# CYCLOADDITION OF ANHYDRO BASES OF HETEROCYCLIC CATIONS. 2.* SYNTHESIS OF SPIROCYCLIC AND CARCASS STRUCTURES IN THE REACTION OF s-TETRAZINES WITH THE ANHYDRO BASE OF A QUATERNARY LEPIDINIUM SALT

**E. G. Kovalev, G. L. Rusinov, G. G. Aleksandrov, V. A. Anufriev, E. O. Sidorov, and A. I. Chernyshev**

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*The anhydro base of an N-methyllepidinium salt reacts with s-tetrazines to give spiro hetarenes with 4,5- and 1,4-dihydropyridazine structures. The regioselectivity of the cycloaddition was established. In addition to spiro annelation, intramolecular cyclization to give compounds with a carcass structure, for which x-ray diffraction analysis was carried out, occurs when s-tetrazines with α-pyridyl substituents are used.*

In a previous paper [1] it was shown that the anhydro bases of 9-alkylacridinium, -xanthylium, and -thioxanthylium salts participate in [4 + 2]-cycloaddition reactions with s-tetrazines by means of their only exocyclic double bond to give spiro hetarenes. The transition from the anhydro bases of acridinium salts to anhydro base A of lepidinium salts I, which is accompanied by structural "liquidation" of one benzene ring, also "reveals" another (cyclic) "substantially localized" [2] double bond, thereby creating the possibility of competitive [4 + 2] cycloaddition to s-tetrazines [3].

The reaction of 3,6-di(2-pyridyl)-s-tetrazine (IIa) with lepidinium methiodide (Ia) in DMF at −20°C in the presence of triethylamine leads to IIIa, the PMR spectrum of which contains two doublets at $\sigma$ 4.60 and 5.85 ppm with J = 8 Hz, which are characteristic for a 1,4-dihydroquinoline structure [4]. In addition to this, at $\sigma$ 3.75 and 3.10 ppm there are two doublets of an AB quartet, with J = 18 Hz, of geminal $H_A$ and $H_{A'}$ protons, which determine the 4,5-dihydropyridazine structure IIIa. This less stable tautomeric form IIIa can also be obtained at a higher temperature (and even in somewhat higher yield) if one uses anhydro base A, which is not formed directly in the reaction mixture but is extracted with benzene in the action of concentrated alkali on methiodide Ia. Thus, despite the symmetrical character of the lowest vacant molecular orbital (LVMO) of the $4\pi$ fragment of s-tetrazine IIa [the coefficients of expansion of the LVMO at the $C_{(3)}$ and $C_{(6)}$ atoms are equal to −0.404) and the symmetrical character of the highest occupied molecular orbital (HOMO) of the $2\pi$ fragment of the exocyclic [−0.588 at the $C_{(1)}$ atom and −0.281 at the $C_{(2)}$ atom] and the cyclic [0.359 at the $C_{(3)}$ atom and 0.340 at the $C_{(4)}$ atom] of the double bond of anhydro base A that are necessary for the symmetry-permitted reverse diene synthesis, exclusively the exocyclic double bond, on the methylene C atom of which the maximum negative charge is concentrated [calculation by the Pariser—Parr—Pople (PPP) method with the parametrization presented in [1], participates in the cycloaddition. Diphenyl derivatives IIIb were obtained by similar methods.

Compounds with the 4,5-dihydropyridazine structure are unstable and readily undergo tautomerization to products with a 1,4-dihydropyridazine structure on heating or under the influence of acids and alkalis [1]. In the case under consideration lepidine derivatives III are also readily converted by the action of alkali or when the reaction is carried out under standard conditions (at room temperature with triethylamine as the base) to spirocycles IVa, b with a 1,4-dihydropyridazine structure, which are characterized by the existence of heteroallyl constant $^4J$ = 2 Hz involving coupling between the $H_{A'}$ proton of the NH proton and the $H_A$ proton of the pyridazine ring [5] (see Table 1). When IV is refluxed in deuteroethanol, the NH proton of the pyridazine ring undergoes complete deuterium exchange, and the proton in the $\beta$ position of the quinoline ring undergoes partial deuterium exchange; this is characteristic for 1,4-dihydroquinolines with an enamine structure. Compounds IVa, b have the photo- and thermochromic properties that are characteristic for spirocyclic compounds [1, 6].

