N-Phenylnaphthalimide (I). This compound was obtained in 78% yield by the method in [3] with subsequent crystallization from methanol. The white crystals had mp 201-202°C. Found: N 5.2%. $C_{18}H_{11}NO_2$. Calculated: N 5.1%. IR spectrum: 1705, 1665 cm^{-1} (imide C=O, symmetrical and asymmetrical). Mass spectrum: M^+ 273.

N-Phenylisonaphthalimide (II). This compound was obtained in 73% yield by the method in [1]. The yellow crystals had mp 162-163°C. Found: N 5.2%. $C_{18}H_{11}NO_2$. Calculated: N 5.1%. IR spectrum: 1770 (C=O), 1680 cm^{-1} (C=N). Mass spectrum: M^+ 273. Isonaphthalimide II was thermally stable and sublimed without isomerization upon heating to 500°C.

Isomerization of N-Phenylisonaphthalimide (II) to N-Phenylnaphthalimide (I). A 0.2-g sample of isomide II was dissolved in 5 ml of benzene, and 3 ml of triethylamine was added. After 1.5 months, 1.8 g of imide I, which was identical to a genuine sample obtained by the method in [3], precipitated.

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CYCLIZATIONS OF N-ALKYLAZINIUM CATIONS WITH BIFUNCTIONAL NUCLEOPHILES. 18.* SYNTHESIS AND STRUCTURE OF HETEROCYCLIC SYSTEMS BASED ON QUINOXALINE

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N-Methylquinoxalinium iodide reacts with ethylenediamine, o-phenylenediamine, and o-aminophenol to give cyclization products of the type involving [2,3-b] annelation of the six-membered heteroring. Two molecules of the quinoxaline participate in the cyclization with 2-aminoethanol to give a complex polycyclic compound.

One-step methods for the synthesis of heterocyclic compounds based on the cyclizations of azines with bifunctional nucleophiles have undergone significant development in recent years [2, 3]. They have found greatest application in series of azine derivatives containing a pyrazine ring, the pronounced capacity of which for diaddition or disubstitution reactions serves as the basis for various sorts of cyclizations with dinucleophiles. The development of research in this field has also been stimulated by the fact that substances with various forms of biological activity have been discovered among pyrazine and quinoxaline derivatives condensed with five- and six-membered heterorings [2, 4-6].

We have previously studied the cyclizations of pyrazinium salts with 1,3-dinucleophiles, which lead to substances with a hydrogenated pyrazine ring fused with five-membered heterorings [3]. In the present research we studied the peculiarities of the annelation of six-membered heterorings to quinoxalines. With this in kind, we investigated the reactions of

*See [1] for communication 17.

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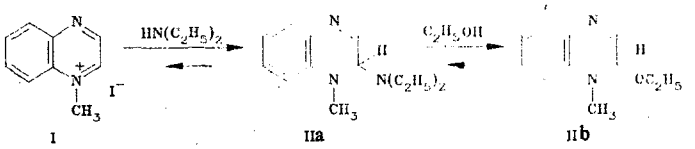
N-methylquinoxalinium iodide (I) with 1,4-N,N- and -N,O-bifunctional nucleophiles such as ethylenediamine, o-phenylene-diamine, o-aminophenol, and 2-aminoethanol.

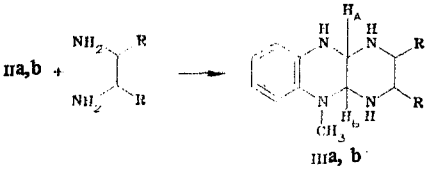
In the course of the investigation we established that the reactions of 1,4-dinucleophiles can be carried out preparatively more conveniently with, instead of N-methylquinoxalinium iodide (I), its covalent adduct (IIa) with diethylamine, which was obtained by the reaction of salt I with diethylamine in ether and chloroform, or with ethoxy adduct IIb, which was formed when IIa was dissolved in ethanol [7]. Dihydroquinoxaline IIa can be isolated from ether solution in the form of a light-yellow oil and can thus be subjected to reaction with dinucleophiles in aprotic solvents such as $CHCl_3$, CCl_4, diethyl ether, DMSO, and others. Ethoxy adduct IIb is formed when adduct IIa is dissolved in ethanol via exchange of the diethylamino group for an alcohol residue; the IIa ⇌ IIb equilibrium is shifted completely to the right [7].



I IIa IIb

In reactions with nucleophiles both adducts IIa, b behave like cation I, but, in contrast to salt I, they are quite soluble in ether, $CHCl_3$, CCl_4, and ethanol, and this makes it possible to create high concentrations of the reagents and thereby ensure rapid cyclization. In addition, the hydriodic acid liberated as a result of the addition of diethylamine to salt I is tied up by excess diethylamine and can be removed from the reaction sphere. The absence of HI in solution is an advantage, since even very small amounts of acids catalyze various transformations of cyclic tetrahydroquinoxalines (particularly regio- and stereo-isomerization), which invariably proceed through a step involving their dissociation to starting salt I and the dinucleophile [8, 9].

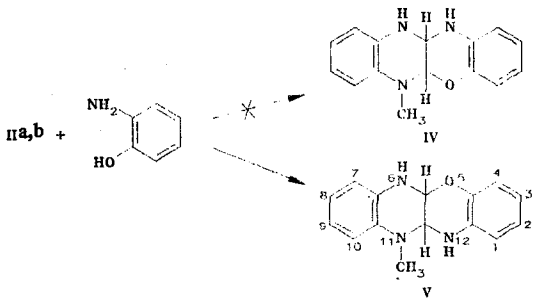
The reactions of adducts IIa, b with ethylenediamine and o-phenylenediamine proceed smoothly in ether, $CHCl_3$, CCl_4, or ethanol at room temperature and lead to cyclic products IIIa, b; owing to the symmetry of the fragment undergoing annelation, the question of its regioorientation does not arise.



