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AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

8.* 1,2-DIARYL-1,1*a*-DIHYDROAZIRINO[1,2-*a*]QUINOXALINES FROM SUBSTITUTE o-PHENYLENEDIAMINES AND CHALCONE DIBROMIDES

V. D. Orlov, N. P. Vorob'eva,
N. N. Demenkova, V. S. Chesnovskii,
and F. G. Yaremenko

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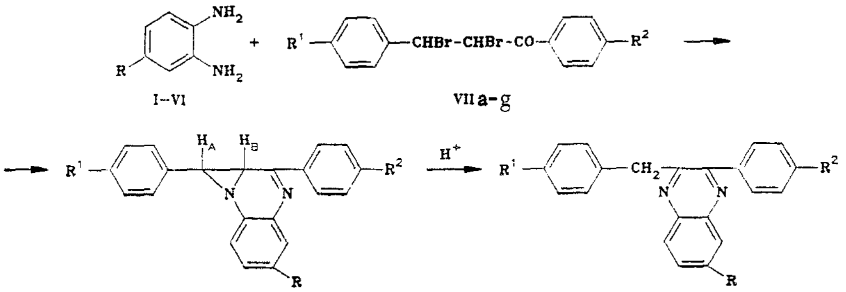
The reaction of 4-R-substituted (R = Br, Cl, OC_2H_5, C≡N, NO_2) 1,2-phenylenediamines with 1,3-diaryl-2,3-dibromo-1-propanones in the presence of triethylamine gave 1,2-diaryl-5-R-1,1*a*-dihydroazirino[1,2-*a*]quinoxalines, which undergo isomerization in an acidic medium to give 2-aryl-3-arylmethylene-7-R-quinoxalines. The dipole moments were measured, and the polarities of the synthesized compounds are discussed.

The interest in the chemistry of azirinoquinoxaline derivatives is due to the photochromism and thermochromisms that are characteristic for them and the high reactivities of the yields formed from them [1-6]. However, until now, only azirinoquinoxalines based on 1,2-phenylenediamine (I) have been described. In developing previous research [1, 5] we set out to study the products of the reaction of I and its 4-R-substituted compounds II-VI with 1,3-diaryl-2,3-dibromo-1-propanones VIIa-g; the reaction was accomplished by refluxing the starting compounds in methanol[†] in the presence of triethylamine:



I–VI

VIIa-g

VIIIa-g; IXa,c,g; Xa-g
XIa-g; XIIa,c,g; XIIIa,g

XIVa,c; XVa,c; XVIa

I, VIII, XIV R=H; II, IX, XV R=Br; III, X R=Cl; IV, XI $R=OC_2H_5$; V, XII, XVI R=CN; VI, XIII $R=NO_2$; VII–XVI a $R^1=R^2=H$; b $R^1=Br$, $R^2=H$; c $R^1=H$, $R^2=Br$; d $R^1=R^2=Br$; e $R^1=H$, $R^2=Cl$; f $R^1=R^2=Cl$; g $R^1=NO_2$, $R^2=H$

In all cases we obtained individual compounds, which, with respect to the results of elementary analysis and the spectral properties, correspond to the structures of 1, 1*a*-dihydroazirino[1,2-*a*]quinoxaline derivatives (Table 1).

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*See [1] for communication 7.

[†] The use of other alcohols entails raising the boiling point of the reaction mixture and, as a consequence, accelerating secondary 1,3-dipolar-addition processes [1].

A. M. Gor'kii Kharkov State University, Kharkov 310,077. Rubezhansk Branch, Scientific-Research Institute of Organic Intermediates and Dyes MNPO, Rubezhnoe 349,870. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3, pp. 328-333, March, 1988. Original article submitted September 2, 1986.