*See [1] for Communication 1.

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TABLE 1. PMR Spectra of Spiro Hetarenes III and IV

| Compound | Chemical shift, δ, ppm | | | | | SSCC, J, Hz | |
|---|---|---|---|---|---|---|---|
| | N—$CH_3$, s | $H_A$, d | $H_{A'}$, d | α-$H_\alpha$, d | β-$H_\beta$, d | $H_A$, $H_{A'}$ | $H_\alpha$, $H_\beta$ |
| III a | 3,15 | 3,1 | 3,75 | 3,85 | 4,60 | 18,0 | 8,0 |
| III b | 3,25 | 3,0, | | 6,15 | 4,50 | — | 8,1 |
| IV a | 3,10 | 5,5 | 9,25 | 5,85 | 4,60 | 2,0 | 8,0 |
| IV b | 3,20 | 4,9 | 10,5 | 6,15 | 4,55 | 2,2 | 8,2 |
| IV c | 3,10 | 4,3* | 9,4 | 6,00 | 4,35 | 2,1; 1,0* | 8,0 |

*The signal shows up in the form of a doublet of quartets with $^4J_{H_AH_{A'}} = 2.1$ Hz and $^4J_{H_A-CH_3} = 1.0$ Hz; The C—$CH_3$ group shows up as a three-proton doublet at δ 1.8 ppm with $^4J_{CH_3-H_A} = 1.0$ Hz.

TABLE 2. Deviations (Δ) of the Atoms of Some Planar Fragments of the Va Molecule from Planes A-E* (See Fig. 1)

| Plane A | | Plane B | | Plane C | | Plane D | | Plane E | | Dihedral angle | < *** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Atom | Δ, Å | Atom | Δ, Å | Atom | Δ, Å | Atom | Δ, Å | Atom | Δ, Å | | |
| $N_{(4)}$ | 0,00 | $C_{(10)}$ | 0,00 | $N_{(1)}$ | −0,01 | $N_{(3)}$ | 0,00 | $N_{(5)}$ | 0,00 | *A—B* | 2,7 |
| $C_{(8)}$ | 0,00 | $C_{(11)}$ | 0,00 | $C_{(1)}$ | 0,02 | $C_{(6)}$ | 0,00 | $C_{(18)}$ | 0,01 | *A—C* | 90,5 |
| $C_{(10)}$ | 0,00 | $C_{(14)}$ | −0,01 | $C_{(2)}$ | −0,01 | $C_{(7)}$ | 0,00 | $C_{(19)}$ | −0,01 | *A—D* | 95,5 |
| $C_{(11)}$ | 0,00 | $C_{(15)}$ | 0,01 | $C_{(3)}$ | 0,00 | $C_{(9)}$ | 0,00 | $C_{(20)}$ | 0,00 | *A—E* | 113,3 |
| $C_{(12)}$** | −0,12 | $C_{(16)}$ | 0,00 | $C_{(4)}$ | 0,00 | $N_{(2)}$** | −0,21 | $C_{(21)}$ | 0,01 | *B—C* | 93,1 |
| $C_{(13)}$** | −0,79 | $C_{(17)}$ | 0,00 | $C_{(5)}$ | 0,00 | $C_{(8)}$** | −0,40 | $C_{(22)}$ | −0,01 | *B—D* | 97,7 |
| | | $C_{(8)}$** | −0,04 | | | | | $C_{(7)}$** | 0,13 | *B—E* | 115,1 |
| | | $C_{(4)}$** | −0,07 | | | | | $C_{(8)}$** | 0,23 | *C—D* | 15,3 |
| | | | | | | | | $C_{(12)}$** | 0,01 | *C—E* | 37,8 |
| | | | | | | | | $C_{(13)}$** | 0,87 | *D—E* | 23,9 |

*A 11.020x − 2.902y + 4.420z −7.227 = 0; B 10.725x − 3.213y + 4.775z − 7.066 = 0; C 4.983x + 7.444y − 2.042z − 4.201 = 0; D 2.744x + 7.746y + 3.004z − 4.260 = 0; E −2.464x + 7.595y + 6.854z − 0.795 = 0.
**Atoms that were not included in the calculation of the given plane.
***The dihedral angle between the planes passing through the $C_{(7)}C_{(8)}C_{(9)}$ and $C_{(10)}C_{(8)}C_{(13)}$ atoms is 89.4°.