IIIa, b

III a R=H, b R=benzo

Alternative structures of the products of reaction with the participation of two molecules of the quinoxaline were rejected on the basis of data from the mass spectra, which contain molecular-ion peaks with M^+ 204 and M^+ 252 for IIIa and IIIb, respectively. Signals of H_A and H_B protons at 4.0-4.7 ppm with $^3J_{A,B}$ = 2.6-2.7 Hz are clearly observed in the ^1H NMR spectra of pyrazino[2,3-b]quinoxaline (IIIa) and quinoxalino[2,3-b]quinoxaline (IIIb) (Table 2). It



IV V

TABLE 1. Characteristics of Annelated Quinoxalines IIIa, b, V, VII, and VIII

Compound	mp*, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIIa	107—108	64,4	7,9	27,7	$C_{11}H_{16}N_4$	64,7	7,9	27,4	90
IIIb	129—130	71,7	6,4	22,7	$C_{15}H_{16}N_4$	71,4	6,4	22,2	70
V	101—102	71,2	6,0	16,6	$C_{15}H_{15}N_3O$	71,1	6,0	16,6	53
VII	175—176	68,8	6,8	20,1	$C_{20}H_{23}N_5O$	68,7	6,6	20,1	60
VIII	124—126	68,5	7,1	23,6	$C_{20}H_{24}N_6$	69,0	6,9	24,1	74

*With decomposition (except for IIIa).

TABLE 2. Spectral Characteristics of Annelated Quinoxalines IIIa, b, V, VII, and VIII

Compound	^{1}H NMR spectrum, *δ, ppm (in $CDCl_3$)			^{13}C NMR spectrum, †δ, ppm
	N–CH_3,s	Nodal protons	aromatic protons,m	
IIIa	2,94	4,04 d (4a-H, $^3J_{4a,10a}$ = =2,6 Hz), 4,31 d (10a-H)	6,4—6,9	—
IIIb	2,90	4,46 m (5a-H, $^3J_{5a,11a}$ = =2,7 Hz), 4,69 m(11a-H)	6,2—6,7	35,4 (N—CH_3), 58,1 (11a-C), 63,9 (5a-C), 111,6, 112,6, 113,4, 117,3, 117,5, 118.1 (8 arom. CH), 130,9, 131,5, 132,6, 132,8 (4 quat. C)
V	2,83	4,49 dd (11a-H, $^3J_{11a,5a}$ = =2,2 Hz), 5,22 dd (5a-H)	6,4—7,0	32,3 (N—CH_3), 62,2 (11a-C), 77,2 (5a-C), 112,7, 113,3, 114,4, 116,1, 118,2, 119,2, 121,2 (8 arom. CH), 130,7, 131,0, 134,2, 142,0 (4 quat. C)
VII	2,93, 2,99	4,35 d (16a-H, $^3J_{16a,5a}$ = =3,2 Hz), 4,62 d (5a-H), 4,52 d (9a-H, $^3J_{9a,15a}$ = =6,2 Hz), 5,54 br.d (15a-H)	6,4—7,0	35,0, 38,0 (two N—CH_3 grps), 46,1 (N—CH_2), 63,7 (O—CH_2), 68,4 (15a-C), 70,4 (16a-C), 81,6 (9a-C)***, 83,5 (5a-C)***, 106,2, 110,6, 112,8, 115,2, 117,5, 118,5, 120,4, 120,8 (8 arom. CH), 131,2, 132,3, 132,3, 137,0 (4 quat. C)
VIII	2,96, 3,05	4,20 d (5a-H, $^3J_{5a,16a}$ = =4,0 Hz), 4,41 d (16a-H), 4,55 d (9a-H, $^3J_{9a,15a}$ = =6,2 Hz), 5,64 d (15a-H)	6,4—7,0	—

*The spectrum of IIIb was obtained in d_6-DMSO.
†The spectra of IIIb and V were recorded in d_6-DMSO, and the spectrum of VII was recorded in $CDCl_3$.
‡ D. D. The assignment of these signals may be just the opposite.

should be immediately noted that the vicinal spin-spin coupling constants (SSCC) in the case of annelation of five-membered heterorings to quinoxalines are 7-10 Hz [10]. The structure of IIIb was also confirmed by ^{13}C NMR spectroscopic data (Table 2).

In the reaction of dihydroquinoxalines IIa, b with o-aminophenol one might have expected the formation of two regioisomeric cycloadducts IV and V; however, the data from the ^{1}H NMR spectra of the reaction mixtures showed the presence of only one product in them. In the ^{1}H NMR spectrum of benzoxazino[1,4][2,3-b]quinoxaline V in $CDCl_3$ (Fig. 1) the signals of the protons of both nodal carbon atoms show up as double doublets at 4.49 ppm (11a-H) and 5.22 ppm, since, in addition to spin-spin coupling with one another with $^3J_{5a,11a}$ = 2.2 Hz, each of them couples with the proton of the adjacent NH group. In the case of exchange of the protons of the NH groups for deuterium the signals of the 5a-H and 11a-H protons take on the form of distinct doublets. These data make it possible to give preference to structure V. More rigorous proof of the mutual regioorientation of the heterorings in cycloadduct V was obtained from the ^{13}C NMR spectra. In the spectrum of V the signals of the C(5a) and C(11a) atoms, which are common to the fused heterorings, have chemical shifts of 77.2 ppm and 62.2 ppm, respectively. The assignment of the signals was made with allowance for the greater electronegativity of the oxygen atom as compared with the nitrogen atom, as well as on the basis of data from the ^{13}C NMR spectrum of IIIb (Table 2). Since the stronger-field signal of the nodal C(11a) atom at 62.2 ppm has a hyperfine structure (hfs) in which, in addition

