Synthesis and study of new 2-aryl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline derivatives

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New derivatives of photochromic 2-aryl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxalines were synthesized by condensation of 4-methyl- and 4,5-dimethyl-1,2-phenylenediamine with 1,3-diaryl-2,3-dibromopropan-1-ones. The reactions of 4-methyl-1,2-phenylenediamine produce mixtures of regioisomers. The chemical properties of the reaction products were studied. The structure of one of the latter was established by X-ray diffraction.

Key words: 1,3-diaryl-2,3-dibromopropan-1-ones, 1,2-diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines, 2-arylquinoxalines, 4-aryl-1,2-bis(4-nitrophenyl)-1,2-dihydro-3a*H*-oxazolo[3,2-*a*]quinoxalines, X-ray diffraction study.

Aziridines are widely used for the synthesis of various practically important compounds.[1] Bicyclic aziridine derivatives have attracted attention primarily due to the presence of the strained three-membered ring, which readily undergoes cleavage under external factors. In particular, the photochromic properties of azireno[1,2-*c*]imidazoles, azireno[1,2-*a*]pyrazines, and azireno[1,2-*a*]quinoxalines are accounted for by the aziridine ring opening.[2]

First data on photochromic fused aziridines[3] were obtained when synthesizing azireno[1,2-*c*]imidazoles by the reactions of *trans*-3-aroyl-2-arylaziridines with aldehydes or ketones in ammonia-saturated alcoholic solutions. Photo-[4] and thermochromic[5] diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines (DAQ) were synthesized from α,β-chalcone dibromides and 1,2-phenylenediamine in the presence of tertiary organic bases (triethylamine and *N*,*N*-dimethylbenzylamine). 1-Fluoroalkyl derivatives[6] also extend the range of known 1,1a-dihydroazireno[1,2-*a*]quinoxalines.

1-(4-Nitrophenyl)-substituted dihydroazirenoquinoxalines are poorly soluble, which hinders their use in light-sensitive composite materials.

In the present study, we report methods for the synthesis of previously unknown methyl- and dimethyl-substituted DAQ (see the preliminary communication[7]). In our opinion, the introduction of additional alkyl and alkoxy substituents can substantially increase the solubility of DAQ.

For the reactions of 4-substituted 1,2-phenylenediamines, the main question is about the reaction pathway. In early studies on this problem,[8,9] only one regioisomer was detected and isolated in moderate yield. Apparently, the second regioisomer was not found because of instrumental limitations.

The reactions of methyl-substituted *o*-phenylenediamines **1** and **2** with *erythro*-1,3-diaryl-2,3-dibromopropan-1-ones **3—9** (Scheme 1) and 2-bromo-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (**21**) afforded new representatives of 1,2-diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines **10—20**. The reactions were carried out by heating the starting compounds in methanol in the presence of triethylamine.

The positions and multiplicities of the signals in the ^{1}H NMR spectra of compounds **10—14** (two doublets with the spin-spin coupling constants of 2.7—2.9 Hz at δ 2.9—3.0 and 3.4—3.5 belonging to the *trans*-aziridine protons at positions 1a and 1, characteristic doublets of the terminal aryl substituents, and singlets of the H(4) (δ 7.32—7.40) and H(7) (δ 7.00—7.19) protons of the annelated phenylene moiety) agree well with the data for various 1,2-diaryl-1,1a-dihydroazireno[1,2-*a*]quinoxalines studied earlier.[4,5,8] The signal at lower field was unambiguously assigned to the proton at position 4 due to the electron-withdrawing effect of the C=N fragment.

The reactions of 4-methyl-1,2-phenylenediamine (**2**) give compounds **15—20** as mixtures of regioisomers **A**

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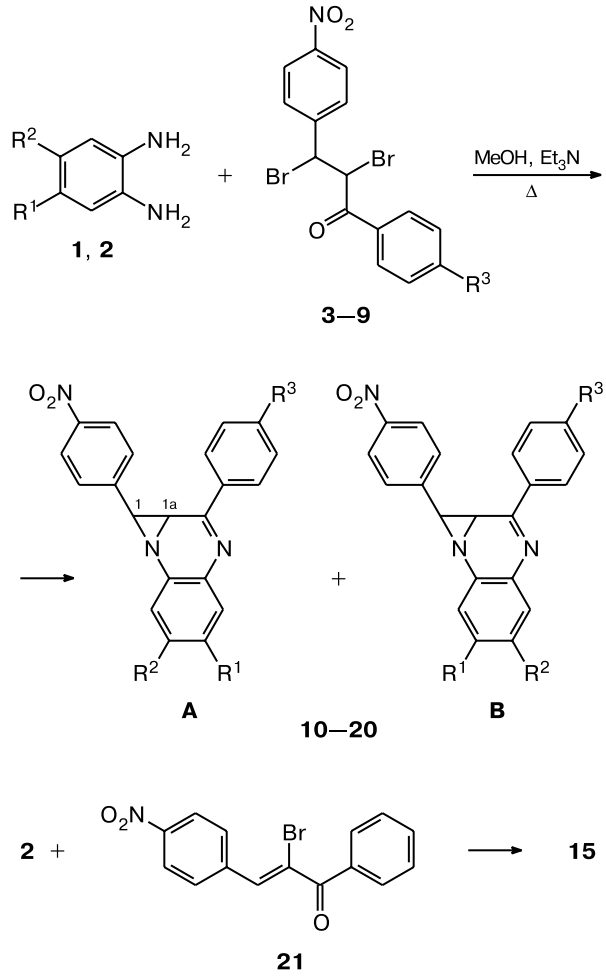
Scheme 1