TABLE 3. Torsion Angles

| Angle | τ° | Angle | τ° | Angle | τ° |
|---|---|---|---|---|---|
| $C_{(8)}C_{(10)}C_{(11)}N_{(4)}$ | −1,0 | $C_{(7)}C_{(8)}C_{(9)}C_{(6)}$ | −29,9 | $C_{(7)}C_{(8)}C_{(13)}C_{(12)}$ | 59,2 |
| $C_{(10)}C_{(11)}N_{(4)}C_{(12)}$ | −4,8 | $C_{(8)}C_{(9)}C_{(6)}N_{(2)}$ | 7,2 | $C_{(8)}C_{(13)}C_{(12)}N_{(5)}$ | −62,7 |
| $C_{(11)}N_{(4)}C_{(12)}C_{(13)}$ | −23,8 | $C_{(9)}C_{(6)}N_{(2)}N_{(3)}$ | 19,6 | $C_{(13)}C_{(12)}N_{(5)}C_{(18)}$ | 35,5 |
| $N_{(4)}C_{(12)}C_{(13)}C_{(8)}$ | 56,8 | $C_{(6)}N_{(2)}N_{(3)}C_{(7)}$ | −19,3 | $C_{(12)}N_{(5)}C_{(18)}C_{(7)}$ | −4,5 |
| $C_{(12)}C_{(13)}C_{(8)}C_{(10)}$ | −59,6 | $N_{(2)}N_{(3)}C_{(7)}C_{(8)}$ | −7,9 | $N_{(5)}C_{(18)}C_{(7)}C_{(8)}$ | 0,0 |
| $C_{(13)}C_{(8)}C_{(10)}C_{(11)}$ | 33,2 | $N_{(3)}C_{(7)}C_{(8)}C_{(9)}$ | 32,1 | $C_{(18)}C_{(7)}C_{(8)}C_{(13)}$ | −28,2 |