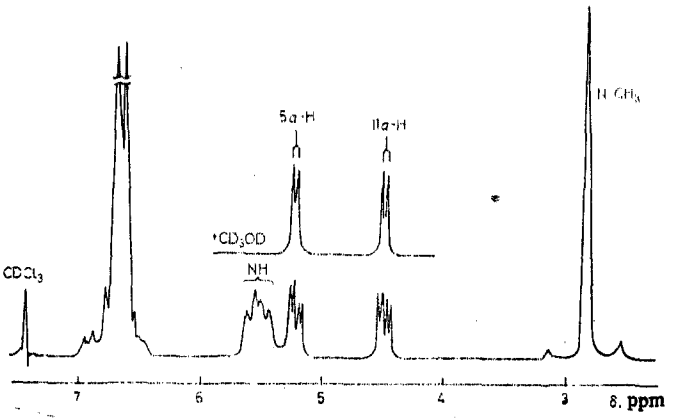


Fig. 1. ^{1}H NMR spectra of benzoxazino[2,3-b]quinoxaline V in $CDCl_3$.

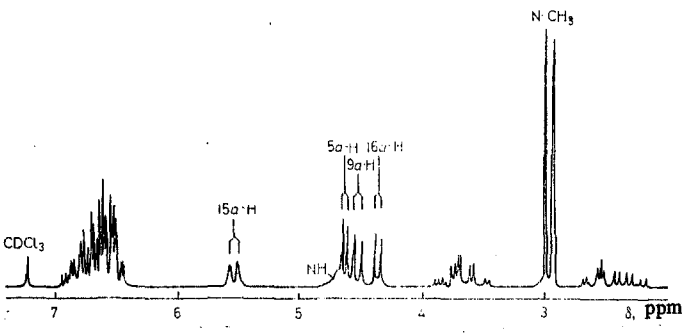
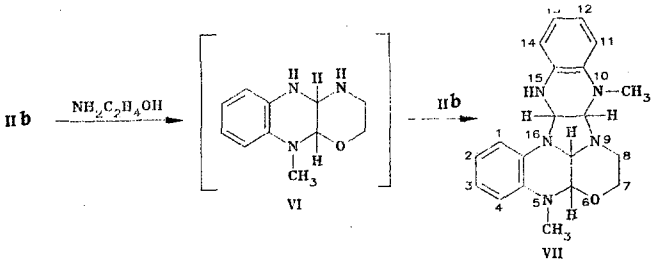


Fig. 2. ^{1}H NMR spectrum of VII in $CDCl_3$.

to the constant of direct spin-spin coupling through one bond $^1J(C_{11a}-H_{11a})$ = 154.9 Hz, long-range coupling with the protons of N-methyl group with $^3J(C_{11a}-HNCH_3)$ = 3 Hz appears, the regioorientation of the benzoxazine fragment in product V is rigorously proved.

The reaction of dihydroquinoxaline IIb with 2-aminoethanol proceeds in a considerably more complex manner. The mass-spectrometric data indicate that two molecules of the quinoxaline and one molecule of the amino alcohol enter into the composition of the resulting VII, which has a molecular-ion peak (M^+) at 349. The low intensity (8.2%) of the molecular-ion peak is explained by the ease of fragmentation of VII under the influence of electron impact. The principal fragmentation pathway is the formation of an N-methylquinoxalinium ion with m/z 145 (100%).



Signals of two N-methyl groups at 2.93 and 2.99 ppm and a multiplet of eight aromatic protons at 6.4-7.0 ppm are observed in the ^{1}H NMR spectrum of VII (Fig. 2 and Table 2); this indicates the presence of two quinoxaline fragments in the molecule. In addition, multiplets of NCH_2 and OCH_2 groups of a morpholine ring with δ values (in parts per million) 2.33 ddd (8-H_a, $^2J_{a,e}$ = 10.6 Hz, $^3J_{a,e}$ = 4.1 Hz, $^3J_{a,a}$ = 11.1 Hz), 2.58 ddd (8-H_e, $^3J_{e,e}$ = 1.9 Hz, $^3J_{e,a}$ = 1.9 Hz), 3.59 ddd (7-H_a, $^2J_{a,e}$ = 11.7 Hz), and 3.79 ddd (7-H_e), as well as a broad signal of the proton of an NH group at 4.64 ppm and two independent spin AB systems of the protons of nodal carbon atoms, are clearly seen in the spectrum. The difference in the vicinal constants between the coupled (in pairs) protons of the fused heterorings makes it

TABLE 3. Coordinates of the Basis Atoms with the Standard Deviations $\cdot 10^4$ ($\cdot 10^3$ for the H atoms) on the Structure of VII

