximately twice the solubilities of the corresponding compounds of the I series.

EXPERIMENTAL

The starting aldehydes (III) were synthesized by the method in [12]. The phosphonium salts were obtained in accordance with [16].

The absorption spectra of solutions of the compounds in toluene (10^{-4}-10^{-5} mole/liter) were measured with an SF-4A spectrophotometer. The fluorescence spectra of the solutions were measured at room temperature with an apparatus for luminescence analysis consisting of a ZMR-3 mirror monochromator, an FÉU-18, an M-95 microammeter, and a DRSh-500 mercury—quartz lamp (the excitation wavelength was 365 nm) with allowance for its spectral sensitivity. The IR spectra of KBr pellets of the compounds were measured with a UR-20 spectrometer.

4',4"-Bis(3,5-diphenyl-2-pyrazolin-1-yl)-1,4-distyrylbenzene (Ia). A 7.5-g (0.008 mole) sample of p-xylylenebistriphenylphosphonium bromide was added to a refluxing solution of 3.3 g (0.01 mole) of 1-(4-formylphenyl)-3,5-diphenyl-2-pyrazoline in 200 ml of absolute isopropyl alcohol, after which a solution of sodium isopropoxide, prepared by dissolving 0.5 g of sodium in 50 ml of absolute isopropyl alcohol, was added in portions in the course of 3 h. The mixture was then refluxed for another hour and allowed to stand overnight. The resulting precipitate was removed by filtration. An additional amount of product was isolated from the mother liquor by the addition of a small amount of water. The product was refluxed with 50 ml of benzene to remove the unchanged aldehyde, after which it was recrystallized twice from chlorobenzene to give a product with mp 289°C in 22% yield.

The remaining I and II were similarly synthesized (Table 1).

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AZIRIDINYL KETONES AND THEIR HETEROANALOGS.

2.* SYNTHESIS AND STUDY OF 5,7-DIARYL-1,4-DIAZABICYCLO[4.1.0]HEPTA-4-ENES

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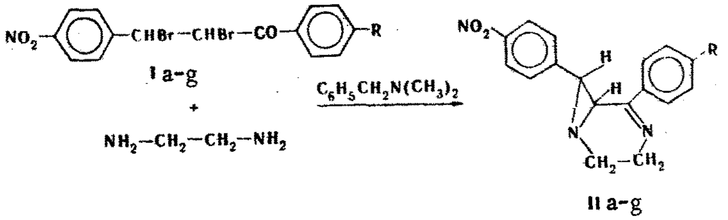
UDC 547.862'717.07:543.422.25.4

5-Aryl-7-(4-nitrophenyl)-1,4-diazabicyclo[4.1.0]hepta-4-enes (I), which have photochromic properties, were synthesized. The structures of the compounds were confirmed by data from the IR, PMR, and mass spectra. The acidolysis of I was investigated, and it was assumed that the mechanism of the reaction includes diprotonation of the bases, while the primary process is the formation of immonium salts. The structures of the photocolored forms of the salts and bases are discussed.

Continuing our study of cyclic anils of aziridinyl ketones [1], we synthesized a number of 5-aryl-7-(4-nitrophenyl)-1,4-diazabicyclo[4.1.0]hepta-4-enes (IIa-g), the interest in which is due to their clearly expressed photochromic properties.

The synthesis of II was accomplished by the method of Heine and Henzel [2] by the reaction of 1-aryl-3-(4-nitrophenyl)-2,3-dibromopropan-1-ones (Ia-g) with ethylenediamine in the presence of N,N-dimethylbenzylamine:



I–II a R = H; b R = CH_3; c R = CH_3O; d R = Cl; e R = Br; f R = NO_2; g R = C_6H_5

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*See [1] for communication 1.

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