1, 10—14: $R^1 = R^2 = Me$
2, 15—20: $R^1 = Me$, $R^2 = H$

Compound	R^3	Yield (%)	Compound	R^3	Yield (%)
3	H	74	**12**	F	39
4	Br	82	**13**	$OCHF_2$	30
5	Et	64	**14**	C_5H_{11}	39
6	C_5H_{11}	66	**15**	H	38
7	F	63	**16**	Br	43
8	Ph	61	**17**	Et	26
9	$OCHF_2$	80	**18**	C_5H_{11}	30
10	H	45	**19**	F	37
11	Br	45	**20**	Ph	16

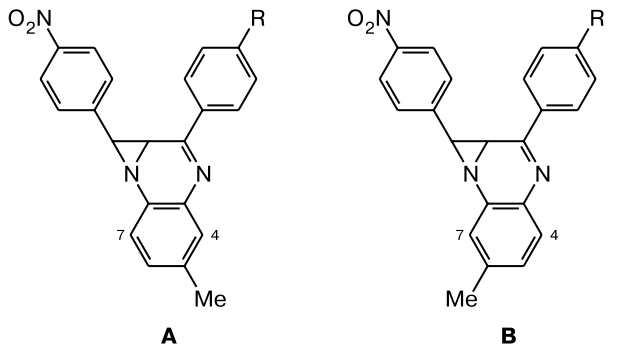
and **B** (see Scheme 1). This is evident from the ^{1}H NMR spectra, in which almost all signals are doubled. Attempts to isolate individual isomers by high-performance liquid chromatography failed. However, control by HPLC demonstrated that the ratio of isomers in solution differs from that in the crystalline product by at most 2%.

For mixtures of isomers **A** and **B** of azireno[1,2-*a*]quinoxalines **15—20**, the ratios of isomers (Table 1) were determined from the ^{1}H NMR spectra by analyzing the

Table 1. Ratio of regioisomers and chemical shifts of the H(4) and H(7) protons in the ^{1}H NMR spectra of compounds **10** and **15—20**

Compound	δ		Ratio of regioisomers (%)	
	H(4) (**A**)	H(7) (**B**)	**A**	**B**
10	7.35	7.18	—	—
15	7.35	7.19	65	35
16	7.33	7.19	60	40
17	7.34	7.18	65	35
18	7.33	7.18	55	45
19	7.32	7.18	60	40
20	7.36	7.19	55	45

integrated intensities of two singlets (or doublets with the coupling constants <2 Hz), which are observed in the resonance region of aromatic protons and belong to the H(4) proton of isomer **A** (δ 7.32—7.36) and the H(7) proton of isomer **B** (δ 7.18—7.19). The assignment of the signals was made based on the above data for 4,5-dimethyl-substituted compounds **10—14**.

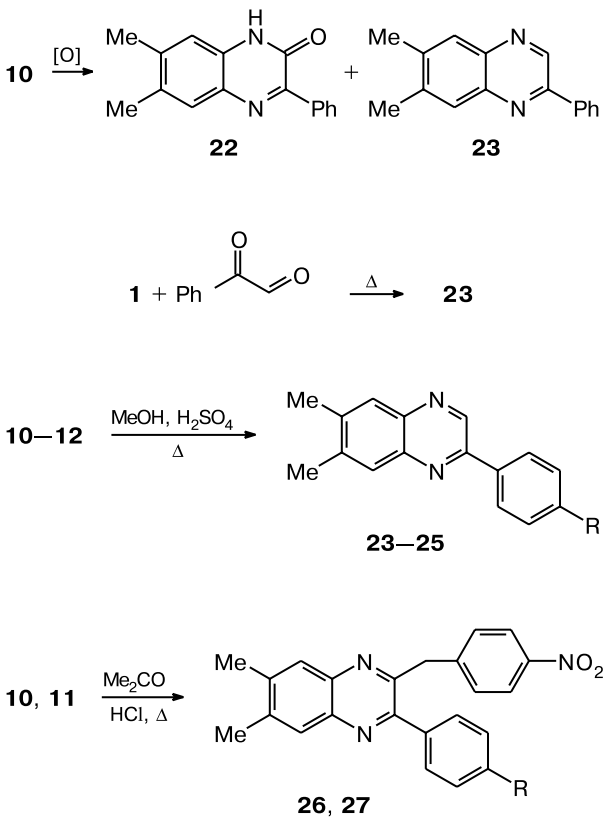


The reaction of α-bromochalcone **21** with diamine **2** afforded the target compound **15** in the same yield and with the same ratio of regioisomers **15A** : **15B** as those obtained in the reaction of dibromochalcone **3**. Consequently, the formation of the aziridine fragment of the bicyclic system is not accompanied by the direct replacement of the β-bromine atom; otherwise the ratio of isomers would be changed. Hence, there is no sense in isolating intermediate α-bromochalcones in the synthesis of DAQ.

Crystalline dihydroazireno[1,2-*a*]quinoxalines **10—20** are reversibly photochromic. Being pale-yellow in the dark, these compounds turned green (R = F or Br) or dark-violet (R = C_5H_{11}) under UV light (or, to a lesser degree, under visible light). Compounds **13**, **14**, **17**, and **18** are highly soluble in usual organic solvents.