Atom*	x	y	z	Atom*	x	y	z
O	9167 (1)	2592 (1)	868 (1)	$C_{(20)}$	9346 (2)	3554 (2)	85 (2)
$N_{(1)}$	9151 (2)	783 (2)	979 (2)	$H_{(1)}$	1020 (2)	208 (2)	2 (2)
$N_{(2)}$	7681 (2)	685 (2)	−790 (2)	$H_{(2)}$	1061 (2)	119 (2)	157 (2)
$N_{(3)}$	6429 (2)	−127 (2)	−2521 (2)	$H_{(3)}$	987 (2)	142 (2)	270 (2)
$N_{(4)}$	8141 (2)	1325 (2)	−3683 (2)	$H_{(4)}$	980 (2)	14 (2)	232 (2)
$N_{(5)}$	8763 (2)	2353 (2)	−1757 (2)	$H_{(5)}$	821 (2)	−22 (2)	305 (2)
$C_{(1)}$	9408 (2)	1763 (2)	211 (2)	$H_{(6)}$	643 (2)	−118 (2)	348 (2)
$C_{(2)}$	9930 (2)	884 (2)	1959 (2)	$H_{(7)}$	516 (2)	−126 (2)	191 (2)
$C_{(3)}$	8059 (2)	243 (2)	1275 (2)	$H_{(8)}$	574 (2)	−42 (2)	0 (2)
$C_{(4)}$	7699 (2)	−261 (2)	2425 (2)	$H_{(9)}$	915 (2)	105 (2)	−148 (2)
$C_{(5)}$	6627 (3)	−834 (2)	2661 (2)	$H_{(10)}$	646 (2)	111 (2)	−138 (2)
$C_{(6)}$	5898 (2)	−879 (2)	1772 (3)	$H_{(11)}$	591 (2)	−61 (2)	−212 (2)
$C_{(7)}$	6232 (2)	−361 (2)	628 (2)	$H_{(12)}$	619 (2)	−227 (2)	−279 (2)
$C_{(8)}$	7309 (2)	199 (2)	358 (2)	$H_{(13)}$	726 (2)	−291 (2)	−408 (2)
$C_{(9)}$	8794 (2)	1495 (2)	−997 (2)	$H_{(14)}$	876 (2)	−167 (2)	−508 (2)
$C_{(10)}$	7017 (2)	851 (2)	−1768 (2)	$H_{(15)}$	925 (2)	33 (2)	−484 (2)
$C_{(11)}$	7063 (2)	−592 (2)	−3151 (2)	$H_{(16)}$	898 (2)	189 (2)	−530 (2)
$C_{(12)}$	6810 (2)	−1738 (3)	−3248 (3)	$H_{(17)}$	975 (2)	224 (2)	−405 (2)
$C_{(13)}$	7432 (3)	−2132 (3)	−3971 (3)	$H_{(18)}$	897 (2)	290 (2)	−432 (2)
$C_{(14)}$	8320 (3)	−1386 (3)	−4554 (3)	$H_{(19)}$	755 (2)	235 (2)	−286 (2)
$C_{(15)}$	8596 (2)	−232 (3)	−4436 (2)	$H_{(20)}$	872 (2)	389 (2)	−150 (2)
$C_{(16)}$	7969 (2)	179 (2)	−3751 (2)	$H_{(21)}$	786 (2)	293 (2)	−62 (2)
$C_{(17)}$	9008 (2)	2139 (2)	−4388 (2)	$H_{(22)}$	1011 (2)	385 (2)	−21 (2)
$C_{(18)}$	7841 (2)	1787 (2)	−2575 (2)	$H_{(23)}$	921 (2)	413 (2)	66 (2)
$C_{(19)}$	8586 (2)	3214 (2)	−991 (2)				

*The numbering of the atoms is presented in Fig. 3.

TABLE 4. Bond Lengths d (Å) in VII

Bond	d	Bond	d	Bond	d
O—$C_{(1)}$	1,424 (4)	$C_{(3)}$—$C_{(8)}$	1,408 (4)	$C_{(4)}$—$H_{(5)}$	0,96 (2)
O—$C_{(20)}$	1,437 (3)	$C_{(4)}$—$C_{(5)}$	1,383 (4)	$C_{(5)}$—$H_{(6)}$	0,98 (2)
$N_{(1)}$—$C_{(1)}$	1,433 (3)	$C_{(5)}$—$C_{(6)}$	1,367 (4)	$C_{(6)}$—$H_{(7)}$	0,94 (2)
$N_{(1)}$—$C_{(2)}$	1,467 (4)	$C_{(6)}$—$C_{(7)}$	1,388 (4)	$C_{(7)}$—$H_{(8)}$	0,94 (2)
$N_{(1)}$—$C_{(3)}$	1,414 (3)	$C_{(7)}$—$C_{(8)}$	1,394 (4)	$C_{(9)}$—$H_{(9)}$	0,96 (2)
$N_{(2)}$—$C_{(8)}$	1,388 (3)	$C_{(10)}$—$C_{(18)}$	1,553 (3)	$C_{(10)}$—$H_{(10)}$	1,03 (3)
$N_{(2)}$—$C_{(9)}$	1,461 (3)	$C_{(11)}$—$C_{(12)}$	1,381 (5)	$C_{(12)}$—$H_{(12)}$	0,99 (2)
$N_{(2)}$—$C_{(10)}$	1,460 (3)	$C_{(11)}$—$C_{(16)}$	1,404 (3)	$C_{(13)}$—$H_{(13)}$	0,94 (3)
$N_{(3)}$—$C_{(10)}$	1,447 (3)	$C_{(12)}$—$C_{(13)}$	1,388 (6)	$C_{(14)}$—$H_{(14)}$	0,99 (3)
$N_{(3)}$—$C_{(11)}$	1,406 (3)	$C_{(13)}$—$C_{(14)}$	1,370 (4)	$C_{(15)}$—$H_{(15)}$	1,00 (2)
$N_{(4)}$—$C_{(16)}$	1,403 (4)	$C_{(14)}$—$C_{(15)}$	1,388 (5)	$C_{(17)}$—$H_{(16)}$	1,03 (2)
$N_{(4)}$—$C_{(17)}$	1,451 (3)	$C_{(15)}$—$C_{(16)}$	1,385 (5)	$C_{(17)}$—$H_{(17)}$	1,04 (3)
$N_{(4)}$—$C_{(18)}$	1,461 (3)	$C_{(19)}$—$C_{(20)}$	1,502 (4)	$C_{(17)}$—$H_{(18)}$	1,00 (3)
$N_{(5)}$—$C_{(9)}$	1,462 (4)	$N_{(3)}$—$H_{(11)}$	0,86 (2)	$C_{(18)}$—$H_{(19)}$	1,00 (3)
$N_{(5)}$—$C_{(18)}$	1,474 (3)	$C_{(1)}$—$H_{(1)}$	1,02 (2)	$C_{(19)}$—$H_{(20)}$	0,98 (2)
$N_{(5)}$—$C_{(19)}$	1,476 (4)	$C_{(2)}$—$H_{(2)}$	0,96 (3)	$C_{(19)}$—$H_{(21)}$	1,00 (2)
$C_{(1)}$—$C_{(9)}$	1,515 (3)	$C_{(2)}$—$H_{(3)}$	1,07 (3)	$C_{(20)}$—$H_{(22)}$	1,01 (3)
$C_{(3)}$—$C_{(4)}$	1,393 (3)	$C_{(2)}$—$H_{(4)}$	0,99 (3)	$C_{(20)}$—$H_{(23)}$	1,03 (3)

