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BISPYRAZOLE[3,4-b:4',3'-e]PYRAZINES AS SELF-CONDENSATION PRODUCTS FROM 4,5-DIAMINOPYRAZOLES

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Bispyrazolo[3,4-b:4',3'-e]pyrazines have been obtained by self-condensation of 4,5-diaminopyrazoles and their structures confirmed by independent synthesis. The spectral data for these compounds is discussed.

We have recently shown [1] that refluxing a toluene solution of 4,5-diamino-3-methyl-1-phenylpyrazole (Ia) leads to self-condensation and formation of 3,5-dimethyl-1,7-diphenylpyrazolo[3,4-b:4',3'-e]pyrazine (IIa). Evidence for similar reactions has only been reported for 5,6-diamino-1,3-dimethyluracil [2].

The aim of this work was an investigation of the self-condensation of diaminopyrazoles to bispyrazolopyrazines which are of interest as luminophores.

It has been shown that diamines Ib,c like Ia, form the bispyrazolopyrazines IIa-c in 40-60% yields when heated for 1-2 h in toluene whereas diamine Id remains unchanged (route A). In methanol diamines Ia,b take part in a cross-ring 4,5-interaction (route B) to form compounds IIIa,b whereas IIc,d are unchanged under these conditions. Prolonged refluxing (15 h) of IIIa in ethylene glycol led to compound IV. The reaction mixture also contained compound IIa, but the mechanism of its formation is not clear. Separation of this mixture was difficult hence IIa and IV were identified by comparison of their R_f values and electronic absorption spectra with standard samples.

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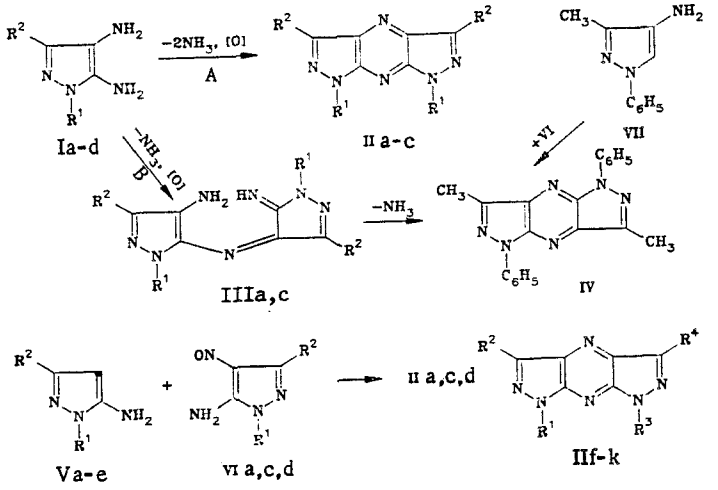

I—III, V, VI a $R^1=C_6H_5$, $R^2=CH_3$; b $R^1=R^2=C_6H_5$; c $R^1=H$, $R^2=C_6H_5$; d $R^1=C_6H_4NO_2$, $R^2=CH_3$; e $R^1=C_6H_4COOH$-4, $R^2=CH_3$; II f $R^1=R^3=C_6H_5$, $R^2=CH_3$, $R^4=H$, g $R^1=R^2=R^4=C_6H_5$, $R^3=CH_3$; h $R^1=R^2=C_6H_5$, $R^3=C_6H_4NO_2$-4, $R^4=CH_3$; i $R^1=C_6H_4NO_2$-4, $R^2=R^3=CH_3$, $R^4=C_6H_5$; j $R^1=C_6H_4NO_2$-4, $R^2=CH_3$, $R^3=R^4=C_6H_5$; k $R^1=C_6H_4COOH$-4, $R^2=R^3=CH_3$, $R^4=C_6H_5$

The structures of compounds IIa-c were confirmed by elemental analytical data, by spectroscopic characteristics (Table 1), and independent synthesis according to [3] in which the authors treated the 5-aminopyrazoles V with their 4-nitroso substituted analogs VI in glacial acetic acid. Changing this solvent to DMF increased the yield of the tricycle IIa from 20-25% to 60%. Compound IId (which could not be prepared by self-condensation of Id) was synthesized in the same way. In addition, the nonsymmetrical compounds IIf-k were prepared by changing the components V and VI.

With the same method we have prepared the bispyrazolopyrazine IV from 4-amino (VII) and 5-amino-4-nitroso-3-methyl-1-phenylpyrazole (VIa).

Compounds IIa and IV are classified as high symmetry systems (their symmetry point groups being C_{2v} and C_{2h}, respectively). The dipole moment of compound IIa was 1.82 D and compound IV zero which was in full agreement with the proposed structures.

The effect of the medium on the course of the self-condensation is probably due to solvation effects. The amino group at the pyrazole 5-position is susceptible to enamine-imine tautomerism [4]. In protic polar solvent (methanol) the tautomeric equilibrium is shifted towards the imino form because of significant solvation effects and the cross reaction is most favored (route B). In aprotic nonpolar solvent (toluene) this solvating effect is absent, the fraction of imino form is small and the synchronous reaction of the diamines (route A) is observed. Self-condensation of diamine Ia in DMF, resulting in formation of IIa and III_a in the ratio 3:1, confirms that mentioned above, DMF causes virtually no solvation of a nucleophilic center [5] hence the relative basicity of the amino groups in diamine Ia is not changed. At the same time, the presence of polar solvents partially promotes stabilization of the imino form leading to formation of a small amount of compound IIIa.