The resulting azirenoquinoxalines are unstable upon storage. Silica gel chromatography of samples, which were obtained upon storage of compound **10** in air for 6—12 months, afforded 6,7-dimethyl-3-phenyl-1,2-dihydroquinoxalin-2-one (**22**) and 6,7-dimethyl-2-phe-

Scheme 2



R = H (**23**, **26**), F (**24**), Br (**25**, **27**)

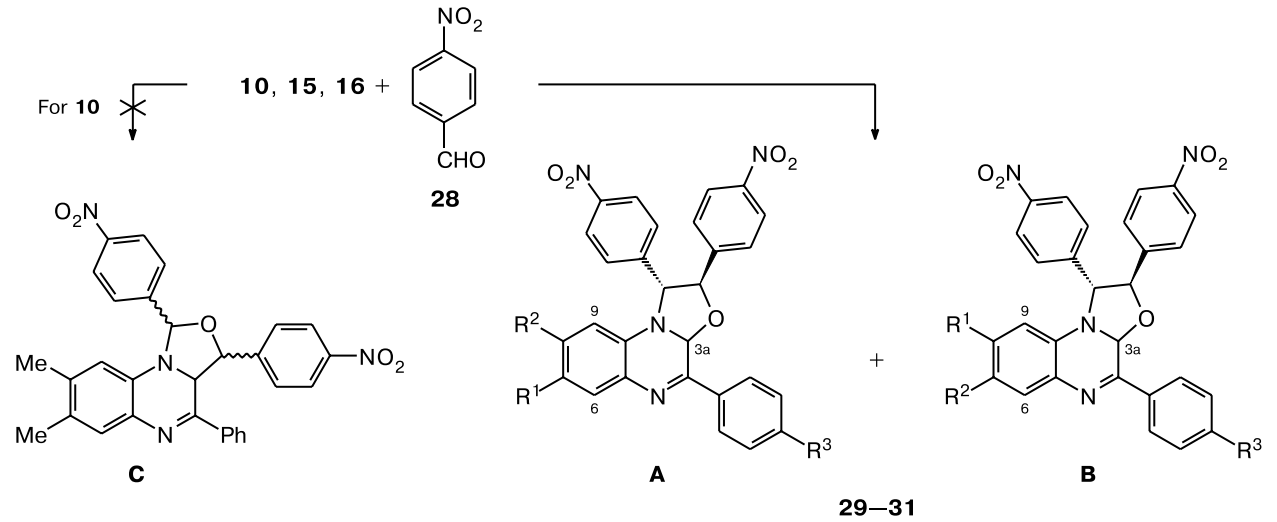
nylquinoxaline (**23**) (Scheme 2). These compounds were identified by ^{1}H NMR spectroscopy and mass spectrometry and by comparing with the data published in the literature.[10,11] Quinoxalines **23—25** were prepared also by refluxing compounds **10—12** in methanol in the presence of sulfuric acid. In refluxing acetone in the presence of traces of hydrochloric acid, azirenoquinoxalines **10** and **11** undergo a known rearrangement[12] into the corresponding 2-aryl-3-(4-nitrobenzyl)quinoxalines **26** and **27**. Quinoxaline **23** was also prepared by the independent synthesis from phenylglyoxal and **1**.

The 1,3-dipolar cycloaddition is typical of cyclic anils of aziridinyl ketones.[4] 4-Nitrobenzaldehyde can serve as an active dipolarophile, which reacts with DAQ to give the corresponding cycloadducts.[5]

The reaction of 7,8-dimethyldihydroazirenoquinoxaline **10** with 4-nitrobenzaldehyde (**28**) produced cycloadduct **29**, whose structure was established by spectroscopic methods (Scheme 3).

In the ^{1}H NMR spectrum of compound **29**, the signals for the protons of the dihydroazole fragment form an AB pair at δ 5.14 and 5.22 with the spin-spin coupling constant of 6.3 Hz. This spectral pattern rules out the structure of regioisomer **C** for the cycloadduct. To make an unambiguous assignment of the singlets at δ 6.41 and 6.46, we used the nuclear Overhauser effect. Additional irradiation at the resonance frequency of the methyl protons at δ 2.08 leads to a decrease in the intensity of the singlet at δ 6.46. Consequently, this signal corresponds to the pro-

Scheme 3



Compound	R^1	R^2	R^3	Yield (%)	Ratio of regioisomers (%)	
					A	**B**
29	Me	Me	H	39	—	—
30	Me	H	H	31	60	40
31	Me	H	Br	53	60	40

ton at position 9, and the singlet at δ 6.41 belongs to the proton at position 3a. This experiment also enabled us to make an unambiguous assignment of the signals of the Me groups. The signal at lower field (δ 2.16) was assigned to the Me group at position 7, and the signal at higher field (δ 2.08) belongs to the Me group at position 8, which is attributed to the anisotropic effect of the adjacent nitrophenyl substituent.

In the cycloaddition reaction, aziridines **15** and **16** were used as mixtures of isomers. Adducts **30** and **31** were also obtained as mixtures of regioisomers, which differ only in the position of the Me group in the dihydroquinoxaline fragment. In particular, this is evidenced by a doubling of the signals of the dihydrooxazole fragment with equal spin-spin coupling constants (~6 Hz) in the ^{1}H NMR spectra. The orientation of the nitrophenyl substituents remains unchanged. The ratio of the regioisomers was estimated from the integrated intensities of the singlets for the H(6) proton of isomer **A** (δ 7.30—7.40) and the H(9) proton of isomer **B** (δ 6.40—6.50), which were also assigned based on the nuclear Overhauser effect. Additional irradiation at the resonance frequency of the methyl protons at δ 2.23 leads to a decrease in the intensity of the singlet at δ 7.32 (H(6), isomer **A**) and the doublet at δ 6.95 (H(8), isomer **A**). The ratio of regioisomers appeared to be identical to that of the starting compounds.