TABLE 1. 1,2-Diaryl-5-R-1,1^{a}-dihydroazirino[1,2-^{a}]quinoxalines

Compound	mp, °C	R_f	UV spectrum, λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)	N found, %	Empirical formula	N calc., %	Yield, %
VIIIa	124	0,53	345 (7,3), 310 (10,9), 257 (33,9)	—		—	39
VIIIb	118	0,62	348 (5,0), 304 (9,0), 254 (24,6)	7,41	$C_{21}H_{15}BrN_2$	7,47	43
VIIIc	121	0,62	350 sh (~7,0), 310 (10,6), 267 (21,9); 249 (24,5)	7,50	$C_{21}H_{15}BrN_2$	7,47	36
VIIId	126	0,72	347 sh (~5,0), 307 (9,6), 265 sh, 255 (27,4)	6,22	$C_{21}H_{14}Br_2N_2$	6,17	52
VIIIe	112	0,65	350 sh (~6,0), 308 (11,7), 263 (22,3), 249 (28,3)	8,54	$C_{21}H_{15}ClN_2$	8,47	40
VIIIf	106	0,80	339 (12,5), ~300 sh, ~265 sh, 255 (27,4)	7,76	$C_{21}H_{14}Cl_2N_2$	7,67	48
VIIIg	136	0,41	352 sh (12,0), 302 sh (~27,4), 257 (39,8)	—		—	38
IXa	108	0,70	355 (5,4), 313 sh (~11,0), ~267 sh, 254 (35,7)	7,54	$C_{21}H_{15}BrN_2$	7,47	40
IXc	132	0,83	348 (7,7), 312 (13,7), 268 (26,3), 253 (27,7)	6,14	$C_{21}H_{14}Br_2N_2$	6,17	44
IXg	143	0,51	362 (8,9), 302 sh (~19,0), 265 (31,1)	10,19	$C_{21}H_{14}BrN_3O_2$	10,00	32
Xa	123	0,74	345 (12,5), ~301 sh., 265 sh, 252 (31,7)	8,43	$C_{21}H_{15}ClN_2$	8,47	29
Xg	135	0,64	352 sh (~5,0), 302 (17,3), 265 (22,6)	11,2	$C_{21}H_{14}ClN_3O_2$	11,19	48
XIa	127	0,48	355 (7,2), 301 (18,3), 254 (28,7)	8,21	$C_{23}H_{20}N_2O$	8,24	27
XIg	142	0,39	398 (7,3), ~302 sh, 270 (27,5)	11,02	$C_{23}H_{19}N_3O_3$	10,91	59
XIIa	140	0,39	359 (7,0), 309 (13,4), 267 (21,7), 249 (26,4)	13,20	$C_{22}H_{15}N_3$	13,08	52
XIIc	151	0,53	350 sh (~8,7), 313 (17,2), 278 (20,2), 247 (28,2)	10,55	$C_{22}H_{14}BrN_3$	10,50	32
XIIg	162	0,21	~352 sh, 302 (28,1), 265 (37,7)	15,47	$C_{22}H_{14}N_4O_2$	15,30	24
XIIIa	154	0,65	396 sh (~6,0), 326 (16,6), 247 (21,5)	12,39	$C_{21}H_{15}N_3O_2$	12,31	34
XIIIg	185	0,48	~393 sh (~7,0), 346 (16,6), 254 (28,5)	14,48	$C_{21}H_{14}N_4O_4$	14,51	38

*Compounds VIIIa,g were described in [4].

Thus the spectra of these compounds in the near-UV region contain no less than three absorption bands that decrease monotonically in intensity with an increase in the wavelength, i.e., the pattern that is typical for the absorption of the $N-C_6H_4-N{=}C-Ar$ chromophore is observed [7]. Characteristics $\nu_{C=N}$ (1600-1615 cm^{-1}), $\nu_{NO_2}{}^{as}$ (1510-1522 cm^{-1}), $\nu_{NO_2}{}^{s}$ (1342-1349 cm^{-1}), and aziridine ring ν^{as} and ν^{s} bands (1010-1025 and 870-882 cm^{-1}, respectively) are noted in the IR spectra. In addition to overlapped multiplets of aromatic protons, two doublets of protons of the aziridine ring with spin-spin coupling constants 3.0-3.1 Hz, which attest to their trans orientation, are observed in the PMR spectra (Table 2).