possible to assign all of the signals in the spectrum. The doublet signals at 4.35 and 4.62 ppm with $^3J_{5a,16a}$ = 3.2 Hz were assigned to the resonance of the protons of the six-membered oxazine ring; the weaker-field signal belongs to the 5a-H proton. The doublet at 4.52 ppm and the broad doublet at 5.54 ppm (broadening is eliminated when the hydrogen of the NH group is exchanged for deuterium) with $^3J_{9a,15a}$ = 6.2 Hz were assigned to the resonance of the protons of the five-membered imidazoline ring. The data from the ^{13}C NMR spectrum of VII, in which all of the structural elements of the molecule appear (Table 2), do not contradict structural formula VII; however, neither the ^1H nor the ^{13}C NMR spectra made it possible to unambiguously determine the structure of the substance and, in particular, to establish the regioorientation of the N-methyltetrahydroquinoxaline fragment relative to the oxazino[2,3-b]quinoxaline system.

We subjected VII to x-ray diffraction analysis. The coordinates of the atoms are presented in Table 3. The structure of the VII molecule is shown in Fig. 3, and the bond lengths and bond angles are presented in Tables 4 and 5, respectively. The principal geometrical parameters of the VII molecule are in agreement with the standard values [11]. As

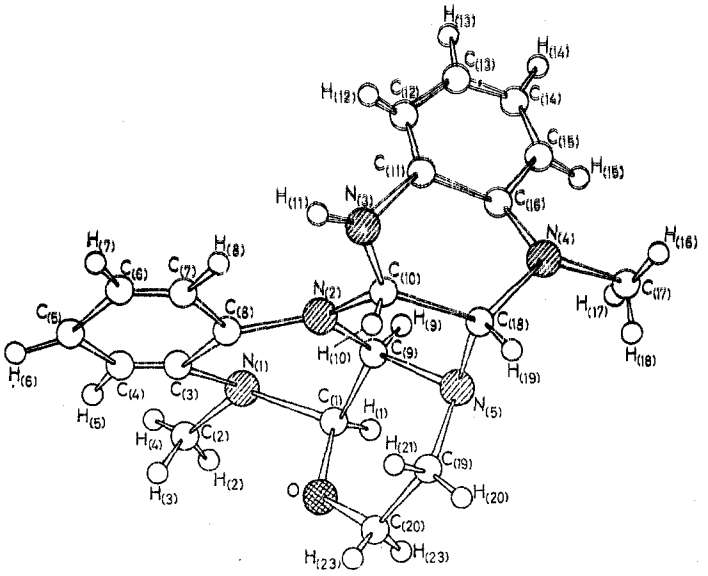
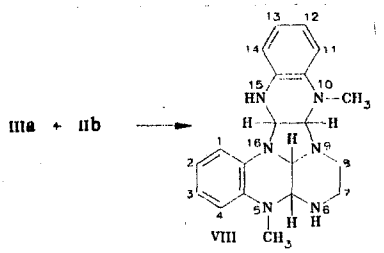


Fig. 3. Structure of the VII molecule.

expected, the oxazine ring exists in the chair conformation; however, both tetrahydropyrazine rings, despite the half-chair conformation postulated in the literature [12] for hydrogenated quinoxalines, have a distorted boat structure. Correlating the results of this research and our previously obtained data from the x-ray diffraction analysis of tetrahydroquinoxalines annelated by both five- and six-membered heterorings, as well as 2,3-disubstituted tetrahydroquinoxalines [13, 14] it may be asserted that a distorted boat conformation is preferred in annelated tetrahydroquinoxalines.

It should also be noted that in the case of annelation of the six-membered oxazine ring to the pyrazine ring the $H(1)C(1)C(9)H(9)$ torsion angle in VII is 43°, whereas in the five-membered imidazoline ring the $H(10)$ and $H(19)$ atoms of the nodal carbon atoms have a pronounced cis orientation, as evidenced by the magnitude of the $H(10)C(10)C(18)H(19)$ torsion angle, which is 23°.

To ascertain the mechanism of the formation of polycyclic VII we synthesized its aza analog VIII. For this, we accomplished the cyclization of pyrazino[2,3-b]quinoxaline IIIa with dihydroquinoxaline IIb.