One crystal of the isomeric mixture of cycloadduct **30** was studied by X-ray diffraction (Fig. 1). This compound was found to have the structure of 8-methyl-1,2-bis(4-nitrophenyl)-4-phenyl-1,2-dihydro-3a*H*-[1.3]oxazolo[3,2-*a*]quinoxaline (minor regioisomer **B**). The dihydropyrazine ring adopts a distorted sofa conformation with

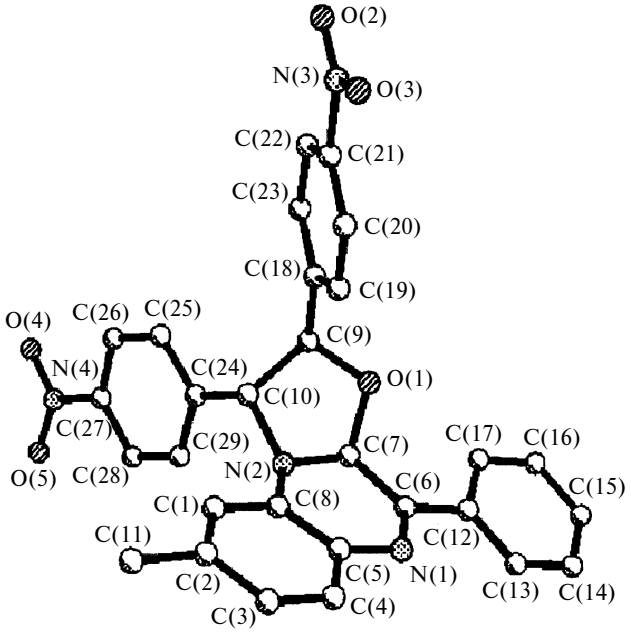


Fig. 1. Structure of compound **30** (minor isomer **B**) established by X-ray diffraction.

the C(6) and C(7) atoms deviating from the mean N(1)C(5)C(8)N(2) plane by −0.08 and −0.20 Å, respectively. The five-membered ring adopts an envelope conformation with the C(7) atom deviating from the plane through the other atoms of the ring by −0.51 Å. The N(2) atom has a pyramidal configuration (the sum of the bond angles is 347.3(4)°). Hence, the partially hydrogenated rings are *cis*-fused (the C(6)—C(7)—N(2)—C(8) and O(1)—C(7)—N(2)—C(10) torsion angles are 12.7(6)° and 35.1(4)°, respectively). As a whole, the tricyclic system adopts a bent conformation (the C(1)—C(8)—N(2)—C(10) torsion angle is 34.5(6)°) due to the presence of the shortened intramolecular H(1)...C(10) (2.70 Å) (the sum of the van der Waals radii is 2.87 Å)[13] and H(1)...H(10) (2.20 Å (2.32 Å)) contacts.

The phenyl group (C(12)...C(17)) is twisted with respect to the N(1)=C(6) bond by 11.4(6)° (the N(1)—C(6)—C(12)—C(13) torsion angle) due, apparently, to the shortened intramolecular H(13)...N(1) (2.48 Å (2.66 Å)) and H(17)...C(7) (2.58 Å) contacts.

The aryl substituents in the five-membered ring are in a *trans* orientation with respect to each other (the C(18)—C(9)—C(10)—C(24) torsion angle is 115.8(4)°). Their mutual repulsion leads to an elongation of the C(9)—C(10) bond to 1.574(6) Å. The phenyl ring (C(18)...C(23)) is in the *sp* conformation relative to the C(9)—H(9) bond (the H(9)—C(9)—C(18)—C(23) torsion angle is 12(1)°).

The nitrophenyl moiety at the C(10) atom is twisted by 58(1)° with respect to the C(10)—H(10) bond in spite of the shortened intramolecular H(29)...N(2) contact (2.48 Å). As a result of this orientation, the Me group at the C(2) atom is located above the plane of the nitrophenyl ring, which accounts for the above-described features of the ^{1}H NMR spectra.

To summarize, the reactions of 4-methyl- and 4,5-dimethyl-1,2-phenylenediamine with 1,3-diaryl-2,3-dibromopropan-1-ones afforded new 2-aryl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline derivatives. It was demonstrated that the reaction of 4-methyl-1,2-phenylenediamine produces a mixture of 5- and 6-methyl-substituted dihydroazireno[1,2-*a*]quinoxalines. The chemical properties of the reaction products were studied. 1,2-Dihydroquinoxalin-2-one, 3-(4-nitrobenzyl)quinoxaline, and 4-aryl-1,2-bis(4-nitrophenyl)-1,2-dihydro-3a*H*-oxazolo[3,2-*a*]quinoxaline derivatives were synthesized. The structures of the resulting compounds were established by ^{1}H NMR spectroscopy, mass spectrometry, and X-ray diffraction.

Experimental

The ^{1}H NMR spectra were recorded on Varian Mercury VX-200 (200 MHz) and Bruker AM-300 (300 MHz) spectrometers in $CDCl_3$ and DMSO-d_6 (Me_4Si as the internal standard).

The mass spectra were obtained on a Varian 1200L instrument (70 eV). The purity of the reaction products was checked by TLC on Silufol UV-254 plates with the use of chloroform, ethyl acetate, or their mixture as the solvent. The ratio of regioisomers was monitored on a Bischoff module liquid chromatograph equipped with a Prontosil 120-3-Si column with the use of dichloromethane as the eluent. The melting points were measured on a Boetius hot-stage apparatus and are uncorrected.

Substituted *o*-phenylenediamines, 4-fluorophenylglyoxal, and 4-nitrobenzaldehyde were commercial reagents (Aldrich), which were used without additional purification.

1,3-Diaryl-2,3-dibromopropan-1-ones **3—9** were synthesized according to a known procedure.[14] The characteristics of new chalcone dibromides are given below.

