The electronic absorption spectra were measured on a Unicam SP-8000 spectrophotometer. The fluorescence spectra were measured on a Jobin–Yvon spectrofluorimeter. The fluorescence spectra were corrected for the spectral sensitivity of the apparatus. The absolute fluorescence quantum yields were determined by a relative method. Quinine bisulfate in 0.1 N sulfuric acid ($\varphi_f = 0.55$ [11]) and 3-aminophthalimide in ethanol ($\varphi_f = 0.6$ [12]) were used as standards.

The fluorescence attenuation time was measured on a pulse nanosecond fluorimeter in a single proton counting regime [13]. The duration of the exciting flash was 1-1.5 nsec. The real attenuation time was determined from the formula $\tau_f = (\tau_{exp}^2 - \tau_{flash}^2)^{1/2}$ [14]. The accuracy of the determination was 10-15%.

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3-ARYL-2-BENZYL -1,2-DIHYDROQUINOXALINES

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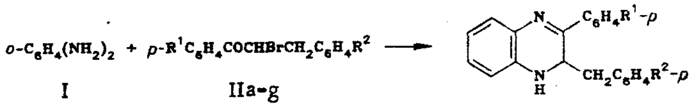
The reaction of 1,2-phenylenediamine with 2-bromo-1,3-diaryl-1-propanones led to stable and crystalline 3-(4-R-phenyl)-2-(4-R'-benzyl)-1,2-dihydroquinoxalines.

Aromatic derivatives of 1,2-dihydroquinoxaline are inherently powerful fluorescing agents with major Stokes shifts [1], but they are chemically unstable. Their tendency to aromatize decreases their practical utility. In our search for increasing the stability of 1,2-dihydroquinoxalines we have synthesized 3-(4-R-aryl)-2-(4-R'-benzyl)-1,2-dihydroquinoxalines (IIIa-g) by treating 1,2-phenylenediamine (I) with 2-bromo-1,3-diaryl-1-propanones (IIa-g) in methanol in the presence of sodium acetate:



I IIa-g IIIa-g.

II, III a, g $R^1=H$, b $R^1=CH_3$, c $R^1=OCH_3$, d $R^1=C_6H_5$, e $R^1=Cl$, f $R^1=Br$; a-e $R^2=H$, g $R^2=Cl$

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TABLE 1. Parameters for Compounds IIIa-g

Compound	mp, °C (methanol)	Absorption, λ_{max} nm ($\varepsilon \cdot 10^{-3}$)		Luminescence λ_{max} nm (Stokes shift, cm^{-1})		IR spectrum cm^{-1} (KBr)		Found: N, %	Empirical formula	Calculated N, %	Yield, %
		in methanol	in toluene	in methanol	in toluene	$\nu_{C=N}$	ν_{N-H}				
IIIa	139—140	395 (5,3)	391	583 (8160)	518 (6270)	1606	3400	9,6	$C_{21}H_{18}N_2$	9,4	34
IIIb	141	392 (5,36)	387	572 (8020)	615 (6420)	1606	3390	9,1	$C_{22}H_{20}N_2$	9,0	18
IIIc	151	387 (6,48)	382	563 (8770)	508 (6490)	1606	3376	8,6	$C_{22}H_{20}N_2O$	8,5	19
IIId	142—143	405 (8,07)	400	595 (7880)	530 (6130)	1608	3376	7,4	$C_{27}H_{22}N_2$	7,5	40
IIIe	136—138	400 (4,99)	395	595 (8190)	529 (6410)	1606	3391	8,4	$C_{21}H_{17}ClN_2$	8,4	33
IIIf	113 with decomposition	404 (5,47)	399	597 (8000)	530 (6190)	1606	3394	7,5	$C_{21}H_{17}BrN_2$	7,3	25
IIIg	135	397 (4,75)	391	586 (8120)	518 (6270)	1608	3390	8,3	$C_{21}H_{17}ClN_2$	8,4	12

The reaction conditions were similar to those described [1] for the reaction of ω-bromoacetophenones with diamine (I) but it occurred more slowly (6 h instead of 2 h) and with a decreased yield of the target product (average decreased yield = 40%). The most likely reasons for this are steric factors or a competing dehydrobromination process. The latter can be excluded because of the absence (TLC) of chalcones which are the main products of dehydrobromination. Additionally, 2-bromo-1,3,3-triarylpropanones (in which the Br atom is shielded by two bulky groups) did not react with 1,2-phenylenediamine. In these conditions a dehydrobromination occurred to give the β-arylchalcones and the diamine remained unchanged. Hence steric factors have a decisive effect on the reaction course.

The structures of IIIa-g were confirmed by elemental analytical data, IR, and UV spectra (Table 1). For compound IIIa a PMR spectrum was also recorded.

The chromophoric system of IIIa-g is related to that of 3-aryl-1,2-dihydroquinoxalines [1]. Thus a considerable effect should be seen in the λ_{max} of the investigated compounds with the introduction of an R substituent and this is, indeed, observed (Table 1). No significant effect is seen when a benzyl radical is placed in position 2 of the heterocycle.

The PMR spectrum of IIIa showed an octet and a quartet signal for the chiral $CH-CH_2$ system at position 2 (2.50-3.00 and 4.45-4.60 ppm), and imino signal (4.05 ppm), and an aromatic proton multiplet (6.4-8.1 ppm).