Considering the similarity in the ^1H NMR spectrum of the compound obtained and the spectrum of VII (Table 2) we assigned structure VIII to it. The formation of polycyclic VIII from pyrazino[2,3-b]quinoxaline IIIa shows that intermediate VI may be a precursor of VII. The reason for the differences in the cyclizations of adducts IIa, b with ethylenediamine and aminoethanol is evidently the higher solubility of intermediate VI, owing to which it reacts rapidly in solution with σ-adduct II. Pyrazino[2,3-b]quinoxaline IIIa, on the other hand, crystallizes from the reaction mixture, and this makes it possible to observe both steps in the formation of heteropolycyclic VIII.

Thus not only additions at the 2 and 3 positions, which lead to annelation of the ring with a new ring, but also more complex cyclizations with the participation of two 1,4-diazine molecules are possible in the reactions of quinoxalinium salts with polyfunctional nucleophiles.

TABLE 5. Bond Angles ω (deg) in VII

Angle	ω	Angle	ω	Angle	ω
$C_{(1)}OC_{(20)}$	110,1 (2)	$N_{(3)}C_{(11)}C_{(16)}$	116,1 (3)	$N_{(2)}C_{(8)}C_{(3)}$	118,2 (2)
$C_{(1)}N_{(1)}C_{(2)}$	114,6 (2)	$C_{(12)}C_{(11)}C_{(16)}$	120,2 (3)	$N_{(2)}C_{(8)}C_{(7)}$	123,0 (2)
$C_{(1)}N_{(1)}C_{(3)}$	114,2 (2)	$C_{(11)}C_{(12)}C_{(13)}$	120,1 (3)	$C_{(3)}C_{(8)}C_{(7)}$	118,8 (2)
$C_{(2)}N_{(1)}C_{(3)}$	118,2 (2)	$C_{(11)}C_{(12)}H_{(12)}$	119 (2)	$N_{(2)}C_{(9)}N_{(5)}$	105,2 (2)
$C_{(8)}N_{(2)}C_{(9)}$	122,3 (2)	$C_{(13)}C_{(12)}H_{(12)}$	121 (2)	$N_{(2)}C_{(9)}C_{(1)}$	112,0 (2)
$C_{(8)}N_{(2)}C_{(10)}$	124,6 (2)	$C_{(12)}C_{(13)}C_{(14)}$	120,2 (3)	$N_{(5)}C_{(9)}C_{(1)}$	115,8 (2)
$C_{(9)}N_{(2)}C_{(10)}$	110,1 (2)	$C_{(12)}C_{(13)}H_{(13)}$	122 (2)	$N_{(2)}C_{(9)}H_{(9)}$	111 (1)
$C_{(10)}N_{(3)}C_{(11)}$	114,5 (2)	$C_{(14)}C_{(13)}H_{(13)}$	118 (2)	$C_{(11)}C_{(16)}C_{(15)}$	118,8 (3)
$C_{(10)}N_{(3)}H_{(11)}$	111 (2)	$C_{(13)}C_{(14)}C_{(15)}$	120,2 (4)	$N_{(4)}C_{(17)}H_{(16)}$	111 (1)
$C_{(11)}N_{(3)}H_{(11)}$	115 (2)	$C_{(13)}C_{(14)}H_{(14)}$	120 (2)	$N_{(4)}C_{(17)}H_{(17)}$	113 (1)
$C_{(16)}N_{(4)}C_{(17)}$	119,0 (2)	$C_{(15)}C_{(14)}H_{(14)}$	120 (2)	$H_{(16)}C_{(17)}H_{(17)}$	107 (2)
$C_{(16)}N_{(4)}C_{(18)}$	120,9 (2)	$C_{(14)}H_{(15)}C_{(16)}$	120,6 (3)	$N_{(4)}C_{(17)}H_{(18)}$	109 (1)
$C_{(17)}N_{(4)}C_{(18)}$	114,3 (2)	$C_{(14)}C_{(15)}H_{(15)}$	122 (2)	$H_{(16)}C_{(17)}H_{(18)}$	112 (2)
$C_{(9)}N_{(5)}C_{(18)}$	102,8 (2)	$C_{(16)}C_{(15)}H_{(15)}$	118 (2)	$H_{(17)}C_{(17)}H_{(18)}$	106 (2)
$C_{(9)}N_{(5)}C_{(19)}$	111,6 (2)	$N_{(4)}C_{(16)}C_{(11)}$	117,2 (3)	$N_{(4)}C_{(18)}N_{(5)}$	111,4 (2)
$C_{(18)}N_{(5)}C_{(19)}$	110,1 (2)	$N_{(4)}C_{(16)}C_{(15)}$	123,9 (2)	$N_{(4)}C_{(18)}C_{(10)}$	111,9 (2)
$OC_{(1)}N_{(1)}$	109,0 (2)	$N_{(1)}C_{(2)}H_{(4)}$	111 (1)	$N_{(5)}C_{(18)}C_{(10)}$	105,7 (2)
$OC_{(1)}C_{(9)}$	112,0 (3)	$H_{(2)}C_{(2)}H_{(4)}$	110 (3)	$N_{(4)}C_{(18)}H_{(19)}$	108 (1)
$N_{(1)}C_{(1)}C_{(9)}$	109,0 (2)	$H_{(3)}C_{(2)}H_{(4)}$	108 (2)	$N_{(5)}C_{(18)}H_{(19)}$	109 (1)
$OC_{(1)}H_{(1)}$	109 (1)	$N_{(1)}C_{(3)}C_{(4)}$	122,7 (3)	$C_{(10)}C_{(18)}H_{(19)}$	111 (1)
$N_{(1)}C_{(1)}H_{(1)}$	109 (1)	$N_{(1)}C_{(3)}C_{(8)}$	118,4 (2)	$N_{(5)}C_{(19)}C_{(20)}$	110,5 (3)
$C_{(9)}C_{(1)}H_{(1)}$	109 (1)	$C_{(4)}C_{(3)}C_{(8)}$	118,9 (2)	$N_{(5)}C_{(19)}H_{(20)}$	109 (1)
$N_{(1)}C_{(2)}H_{(2)}$	106 (2)	$C_{(3)}C_{(4)}C_{(5)}$	121,3 (3)	$C_{(20)}C_{(19)}H_{(20)}$	108 (1)
$N_{(1)}C_{(2)}H_{(3)}$	111 (2)	$C_{(3)}C_{(4)}H_{(5)}$	119 (1)	$N_{(5)}C_{(19)}H_{(21)}$	112 (1)
$H_{(2)}C_{(2)}H_{(3)}$	112 (2)	$C_{(5)}C_{(4)}H_{(5)}$	120 (1)	$C_{(20)}C_{(19)}H_{(21)}$	106 (1)
$N_{(5)}C_{(9)}H_{(9)}$	107 (1)	$C_{(4)}C_{(5)}C_{(6)}$	119,8 (2)	$H_{(20)}C_{(19)}H_{(21)}$	111 (2)
$C_{(1)}C_{(9)}H_{(9)}$	106 (1)	$C_{(4)}C_{(5)}H_{(6)}$	117 (1)	$OC_{(20)}C_{(19)}$	109,6 (2)
$N_{(2)}C_{(10)}N_{(3)}$	116,1 (2)	$C_{(6)}C_{(5)}H_{(6)}$	123 (1)	$OC_{(20)}H_{(22)}$	108 (2)
$N_{(2)}C_{(10)}C_{(18)}$	102.2 (2)	$C_{(5)}C_{(6)}C_{(7)}$	120,2 (3)	$C_{(19)}C_{(20)}H_{(22)}$	111 (1)
$N_{(3)}C_{(10)}C_{(18)}$	110.5 (2)	$C_{(5)}C_{(6)}H_{(7)}$	122 (1)	$OC_{(20)}H_{(23)}$	104 (1)
$N_{(2)}C_{(10)}H_{(10)}$	110 (1)	$C_{(7)}C_{(6)}H_{(7)}$	118 (1)	$C_{(19)}C_{(20)}H_{(23)}$	112 (1)
$N_{(3)}C_{(10)}H_{(10)}$	106 (1)	$C_{(6)}C_{(7)}C_{(8)}$	121,0 (3)	$H_{(22)}C_{(20)}H_{(23)}$	112 (2)
$C_{(18)}C_{(10)}H_{(10)}$	112 (1)	$C_{(6)}C_{(7)}H_{(8)}$	121 (1)		
$N_{(3)}C_{(11)}C_{(12)}$	123,6 (2)	$C_{(8)}C_{(7)}H_{(8)}$	118 (1)		