2,3-Dibromo-3-(4-nitrophenyl)-1-(4-pentylphenyl)propan-1-one (6). The yield was 66%, m.p. 143—144 °C (from an MeOH—$CHCl_3$ mixture). Found (%): N, 2.88. $C_{20}H_{21}Br_2NO_3$. Calculated (%): N, 2.90. ^{1}H NMR (DMSO-d_6), δ: 0.85 (t, 3 H, $\underline{Me}(CH_2)_4$, J = 6.6 Hz); 1.24—1.36 (m, 4 H, $MeC\underline{H}_2C\underline{H}_2(CH_2)_2$); 1.61 (quint, 2 H, $Me(CH_2)_2C\underline{H}_2CH_2$, J = 7.2 Hz); 2.68 (t, 2 H, $Me(CH_2)_3C\underline{H}_2$, J = 7.5 Hz); 5.95 (d, 1 H, C(3)H, J = 11.3 Hz); 6.73 (d, 1 H, C(2)H, J = 11.3 Hz); 7.45 and 8.19 (both d, 2 H each, $C_6\underline{H}_4C_5H_{11}$, J = 8.2 Hz); 8.14 and 8.29 (both d, 2 H each, $C_6H_4NO_2$, J = 8.9 Hz).

2,3-Dibromo-1-(4-fluorophenyl)-3-(4-nitrophenyl)propan-1-one (7). The yield was 63%, m.p. 182—184 °C (from an MeOH—$CHCl_3$ mixture). Found (%): N, 3.21. $C_{15}H_{10}Br_2FNO_3$. Calculated (%): N, 3.25. ^{1}H NMR (DMSO-d_6), δ: 5.96 (d, 1 H, C(3)H, J = 11.3 Hz); 6.78 (d, 1 H, C(2)H, J = 11.3 Hz); 7.44—7.53 and 8.34—8.42 (both m, 2 H each, C_6H_4F); 8.13 and 8.30 (both d, 2 H each, $C_6H_4NO_2$, J = 8.9 Hz).

2,3-Dibromo-1-(4-difluoromethoxyphenyl)-3-(4-nitrophenyl)propan-1-one (9). The yield was 80%, m.p. 108—110 °C (from an MeOH—$CHCl_3$ mixture). Found (%): N, 2.95. $C_{16}H_{11}Br_2F_2NO_4$. Calculated (%): N, 2.92. ^{1}H NMR (DMSO-d_6), δ: 5.96 (d, 1 H, C(3)H, J = 11.1 Hz); 6.77 (d, 1 H, C(2)H, J = 11.1 Hz); 7.47 (t, 1 H, $OCHF_2$, J = 73.2 Hz); 7.40 and 8.37 (both d, 2 H each, $C_6\underline{H}_4OCHF_2$, J = 8.5 Hz); 8.13 and 8.29 (both d, 2 H each, $C_6H_4NO_2$, J = 8.9 Hz).

5,6-Dimethyl-1-(4-nitrophenyl)-2-phenyl-1,1a-dihydroazireno[1,2-*a*]quinoxaline (10). A solution of chalcone dibromide **3** (12 g, 29 mmol), diamine **1** (3.95 g, 29 mmol), and triethylamine (8.16 mL, 116 mmol) in methanol (460 mL) was refluxed for 50 min and then kept at ~20 °C in the dark for 1 day. The precipitate that formed was filtered off and washed with methanol (10 mL) and 50% aqueous methanol (20 mL). The mother liquor was concentrated under reduced pressure to 1/3 of the initial volume. After 1 day, the second portion of the reaction product was filtered off and also washed with methanol and aqueous methanol. The portions were combined. Compound **10** was obtained in a yield of 5.0 g (45%), m.p. 141—143 °C (from acetone). ^{1}H NMR ($CDCl_3$), δ: 2.30 and 2.31 (both s, 3 H each, Me); 3.00 (d, 1 H, C(1a)H, J = 2.7 Hz); 3.51 (d, 1 H, C(1)H, J = 2.7 Hz); 7.18—8.30 (m, 11 H, H arom.).

Compounds **11—20** were synthesized analogously.

2-(4-Bromophenyl)-5,6-dimethyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (11). The yield was 45%, m.p. 150—154 °C (from acetone). Found (%): N, 9.39. $C_{23}H_{18}BrN_3O_2$. Calculated (%): N, 9.37. ^{1}H NMR ($CDCl_3$), δ: 2.26 and 2.27 (both s, 3 H each, Me); 2.95 (d, 1 H, C(1a)H, J = 2.8 Hz); 3.41 (d, 1 H, C(1)H, J = 2.8 Hz); 7.14—8.27 (m, 10 H, H arom.).

2-(4-Fluorophenyl)-5,6-dimethyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (12). The yield was 39%, m.p. 139—145 °C (from acetone). Found (%): N, 10.82. $C_{23}H_{18}FN_3O_2$. Calculated (%): N, 10.85. ^{1}H NMR ($CDCl_3$), δ: 2.26 and 2.27 (both s, 3 H each, Me); 2.95 (d, 1 H, C(1a)H, J = 2.8 Hz); 3.43 (d, 1 H, C(1)H, J = 2.8 Hz); 7.10—8.27 (m, 10 H, H arom.).

2-(4-Difluoromethoxyphenyl)-5,6-dimethyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (13). The yield was 30%, m.p. 127—130 °C (from acetone). Found (%): N, 9.66. $C_{24}H_{19}FN_3O_3$. Calculated (%): N, 9.65. ^{1}H NMR ($CDCl_3$), δ: 2.29 and 2.30 (both s, 3 H each, Me); 2.96 (d, 1 H, C(1a)H, J = 2.8 Hz); 3.44 (d, 1 H, C(1)H, J = 2.8 Hz); 6.58 (t, 1 H, $OCHF_2$, J = 73.0 Hz); 7.17—8.27 (m, 10 H, H arom.).