The course of the self-condensation reaction depends upon the substituents introduced into the heterocyclic ring. 4,5-Diamino-3-methyl-(4-nitrophenyl)pyrazole (Id) did not self-condense, probably because the electron accepting nitrophenyl radical significantly lowers the nucleophilicity of the amino groups. For 4,5-diamino-3-phenylpyrazole (Ic) the nucleophilicity of both amino groups remains high (according to CNDO/2 calculations $q_{5\text{-}NH_2}$ = −0.218 and $q_{4\text{-}NH_2}$ = −0.252) but there is also a significant lowering of the fraction of the imino form (preferential equilibrium occurs via the endo-imino group) which hinders the self-condensation of Ic in methanol.

The bispyrazolopyrazines II show intense yellow-green fluorescence in toluene solution. A rigid relationship between the electronic character of the introduced substituents R^1—R^4 and the λ_{max} fluorescence values (Table 1) was not observed. Because introduction of the substituents generally has identical effects on the absorption and the fluorescence spectra there is little change in the Stokes shift (with the exclusion of the values for

TABLE 1. Parameters for Bispyrazolo[3,4-b:4',3'-e]pyrazines (IIa-k, IV)

Compound	mp, °C	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	Fluoresence spectrum, λ_{max}, nm	Stokes shift, cm^{-1}	Quantum yield, %	Found N, %	Empirical formula	Calculated N, %	Yield, % B(A)
IIa	202	401 (2,6), 364 (9,2)	492	4610	0,17	24,3	$C_{20}H_{16}N_6$	24,7	60 (69)
IIb	340	439 (3,2), 388 (8,2), 355 (6,7)	524	3700	0,36	18,2	$C_{30}H_{20}N_6$	18,1	— (53)
IIc	220 (dec.)	413 (1,5), 358 (3,1), 327 (3,7)	506	4450		27,0	$C_{18}H_{12}N_6$	26,9	57 (10)
IId	272...274	434 (8,6), 342 (26,3), 322 (27,7)	473	1900		26,3	$C_{20}H_{14}N_8O_4$	26,0	52
IIf	207...208	417 (3,4), 376 (9,2)	510	4370	0,59	25,7	$C_{19}H_{14}N_6$	25,8	83
IIg	202...203	420 (3,9), 375 (8,9)	504	3970	0,59	20,8	$C_{25}H_{18}N_6$	20,9	45
IIh	279...280	427 (8,4), 349 (22,5)	519	5150		20,1	$C_{25}H_{17}N_7O_2$	20,4	58
IIi	320	401 sh, 352 (23,3)	500	—		25,8	$C_{20}H_{15}N_7O_2$	25,5	52
IIj	268...269	435 (12,0), 346 (22,1)	486	2410		26,5	$C_{19}H_{13}N_7O_2$	26,4	40
IIk	186...187	405 (2,6), 363 (9,2)	498	4600		21,6	$C_{21}H_{16}N_6O_2$	21,9	52
IV*	262	444 (4,0), 316 (10,8)	506	2760	0,41	25,0	$C_{20}H_{16}N_6$	24,7	53

*According to [3]: mp 260°C, λ_{max}^{abs} 320 nm, λ_{max}^{fluor} 510 nm.

compounds IId,j which contained a nitrophenyl group). The fluorescence of these nitro compounds is unusual [6]. It seems likely that the contribution of the N-aryl radicals to the electronic transitions, responsible for their long wavelength absorption and corresponding emission, is small.

The quantum yields are given in Table 1 for some of the synthesized compounds measured in toluene. It was interesting to note that the fluorescence quantum yields for isomeric molecules IIa and IV differ by almost 2.5 times but a clear dependence of this characteristic on the structure of II is not observed.

The generating ability of compounds IIa,e,f* is absent, probably because of the low intensity of the long wave absorption of the compounds studied [$\varepsilon = (2\text{-}4)\cdot10^{-3}$].

EXPERIMENTAL

UV absorption spectra were measured using a Specord UV-vis spectrophotometer for toluene solutions of $1\text{-}3\cdot10^{-5}$ M. IR spectra were taken on a Specord IR-75 spectrophotometer (in KBr tablets) and PMR spectra on a Tesla BS-2487-B (80 MHz) in $CDCl_3$ with TMS internal standard. Fluorescence spectra were measured on apparatus consisting of a monochromator from an SF-4A spectrophotometer, an FÉU-38 radiation detector, V7-16 digital voltmeter, recorder, and DRSh-500 mercury lamp as light source. Measured spectra were corrected through the spectral sensitivity of the apparatus. Fluorescence quantum yields were measured by method [7] using quinine bisulfate in 1.0 N H_2SO_4 as standard with a quantum yield of 0.546 [7]. Dipole moments were measured in benzene at 25°C by method [8]. Quantum chemical calculations of electronic distributions by diamine Ic used the CNDO/2 method with standard parameters. Preparative chromatographic separation of the compounds obtained was carried out on an Al_2O_3 grade III activity (1 cm diameter, packing height 10 cm) using $CHCl_3$ as eluent.