EXPERIMENTAL

The ^1H NMR spectra of the compounds in $CDCl_3$ and d_6-DMSO were recorded with Perkin–Elmer R-12B (60 MHz) and Bruker WH-90 (90 MHz) spectrometers with tetramethylsilane (TMS) and hexamethyldisiloxane (HMDS) as the internal standards. The ^{13}C NMR spectra of solutions in $CDCl_3$ and d_6-DMSO were recorded at 30-40°C with a Bruker WH-90 (22.62 MHz) spectrometer. The ^{13}C chemical shifts were measured with respect to the signals of the solvents ($\delta CDCl_3$ 77.0 ppm and δd_6-DMSO 39.7 ppm). The ^{13}C NMR spectra were recorded under conditions of complete decoupling of the spin-spin coupling of the protons with the carbon atoms with retention of the true values of the constant with partial intensification of the signals of the carbon atoms due to the Overhauser effect, as well as with selective decoupling of the coupling of the individual groups of protons with the carbon atoms.

The mass spectra were recorded with a Varian MAT spectrometer with direct introduction of the samples into the ion source at an accelerating voltage of 3.6 kV, an ionizing-electron energy of 30 eV, a cathode emission current of 1.5 mA, and a sample-vaporization temperature of 190-220°C.

X-Ray diffraction analysis was carried out with a DAR-UMB diffractometer in MoK_α emission. The colorless transparent single crystals of VII with a lamellar habitus belong to monoclinic syngony. The unit cell parameters were as follows: a = 13.680 (9), b = 12.882 (8), c = 10.752 (7) Å, γ = 113.1 (3)°, v = 1743 (3) Å^3, and $P2_1/n$. In the calculations we used 1345 independent reflections with $I > 2\sigma(I)$, obtained from a 0.25 by 0.10 by 0.95 mm sample.

The structure was solved by the direct method and was refined by the method of least squares within the anisotropic approximation (within the isotropic approximation for the hydrogen atoms) with the aid of an experimental weight scheme. Final divergence factors R = 0.035 and R_W = 0.036. All of the calculations were made from the YANX program [15].

N-Methylquinoxalinium iodide (I) was obtained by the method in [14], and dihydroquinoxalines IIa, b were obtained as described in [7].

The spectral characteristics of III, V, VII, and VIII are presented in Table 2.