5,6-Dimethyl-1-(4-nitrophenyl)-2-(4-pentylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (14). The yield was 39%, m.p. 123—127 °C (from acetone). Found (%): N, 9.60. $C_{28}H_{29}N_3O_2$. Calculated (%): N, 9.56. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, $\underline{Me}(CH_2)_4$, J = 6.8 Hz); 1.28—1.34 (m, 4 H, $MeC\underline{H}_2C\underline{H}_2(CH_2)_2$); 1.59—1.67 (m, 2 H, $Me(CH_2)_2C\underline{H}_2CH_2$); 2.29 and 2.30 (both s, 3 H each, Me); 2.62 (t, 2 H, $Me(CH_2)_3C\underline{H}_2$, J = 7.7 Hz); 2.96 (d, 1 H, C(1a)H, J = 2.8 Hz); 3.44 (d, 1 H, C(1)H, J = 2.8 Hz); 7.17—8.27 (m, 10 H, H arom.).

5(6)-Methyl-1-(4-nitrophenyl)-2-phenyl-1,1a-dihydroazireno[1,2-*a*]quinoxaline (15) (a mixture of isomers **A** and **B**). The yield was 38%, m.p. 135—136 °C (from acetone). Found (%): N, 11.87. $C_{22}H_{17}N_3O_2$. Calculated (%): N, 11.82. ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, Me (**B**)); 2.36 (s, 3 H, Me (**A**)); 2.98 (d, 1 H, C(1a)H (**A**), J = 2.8 Hz); 3.01 (d, 1 H, C(1a)H (**B**), J = 2.8 Hz); 3.47 (d, 1 H, C(1)H (**B**), J = 2.8 Hz); 3.48 (d, 1 H, C(1)H (**A**), J = 2.8 Hz); 7.02—8.28 (m, 12 H, H arom. (**A** + **B**)). MS, m/z (I_{rel} (%)): 355 $[M]^+$ (100), 308 $[M - NO_2 - H]^+$ (20), 270 (13), 233 $[M - C_6H_4NO_2]^+$ (19), 220 $[M - CHC_6H_4NO_2]^+$ (60), 193 (12), 192 (14), 178 (11), 165 (21).

2-(4-Bromophenyl)-5(6)-methyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (16) (a mixture of isomers **A** and **B**). The yield was 43%, m.p. 136—140 °C (from acetone). Found (%): N, 9.73. $C_{22}H_{16}BrN_3O_2$. Calculated (%): N, 9.68. ^{1}H NMR ($CDCl_3$), δ: 2.36 (s, 3 H, Me (**B**)); 2.37 (s, 3 H, Me (**A**)); 2.97 (d, 1 H, C(1a)H (**A**), J = 2.8 Hz); 3.00 (d, 1 H, C(1a)H (**B**), J = 2.8 Hz); 3.43 (d, 1 H, C(1)H (**A** + **B**), J = 2.8 Hz); 7.03—8.28 (m, 11 H, H arom. (**A** + **B**)).

2-(4-Ethylphenyl)-5(6)-methyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (17) (a mixture of isomers **A** and **B**). The yield was 26%, m.p. 132—142 °C (from acetone). Found (%): N, 10.89. $C_{24}H_{21}N_3O_2$. Calculated (%): N, 10.96. ^{1}H NMR ($CDCl_3$), δ: 1.25 (t, 3 H, $CH_2\underline{Me}$ (**A** + **B**), J = 7.5 Hz); 2.34 (s, 3 H, Me (**B**)); 2.36 (s, 3 H, Me (**A**)); 2.70 (quart, 2 H, $C\underline{H}_2Me$ (**A** + **B**), J = 7.5 Hz); 2.96 (d, 1 H, C(1a)H (**A**), J = 2.8 Hz); 2.99 (d, 1 H, C(1a)H (**B**), J = 2.8 Hz); 3.47 (d, 1 H, C(1)H (**B**), J = 2.8 Hz); 3.48 (d, 1 H, C(1)H (**A**), J = 2.8 Hz); 7.00—8.27 (m, 11 H, H arom. (**A** + **B**)).

5(6)-Methyl-1-(4-nitrophenyl)-2-(4-pentylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (18) (a mixture of isomers **A** and **B**). The yield was 30%, m.p. 116—118 °C (from hexane). Found (%): N, 9.88. $C_{27}H_{27}N_3O_2$. Calculated (%): N, 9.87. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, $\underline{Me}(CH_2)_4$ (**A** + **B**), J = 6.8 Hz); 1.28—1.34 (m, 4 H, $MeC\underline{H}_2C\underline{H}_2(CH_2)_2$ (**A** + **B**)); 1.59—1.67 (m, 2 H, $Me(CH_2)_2C\underline{H}_2CH_2$ (**A** + **B**)); 2.35 (s, 3 H,

Me (**B**)); 2.36 (s, 3 H, Me (**A**)); 2.65 (t, 2 H, $Me(CH_2)_3C\underline{H}_2$ (**A** + **B**), J = 7.6 Hz); 2.96 (d, 1 H, C(1a)H (**A**), J = 2.8 Hz); 2.99 (d, 1 H, C(1a)H (**B**), J = 2.8 Hz); 3.47 (d, 1 H, C(1)H (**B**), J = 2.8 Hz); 3.48 (d, 1 H, C(1)H (**A**), J = 2.8 Hz); 7.00—8.27 (m, 11 H, H arom. (**A** + **B**)).