Compounds IIa and IIIa are described in [1].

3,5-Diphenylbispyrazolo[3,4-b:4,'3'-e]pyrazine (IIc). A. A solution of diamine Ic (0.28 g, 1.6 mmole) in toluene (50 ml) was refluxed for 2 h, the solvent distilled off, and the residue chromatographed collecting the luminescent fraction (0.1 g) with R_f 0.38.

Compound IIb was obtained similarly.

B. A solution of amine Vc (0.3 g, 1.7 mmole) and 5-amino-4-nitroso-3-phenylpyrazole (VIc, 0.35 g, 1.7 mmole) in DMF (1 ml) was refluxed for 3h, cooled, and the precipitated solid was filtered off and chromatographed to give IIc (0.34 g).

Compounds IIa,d,f-k, and IV were obtained similarly.

Condensation of Diamine I with DMF. A solution of Ia (0.3 g, 1.6 mmole) in DMF (1 ml) was refluxed for 2 h, cooled, and the precipitated solid was filtered off and chromatographed. The first luminescent fraction (0.18 g, 60%) had R_f 0.62 and was compound IIa. The second fraction (0.06 g, 20%) with R_f 0.45 was compound IIIa.

1,3-Diphenyl-5-imino-4-(1,3-diphenyl-4-aminopyrazol-5-yl)-imino-2-pyrazoline (IIIb). A solution of diamine Ib (0.3 g, 1.2 mmole) in methanol (15 ml) was allowed to stand overnight at 20°C. The precipitate was filtered off and crystallized from chloroform to give the product (0.12 g, 40%) with mp 248°C. IR spectrum: 3290, 3415 cm^{-1} (NH, NH_2). UV Spectrum (in alcohol), λ_{max}: 450 nm. Found, %: N 20.1. $C_{30}H_{23}N_7$. Calculated, %: N 20.4.

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OXIDATIVE CYCLIZATION OF 2-AMINO-1-ARYLIDENEAMINO-BENZIMIDAZOLES INTO 1,2,4-TRIAZOLO[1,5-*a*]BENZIMIDAZOLES

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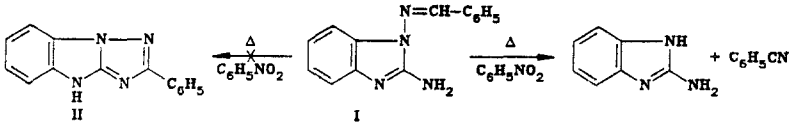
When heated in nitrobenzene, 1-arylideneamino-2-methylaminobenzimidazoles convert in a 20...30% yield into 2-aryl-3-methyl-1,2,4-triazolo[1,5-*a*]-benzimidazoles. In addition, 2-methylaminobenzimidazole and the corresponding benzonitrile are formed as a result of a thermal splitting of the N–N bond. Under the same conditions, 2-amino-1-arylideneaminobenzimidazoles and 1-arylideneamino-3-methylbenzimidazoline-2-imines give only products of spiltting off of the nitrile. In several cases, the subsequent reaction of the nitrile with 2-amino-1-methylbenzimidazole leads to the formation of benzamidines.

2-Aryl-1,2,4-triazolo[1,5-*a*]benzimidazoles are usually synthesized from 1,2-diaminobenzimidazoles and anhydrides or acid chlorides of aromatic acids [1-4]. Another theoretically possible method for the preparation of these compounds could be the oxidative cyclization of 2-amino-1-arylideneaminobenzimidazoles, similar to the transformation of o-phenylenediamine anils into 2-arylbenzimidazoles [5]. It should be noted, however, that an attempt to oxidize 2-amino-1-benzylideneaminobenzimidazole (I) into 2-phenyl-1,2,4-triazolo-[1,5-*a*]benzimidazole (II) by the action of copper acetate [6] was unsuccessful. In the present article, we describe the results of our experiments on the cyclization of 2-amino-1-arylideneaminobenzimidazoles in nitrobenzene medium. This oxidant gives good results in the preparation of 2-arylbenzimidazoles from o-phenylenediamine anils [7].

Boiling compound I in nitrobenzene leads to partial resinification and formation of a complex mixture of compounds, which does not include 2-phenyl-1,2,4-triazolo[1,5-a]-benzimidazole (II). However, an appreciable amount of 2-aminobenzimidazole can be detected in this mixture. This compound is clearly formed as a result of splitting of the N–N bond, as in the case of the N-aminopyridinium hydrazone series [8].



We assumed that this course of reaction can be explained by the lower nucleophilicity of the 2-amino group in compound I, as a result of which the elimination of nitrile, competing with the cyclization, proceeds much more rapidly. To increase the probability of closing the triazole ring, we decided to increase the nucleophilicity of the amino group by introducing a methyl substituent into it, and also by converting it into a fixed imine.

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