Compounds IIIa-g were quite stable in the solid state but solutions stored at 20°C for greater than a month showed oxidation to 3-aryl-2-benzylquinoxalines. The same compounds were obtained by acidolysis of 1,1a-dihydroazirino[1,2-a]quinoxalines [2]. Analysis of a Dreiding model of 3-phenyl-1,2-dihydroquinoxaline showed that the bicycle had a near envelope conformation in which an orientation of the p-orbitals of the amino nitrogen favorable to conjugation with the π-electrons was achieved. The atoms $N_1-C_6H_4-N_4$ and C_3 are virtually planar while C_2 is 0.8-0.9 Å removed. Introduction of the benzyl radical at 2 did not introduce significant perturbing effects on account of its quasi-axial alignment (besides achieving a maximum, mutual separation of all bulky aromatic nuclei). The flattening of the bicycle, which occurs on aromatization, causes approach of these nuclei and increase in steric hindrance. This may, then, account for the 3-aryl-1,2-dihydroquinoxalines bearing a 2-benzyl substituent showing an enhanced stability.

All of the compounds prepared showed intense fluorescence as methanol or toluene solutions The large hypsofluoric spectral shifts on changing from methanol to toluene were not reflected in their absorption spectra. This large solvent-related Stokes shift is discussed further in [1].

TABLE 2. 2-Bromo-1,3-diarylpropanones (IIa-g)

Compound	mp, °C	$\nu_{C=O}$, cm^{-1}	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	Br		C	H	Br	
II a	58	1675	62,1	4,3	27,7	$C_{15}H_{13}BrO$	62,3	4,5	27,6	87
IIb	63	1672	63,2	5,2	26,7	$C_{16}H_{15}BrO$	63,4	5,0	26,4	90
IIc	59	1668	60,4	4,8	25,2	$C_{16}H_{15}BrO_2$	60.2	4,7	25,0	85
IId	99	1675	69,4	4,7	21,7	$C_{21}H_{17}BrO$	69,1	4,7	21,9	90
IIe	92	1677	55,4	3,5	—	$C_{13}H_{12}BrClO$	55,7	3,7	—	85
IIf	86	1676	48,6	3,2	—	$C_{15}H_{12}Br_2O$	48,9	3,3	—	85
IIg	82	1678	55,5	3,6	—	$C_{15}H_{12}BrClO$	55,7	3,7	—	82

EXPERIMENTAL

IR spectra were measured on a Specord IR-75 (KBr tablets), electronic absorption spectra on a Specord UV-vis (in methanol and toluene), and fluorescence spectra in the same solvents using an SF-4A spectrometer monochromator, an FEU-38 detector, and a DRS-500 mercury lamp source. The fluorescence spectra were corrected. Absorbance at long-wave excitation did not exceed 0.2. PMR spectra for IIIa were measured on a Varian XL-100 instrument using TMS as internal standard.

2-Bromo-1,3,3-triarylpropanones have been described in [3]. Dihydrochalcone was obtaine by method [4].

2-Bromo-1,3-diphenylpropanone (IIa). A solution of 1,3-diphenylpropanone (2 g, 9.5 mmol in glacial acetic acid (15 ml) was heated to 50°C and bromine (5 ml) was added cautiously wit stirring. When the solution had become light yellow, it was poured into iced water (100 g). The precipitated solid was filtered off and crystallized from methanol to give 2.4 g (87%) with mp 58°C.

Compounds IIb-g were obtained similarly (Table 2).

3-Aryl-2-benzyl-1,2-dihydroquinoxaline (IIIa). A mixture of 1,2-phenylenediamine (1.1 g 10 mmole), 2-bromo-1,3-diphenylpropanone (2.9 g, 10 mmole), and sodium acetate (0.83 g, 10 mmole) in methanol (50 ml) was refluxed with continuous passage of a stream of methane or carbon gas for 6 h. The salt was filtered off and the filtrate cooled to 5°C. Filtration then gave a crystalline product (1.0 g, 34%) with mp 139-140°C (from methanol).

IIIb-g were prepared in the same way.

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SYNTHESIS OF AZOTRIAZINES

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Condensation of 4-nitroso-3-thio-6-phenyl-1,2,4-triazin-5-one with aromatic amines led to azotriazines.

Substituted 1,2,4-triazin-5-ones have found wide usage as herbicides. The majority of these herbicides have a substituent (alkyl, amino) in the 4-position of the triazine ring [1] but others (e.g., azo groups) have been little studied.

This study was aimed at the preparation of azotriazines by condensation of 4-nitroso-1,2,4-triazin-5-ones with aromatic amines. The usual method for such compounds involving azo coupling of an aromatic amine of phenol with a diazonium salt was unacceptable because of the instability of triazine diazonium salts. Reaction of nitrous acid with 4-amino-1,2,4-triazin-5-one leads to cleavage of the amino group [2]. In view of the weak electrophilicity of $Ph\text{-}N_2^+$, together with the rather poor activity of 1,2,4-triazin-5-ones in electrophilic substitutions, the reaction of phenyldiazonium salts with 1,2,4-triazin-5-ones showed little

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