The individuality of VIII-XIII, which was confirmed by TLC (Table 1), attests to the high regiospecificity of the reaction of phenylenediamines I-VI with the chalcone dibromides, and the question of the specificity of the investigated processes therefore arises. The effect of substituents introduced into the 5 or 6 position of the three-ring system on the properties of azirinoquinoxalines VIII-XIII should not differ substantially. This also applies to the spectral properties. For example, the PMR spectra (100 MHz), which give an unequivocal answer regarding the structure of dihydroquinoxalines that are substituted in the annelated benzene ring [8], are not informative in this case. One can form a judgment regarding the position of R only from the PMR spectrum of XIIIa, in which, under the influence of two electron-acceptor groups (NO_2 and C=N), the protons of the annelated ring display signals at weak fields and can be reliably identified. The characteristics of these protons [δ (ppm), J (Hz)] are as follows: 4-H 8.17 (d), 2.5; 6-H 8.02 (dd), 8.0 and 2.5; 7-H 7.52 (d), 8.0. They correspond to the only possible structure with R in the 5 position; the fact that the nitrogen atom of the aziridine ring displays electron-donor properties with respect to the annelated phenylene ring and that the signal of the 7-H proton consequently should experience the greatest diamagnetic effect is taken into account in this analysis.

The problem regarding the position of substituent R in VIII-XIII can be solved most reliably only on the basis of an analysis of their vector characteristics. For this, we measured the dipole moments of a number of compounds that contain regular groups as the R, R^1, and R^2 substituents (Table 2).

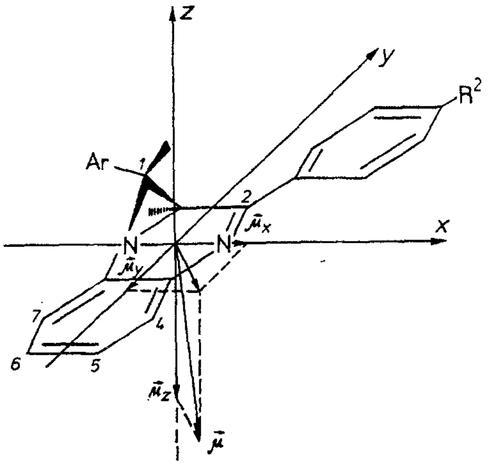

Fig. 1. Orientation of the **azirino**quinoxaline three-ring system and the vector of its dipole moment in a system of rectangular coordinates.

TABLE 2. 1,2-Diaryl-5-R-1,1*a*-dihydroazirino[1,2-*a*]quinoxalines

Compound	PMR spectrum*			μ, D		
	δ_{H_A}	δ_{H_B}	J_{AB}	exptl.	calc. (5-R)	calc. (6-R)
VIIIa	3,39	2,90	3,0	1,77	1,77	
VIIIb				1,73	1,64	
VIIIc	3,39	2,99	3,0	1,89	1,89	
VIIId				1,06	1,78	
VIIIe	3,41	3,00	3,0	1,87	1,91	
VIIIg	3,49	3,03	3,0			
IXa	3,49	3,03	3,0	3,02	3,02	2,76
IXc	3,39	2,95	3,0	2,82	2,67	1,77
Xa	3,52	3,00	3,0			
XIIa	3,49	3,03	3,1	5,57	5,35	4,98
XIIc				4,34	4,78	3,53
XIIIa	3,49	3,06	3,1	5,51	5,30	4,93

*The solvent was $CDCl_3$, except for VIIIa, IXa, and Xa, for which the solvent was $CDCl_3$ with added D_5-pyridine.