2-(4-Fluorophenyl)-5(6)-methyl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (19) (a mixture of isomers **A** and **B**). The yield was 37%, m.p. 133—140 °C (from acetone). Found (%): N, 11.31. $C_{22}H_{16}FN_3O_2$. Calculated (%): N, 11.25. ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, Me (**B**)); 2.36 (s, 3 H, Me (**A**)); 2.97 (d, 1 H, C(1a)H (**A**), J = 2.6 Hz); 3.00 (d, 1 H, C(1a)H (**B**), J = 2.6 Hz); 3.43 (d, 1 H, C(1)H (**B**), J = 2.6 Hz); 3.44 (d, 1 H, C(1)H (**A**), J = 2.6 Hz); 7.02—8.24 (m, 11 H, H arom. (**A** + **B**)).

5(6)-Methyl-1-(4-nitrophenyl)-2-(4-phenylphenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline (20) (a mixture of isomers **A** and **B**). The yield was 16%, m.p. 123—130 °C (from acetone). Found (%): N, 9.71. $C_{28}H_{21}N_3O_2$. Calculated (%): N, 9.74. ^{1}H NMR ($CDCl_3$), δ: 2.36 (s, 3 H, Me (**B**)); 2.37 (s, 3 H, Me (**A**)); 3.00 (d, 1 H, C(1a)H (**A**), J = 2.7 Hz); 3.03 (d, 1 H, C(1a)H (**B**), J = 2.7 Hz); 3.53 (d, 1 H, C(1)H (**A** + **B**), J = 2.7 Hz); 7.02—8.28 (m, 16 H, H arom. (**A** + **B**)).

2-(4-Fluorophenyl)-6,7-dimethylquinoxaline (24). Compound **12** (330 mg, 0.85 mmol) was refluxed in methanol (150 mL) in the presence of concentrated H_2SO_4 (0.15 mL) for 50 min. The reaction solution was concentrated under reduced pressure to 5 mL, neutralized with a 25% aqueous ammonia solution, and cooled. The precipitate that formed was filtered off and washed on a filter with methanol. Compound **24** was obtained in a yield of 155 mg (73%), m.p. 168 °C (from methanol). Found (%): N, 11.07. $C_{16}H_{13}FN_2$. Calculated (%): N, 11.10. ^{1}H NMR (DMSO-d_6), δ: 2.48 (s, 6 H, Me); 7.41 (t, 2 H, *m*-H arom., J = 8.7 Hz); 7.86 and 7.88 (both s, 1 H each, H(5), H(8)); 8.35 (dd, 2 H, *o*-H arom., ^3J = 8.7 Hz, ^4J = 6.1 Hz); 9.42 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 252 $[M]^+$ (100), 237 $[M - CH_3]^+$ (28), 225 $[M - CCH_3]^+$ (24), 210 $[M - CCH_3 - CH_3]^+$ (17), 183 (6), 121 (22), 103 (51).

Compounds **23** and **25** were synthesized analogously. The characteristics of the previously unknown compound **25** are given below.

2-(4-Bromophenyl)-6,7-dimethylquinoxaline (25). The yield was 77%, m.p. 141—142 °C (from MeOH). Found (%): N, 8.97. $C_{16}H_{13}BrN_2$. Calculated (%): N, 8.94. ^{1}H NMR (DMSO-d_6), δ: 2.47 (s, 6 H, Me); 7.77 (d, 2 H, *m*-H arom., J = 8.8 Hz); 7.87 and 7.89 (both s, 1 H each, H(5), H(8)); 8.24 (d, 2 H, *o*-H arom., J = 8.8 Hz); 9.44 (s, 1 H, H(3)). MS, m/z (I_{rel} (%)): 314, 312 $[M]^+$ (100); 299 (5), 297 (6) $[M - CH_3]^+$; 287, 285 $[M - CCH_3]^+$ (4); 233 $[M - Br]^+$ (80); 218 $[M - Br - CH_3]^+$ (12); 206 $[M - Br - CCH_3]^+$ (23); 191 $[M - Br - CCH_3 - CH_3]^+$ (24); 183 (26), 181 (30); 157 (16); 103 (51).

3-Aryl-6,7-dimethyl-2-(4-nitrobenzyl)quinoxalines 26 and **27** were synthesized according to a known procedure.[12]

6,7-Dimethyl-2-(4-nitrobenzyl)-3-phenylquinoxaline (26). The yield was 74%, m.p. 167—168 °C. Found (%): N, 11.34. $C_{23}H_{19}N_3O_2$. Calculated (%): N, 11.37. ^{1}H NMR ($CDCl_3$), δ: 2.54 and 2.56 (both s, 3 H each, Me); 4.50 (s, 2 H, CH_2); 7.17—8.07 (m, 11 H, H arom.). MS, m/z (I_{rel} (%)): 252 $[M]^+$ (100), 237 $[M - CH_3]^+$ (28), 225 $[M - CCH_3]^+$ (24), 210 $[M - CCH_3 - CH_3]^+$ (17).

3-(4-Bromophenyl)-6,7-dimethyl-2-(4-nitrobenzyl)quinoxaline (27). The yield was 72%, m.p. 160 °C. Found (%): N, 9.40. $C_{23}H_{18}BrN_3O_2$. Calculated (%): N, 9.37. ^{1}H NMR (DMSO-d_6), δ: 2.47 (s, 6 H, Me); 4.51 (s, 2 H, CH_2); 7.28—8.09 (m, 10 H, H arom.).