5-Methyl-1,2,3,4,4a,5,10,10a-octahydropyrazino[2,3-b]quinoxaline (IIIa). A) A 0.65-ml (0.01 mole) sample of anhydrous ethylenediamine was added with stirring at 20°C to a solution of 2.1 g (0.01 mole) of the adduct of the N-methylquinoxalinium ion with diethylamine, viz., IIa, which was obtained from 0.01 mole of salt I by the method in [7], in 10 ml of absolute diethyl ether, after which the reaction mixture was maintained at room temperature for 1 h, and the precipitated IIIa was removed by filtration to give 1.8 g (90%) of colorless needles from ethyl acetate with mp 107-108°C. Mass spectrum, m/z (I ≥ 20%): 42 (32), 43 (27), 44 (28), 50 (25), 65 (21), 71 (56), 76 (48), 77 (34), 83 (31), 84 (70), 92 (29), 103 (58), 130 (72), 131 (37), 133 (90), 144 (23), 145 (100), 146 (37), 147 (25), 160 (68), 204 (90, M^+).

B) A solution of 2.1 g (0.01 mole) of dihydroquinoxaline IIa in absolute ether [7] was evaporated to dryness *in vacuo* at room temperature, and the residue was dissolved in 10 ml of absolute ethanol. A 0.65-ml (0.01 mole) sample of ethylenediamine was added with stirring at room temperature to the resulting alcohol solution of ethoxy adduct IIb [7], after which the mixture was allowed to stand at room temperature for 5-10 min, after which it was cooled to 0°C in a refrigerator. The precipitated IIIa was removed by filtration and washed with ether to give 1.7 g (85%) of product.

The identical character of the substances obtained by methods A and B was confirmed by the lack of a depression of the melting point of a mixture of the samples and also by the coincidence of their spectral characteristics (Table 2).

6-Methyl-5,5a,6,11,11a,12-hexahydroquinoxalino[2,3-b]quinoxaline (IIIb). A 1.1-g (0.01 mole) sample of o-phenylenediamine was added with stirring at room temperature to a solution of 2.1 g (0.01 mole) of dihydroquinoxaline IIa in 15 ml of absolute diethyl ether, after which 1 ml of ethanol was added to the reaction mixture to dissolve the starting diamine (conversion of dihydroquinoxaline IIa to ethoxy adduct IIb is also possible in this case). After 30 min, the resulting precipitate was removed by filtration to give 1.9 g (70%) of colorless needles from acetone with mp 129-130°C (dec.). Mass spectrum, m/z (I ≥ 20%): 50 (36), 51 (26), 52 (21), 65 (31), 77 (44), 80 (50), 92 (23), 103 (64), 107 (49), 108 (62), 119 (44), 122 (54), 130 (98), 131 (77), 132 (36), 133 (41), 145 (100), 146 (54), 252 (19, M^+).

11-Methyl-5,5a,6,11,11a,12-hexahydrobenzoxazino[1,4][2,3-b]-quinoxaline (V). This compound was obtained from dihydroquinoxaline IIa and o-aminophenol by the method described above for IIIb. Workup gave light-gray needles (53% yield) from ethanol with mp 101-102°C (dec.). Mass spectrum, m/z (I ≥ 20%): 32 (22), 76 (39), 80 (42), 103 (46), 109 (100), 130 (71), 131 (34), 145 (42), 146 (41), 254 (10, M^+).

5,10-Dimethyl-15H-5,5a,6,7,8,9,9a,10,15,15a,15,16a-dodecahydroquinoxalino[2',3':4,5]-imidazo[1,2,3-d,e][1,4]oxazino[2,3-b]-quinoxaline (VII). A 2-ml (0.02 mole) sample of triethylamine was added to a suspension of 2.7 g (0.01 mmole) of N-methylquinoxalinium iodide (I) to 5 ml of ethanol, and the mixture was stirred at room temperature until the starting salt had dissolved (5-10 min), during which ethoxy adduct IIb [7] formed in the solution, to which 0.7 ml (0.01 mole) of 2-aminoethanol was added. This mixture was then stirred for 5 min and allowed to stand for 2 h for crystallization. All of the operations were carried out at room temperature. The precipitated VII was removed by filtration to give 1.1 g (60%) of long colorless needles from ethanol with mp 175-176°C (dec.). Mass spectrum, m/z (I ≥ 20%): 103 (23), 130 (28), 131 (26), 133 (36), 145 (100), 146 (44), 349 (8.2, M^+).

The yield of VII increased to 65-75% when an alcohol solution of adduct IIb that did not contain triethylammonium iodide was used. To obtain it an ether solution of the adduct of the N-methylquinoxalinium ion with diethylamine was prepared by the method in [7], the ether was evaporated to dryness *in vacuo* at room temperature, the residue was dissolved in absolute ethanol, and the reaction with 2-aminoethanol was then carried out as described above.

5,10-Dimethyl-15H-5,5a,6,7,8,9,9a,10,15,15a,16,16a-dodecahydroquinoxalino[2',3':4,5]-imidazo[1,2,3-d,e]pyrazino[2,3-b]quinoxaline (VIII). A 2.1-g (0.01 mole) sample of adduct IIa, obtained by the method in [7], was dissolved in 10 ml of absolute ethanol, thereby converting it to ethoxy adduct IIb [7], and a solution of 2 g (0.01 mole) of pyrazino[2,3-b]-quinoxaline IIIa in 4 ml of absolute ethanol was added with stirring at room temperature. The reaction mixture was allowed to stand at room temperature for 24 h for crystallization, after which the precipitated VIII was separated and recrystallized from ethanol to give 2.6 g

(74%) of colorless needles with mp 124-126°C (dec.). Mass spectrum, m/z ($I \geq 20\%$): 42 (21), 43 (38), 44 (45), 50 (53), 51 (37), 55 (23), 57 (40), 69 (21), 71 (38), 76 (54), 77 (48), 83 (21), 92 (29), 103 (71), 104 (20), 105 (23) 130 (68), 131 (46) 133 (79), 144 (20), 145 (100), 146 (64), 149 (21), 160 (21) 204 (27), 273 (25), 348 (17, M^+).

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