The position of the bromine atom in the phenylene ring of the azirinoquinoxalines can be judged on the basis of the μ_{exp} values of VIIIa,c and IXa,c; the results of an analysis of Dreiding models, according to which the investigated three-ring systems are conformationally rigid systems with a compressed dihydroquinoxaline fragment, are taken into account. The dipole moment of VIIIa is 1.77 D. The introduction of a bromine atom as substituent R^2 (VIIIc) increases μ by 0.12 D, whereas its introduction as substituent R (IXa) increases μ by 1.25 D. As regards the μ value of dibromo derivative IXc, it is 2.82 D, i.e., close to the moment of IXa rather than VIIIa. This means that substituent R = Br is located in the 5 position of the three-ring system rather than in the 6 position; in the latter case the bond moment of this bromine atom would completely compensate the moment for R^2 = Br (as a consequence of their antiparallel character), and the expected μ_{calc} value of IXc would be close to 1.77 D.

This conclusion is confirmed by the μ_{calc} values of VIIIb,d and IXc. In the calculations of these values the moment of the three-ring system was assumed to be equal to the μ_{exp} value of VIIIa, while its direction was evaluated by means of unit vectors calculated on the basis of the μ_{exp} values of VIIIa,c and IXa. The orientation of the azirinoquinoxaline molecule in a system of coordinates is shown in Fig. 1. The calculated values of the unit vectors $\vec{\mu}_x = 0.48$, $\vec{\mu}_y = -1.02$, and $\vec{\mu}_z = -1.37$. The μ_{calc} values of VIIIb,d and IXc were determined taking these data into account (Table 2); their good agreement with the μ_{exp} values confirms the correctness of the determination of the position of R = Br in the phenylene ring.

The dipole moments of XIIa,c (R=C≡N) and XIIIa ($R=NO_2$) were calculated on the basis of the same values of the unit vectors of the moment of the heterocycle. It is apparent from

TABLE 3. 3-Benzyl-2-(R^2-phenyl)-7-R-quinoxalines

Compound	mp, °C	R_f	UV spectrum, λ_{max}, ($\varepsilon \cdot 10^{-3}$)	μ_{exp}, D	N found, %	Empirical formula	N calc, %	Yield, %
XIVa	98 [11]	0,41	327 (8,9), 241 (30,1)	0,83	9,58	$C_{21}H_{16}N_2$	9,46	80
XIVc	131	0,44	326 (11,3), 239 (38,4)	1,88	7,61	$C_{21}H_{15}BrN_2$	7,47	84
XVa	82	0,47	322 (13,1), 240 (41,8)	2,40	7,52	$C_{21}H_{15}BrN_2$	7,47	81
XVc	148	0,53	322 (12,1), 243 (45,3)	2,00	6,29	$C_{21}H_{14}Br_2N_2$	6,17	90
XVIa	131	0,40	333 (11,6), 244 (46,3)	4,43	13,19	$C_{22}H_{15}N_3$	13,08	86

Table 2 that better agreement between μ_{calc} and μ_{exp} is also achieved for the 5-substituted compounds. The conclusion regarding the structure that was drawn on the basis of an analysis of the PMR spectrum is thereby confirmed in the case of XIIIa.

Fundamental differences in the chemical behavior of 4-bromo- and 4-chloro-1,2-phenylenediamine are not observed, and the structures of IXa,g and Xa,g should therefore be identical. As regards the position of substituent R = OC_2H_5 in XIa,g, it is difficult to obtain an unequivocal answer to this question (the method of dipole moments does not give an unequivocal answer because of the irregularity of the epoxy group).

The participation of the more basic amino group of substituted 1,2-phenylenediamines is preferable in the addition to the intermediate 1,3-diaryl-2-bromopropen-1-ones formed by the action of triethylamine on chalcone dibromides VIIa-g. For II-IV this is the amino group in the 1 position, and it should therefore be expected that substituent R in XIa,g is also located in the 5 position.

The behavior of 4-cyano- and 4-nitro-1,2-phenylenediamine (V and VI), which contain strong electron-acceptor groups, does not follow this principle. The chief factor that determines the direction of processes in which they participate is most likely retention of the conjugation of substituent R with the amino group in the 1 position, which is achieved in XII and XIII but would be disrupted under the condition of conversion of this group to an azomethine group (i.e., in the isomeric compounds with the R group in the 6 position).