7,8-Dimethyl-1,2-bis(4-nitrophenyl)-4-phenyl-1,2-dihydro-3a*H*-[1.3]oxazolo[3,2-*a*]quinoxaline (29). A solution of compound **10** (1.0 g, 2.58 mmol) and 4-nitrobenzaldehyde (**28**) (0.39 g, 2.6 mmol) in toluene (30 mL) was refluxed for 30 min. Then the reaction solution was concentrated to one-half of the initial volume and kept at ~20 °C for 2 days. The precipitate that formed was filtered off and washed on a filter with acetone. The mother liquor was concentrated under reduced pressure to 1/3 of the initial volume and the second portion of the reaction product was isolated. The portions were combined. Compound **29** was obtained in a yield of 0.52 g (39%), m.p. 183—186 °C (from a MeCN—$PhCH_3$ mixture, 10 : 1). Found (%): N, 10.81. $C_{30}H_{24}N_4O_5$. Calculated (%): N, 10.76. ^{1}H NMR (DMSO-d_6), δ: 2.08 and 2.16 (both s, 3 H each, Me); 5.14 and 5.22 (both d, 1 H each, H(1), H(2), J = 6.3 Hz); 6.41 (s, 1 H, H(3a)); 6.46 (s, 1 H, H(9)); 7.31 (s, 1 H, H(6)); 7.50—8.33 (m, 13 H, H arom.). MS, m/z (I_{rel} (%)): 518 $[M - 2 H]^+$ (14), 370 (19), 234 $[M - (C_6H_4NO_2)_2CHCHO]^+$ (94), 233 (42), 219 (17), 207 (14), 192 (9), 151 (16), 150 (17), 103 (86).

7(8)-Methyl-1,2-bis(4-nitrophenyl)-4-phenyl-1,2-dihydro-3a*H*-[1.3]oxazolo[3,2-*a*]quinoxaline (30) (a mixture of isomers **A** and **B**). A solution of compound **15** (2.5 g, 7 mmol) and 4-nitrobenzaldehyde (**28**) (1.1 g, 7.3 mmol) in toluene (25 mL) was refluxed for 45 min and then kept at ~20 °C for 2 days. The precipitate that formed was filtered off and washed on a filter with acetone. Compound **30** was obtained in a yield of 1.1 g (31%), m.p. 179—182 °C (from MeCN). Found (%): N, 11.07. $C_{29}H_{22}N_4O_5$. Calculated (%): N, 11.06. ^{1}H NMR ($CDCl_3$), δ: 2.22 (s, 3 H, Me (**B**)); 2.33 (s, 3 H, Me (**A**)); 4.90—5.00 (m, 2 H, H(1), H(2) (**A** + **B**)); 6.20 (s, 1 H, H(3a) (**B**)); 6.28 (s, 1 H, H(3a) (**A**)); 6.34—8.35 (m, 16 H, H arom. (**A** + **B**)). MS, m/z (I_{rel} (%)): 504 $[M - 2 H]^+$ (5), 371 (4), 356 (5), 355 (5), 220 $[M - (C_6H_4NO_2)_2CHCHO]^+$ (100), 192 (15), 165 (15).

4-(4-Bromophenyl)-7(8)-methyl-1,2-bis(4-nitrophenyl)-1,2-dihydro-3a*H*-[1.3]oxazolo[3,2-*a*]quinoxaline (31) (a mixture of isomers **A** and **B**). A solution of compound **16** (550 mg, 1.27 mmol) and 4-nitrobenzaldehyde (**28**) (196 mg, 1.3 mmol) in toluene (15 mL) was refluxed for 30 min. Then the reaction solution was concentrated to one-half of the initial volume and kept at ~20 °C for 2 days. The precipitate that formed was filtered off and washed on a filter with acetone. Compound **31** was obtained in a yield of 400 mg (53%), m.p. 179—185 °C (from an MeCN—$CHCl_3$ mixture). Found (%): N, 9.61. $C_{29}H_{21}BrN_4O_5$. Calculated (%): N, 9.57. ^{1}H NMR (DMSO-d_6), δ: 2.15 (s, 3 H, Me (**B**)); 2.23 (s, 3 H, Me (**A**)); 5.13—5.23 (m, 2 H, H(1), H(2) (**A** + **B**)); 6.42—8.32 (m, 16 H, H(3a) (**A** + **B**) + H arom. (**A** + **B**)). MS, m/z (I_{rel} (%)): 584, 582 $[M - 2 H]^+$ (2); 434 (10); 300 (45), 298 $[M - (C_6H_4NO_2)_2CHCHO]^+$ (46); 219 (22); 165 (16).

X-ray diffraction study. X-ray diffraction data were collected from one single crystal, which was grown by crystallization of a mixture of isomers **30** from acetonitrile. The crystals belong to the orthorhombic system. At 20 °C, a = 36.98(2) Å, b = 10.552(7) Å, c = 13.016(9) Å, V = 5079(6) Å^3, d_{calc} = 1.325 g cm^{-3}, space group *Pbcn*, Z = 8. The unit cell parameters and intensities of 4384 independent reflections (R_{int} = 0.038) were measured on an automated Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning

technique, $2\theta_{max} = 50°$). The profile analysis of the X-ray diffraction data was performed with the use of the PROFIT program.

The structure was solved by direct methods with the use of the SHELXTL PLUS program package.[15] The positions of the H atoms were calculated geometrically and refined using a riding model with fixed $U_i = nU_{eq}$ of the corresponding pivot nonhydrogen atoms (n = 1.5 for Me groups and 1.2 for other H atoms). The structure was refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for all nonhydrogen atoms to $wR_2 = 0.208$ ($R_1 = 0.084$ based on reflections with $F > 4\sigma(F)$, $S = 1.00$).

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