The acid-catalyzed isomerization of dihydroazirinoquinoxalines to quinoxaline derivatives was studied in detail in [4, 6]. We accomplished this process for some of the compounds that we studied and obtained 2-aryl-3-(4-R^1-benzyl)-7-R-quinoxalines, the properties of which are presented in Table 3. The reaction proceeds in high yields by brief heating of acetone solutions of VIIIa,c, IXa,c, and XIIa containing added concentrated HCl.

The position of the substituent in the phenylene fragment of quinoxaline does not change during isomerization, and the establishment of the structures of XIV-XVI therefore can serve as additional evidence for the orientation of R in the starting azirinoquinoxalines. With this end in mind, we measured the dipole moments of XIV-XVI (Table 3) and 2-phenylquinoxaline (XVII, μ_{exp} = 0.83 D). It follows from an analysis of these values that the simultaneous introduction of two bromine atoms into **quinoxaline** derivative XVc, as in the case of IXc, is not accompanied by compensation of the moments of the C—Br bonds. Consequently, substituent R = Br can occupy only the 7 position in the XVc molecule.

The direction of the moment of quinoxaline (0.51 D [9]) should coincide with its symmetry axis. The introduction of a phenyl ring (XVII) and a benzyl radical (XIVa) has little effect on the dipole moment of the heterocycle. However, the effect of bromine atoms on the polarization of the heterocycle probably depends on the site at which they are introduced; this may explain the failure of attempts to calculate the unit vectors of the moment of the heterocycle on the basis of bromine-substituted compounds XIVc and XVa,c.

In conclusion, let us note that all of the investigated dihydroazirinoquinoxalines VIII-XIII have clearly expressed photochromism: under the influence of UV light their color changes from light yellow to blue (compounds of the g group, R^1 = NO_2) or red.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Specord IR-75 spectrometer. The electronic absorption spectra of solutions in methanol at concentrations of $(2-4) \cdot 10^{-5}$ M were recorded with a Specord UV-vis spectrophotometer. The PMR spectra were recorded with Tesla BS-487B and Varian XL-100 spectrometers with tetramethylsilane as the internal standard. The individuality of the compounds was monitored by TLC on Silufol UV-254 plates with elution by chloroform.

Data on chalcone dibromides VIIa-g are presented in [10].

1-(4-Nitrophenyl)-2-phenyl-5-ethoxy-1,1*a*-dihydro[1,2-*a*]quinoxaline (XIg). A mixture of 4.0 g (9.7 mmole) of VIIg, 2.0 g (12.9 mmole) of diamine IV, and 3 ml (21.4 mmole) of $(C_2H_5)_3N$ in 65 ml of methanol was refluxed for 1 h, after which it was allowed to stand at room temperature for 24 h. The resulting precipitate was removed by filtration, washed with aqueous methanol (1:1), and dried to give 2.2 g (59%) of XIg, which was homogeneous with respect to TLC. After purification by column chromatography on silica gel L 100/250 with chloroform as the eluent, the product had mp 142°C (with decomposition).

Compounds VIII-XIII were similarly obtained.

2-Phenyl-3-benzyl-7-cyanoquinoxaline (XVIa). A 0.1-ml sample of concentrated HCl was added to a refluxing solution of 1.07 g (3.3 mmole) of VIIIa in 50 ml of acetone, during which the reaction mixture became red. The acetone was evaporated with a rotary evaporator, and the residue was crystallized by trituration with 5 ml of cold methanol. Crystallization from alcohol gave 0.92 g (86%) of XVIa in the form of silky filaments with mp 131°C. IR spectrum: 2963, 2916, 1451 (CH_2), 2226 cm^{-1} ($C{\equiv}N$). PMR spectrum ($CDCl_3$): 4.42 (2H, s, CH_2), 8.50 (1H, d, J = 2 Hz, 8-H), 8.20 (1H, d, J = 8 Hz, 5-H), 7.88 (1H, dd, J = 8 and 2 Hz, 6-H).

Compounds XIVa,c and XVa,c were similarly obtained.

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