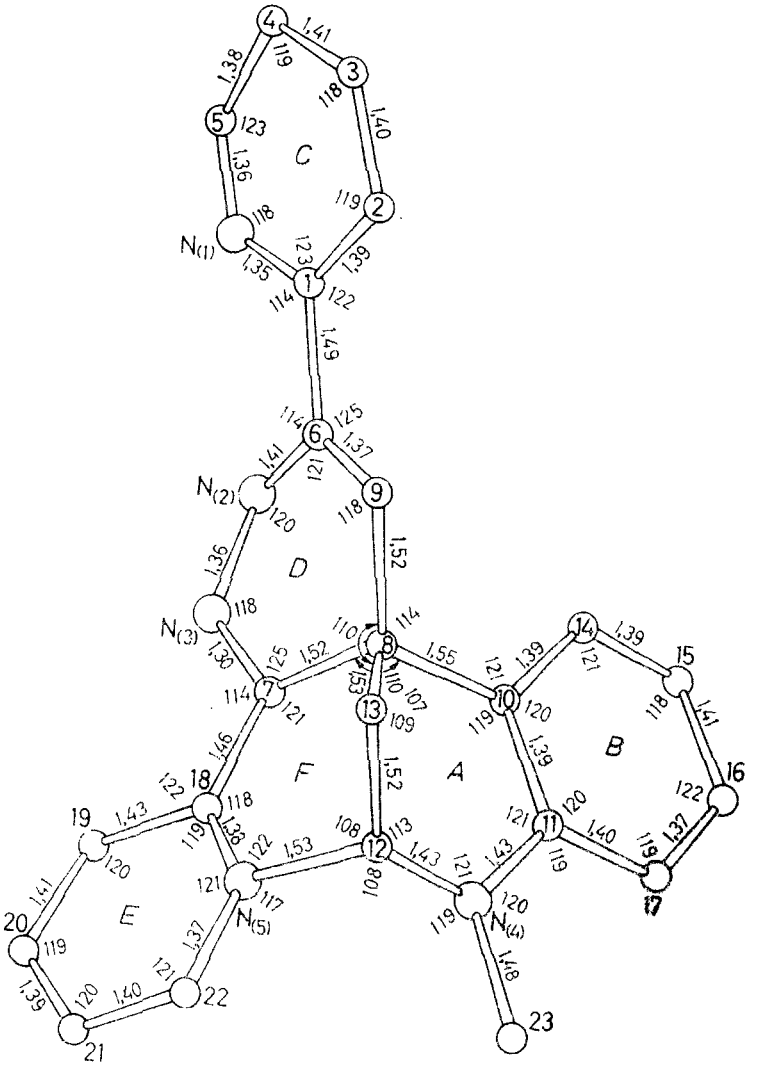
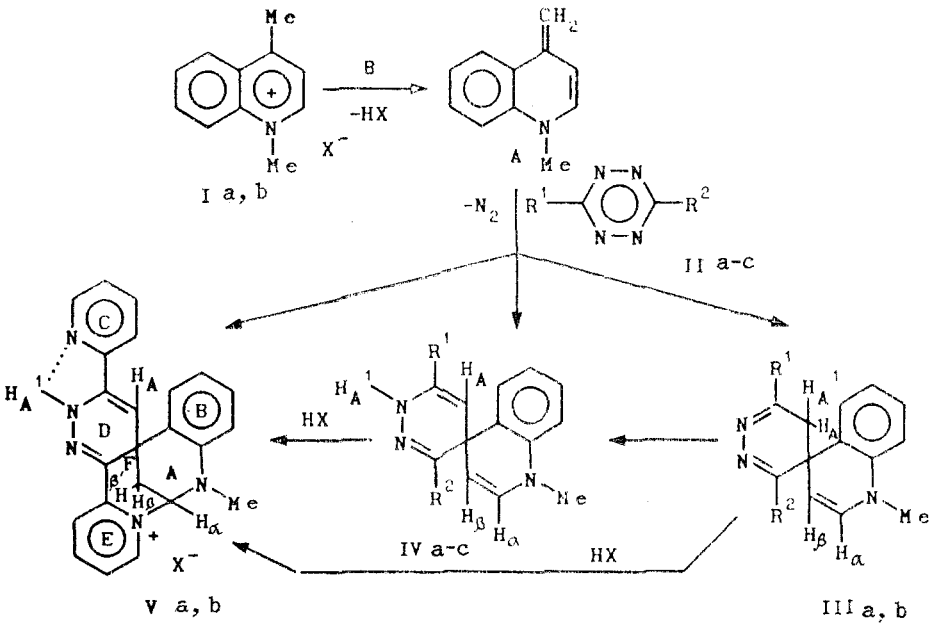


Fig. 1. Structure of the Va molecule.

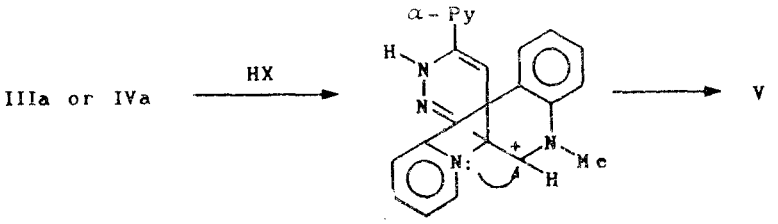


I, V a X=I, b X=$ClO_4$; II—IV a $R^1=R^2=\alpha$-Py, b $R^1=R^2=C_6H_5$; II, IV c $R^1=CH_3$, $R^2=C_6H_5$

3-Methyl-6-phenyl-s-tetrazine (IIc), the unsymmetrical character of the substitution of which is used to study the regioselectivity of cycloaddition [1], does not react with the lepidinium anhydro base at low temperatures, but under relatively more severe conditions (at room temperature) the reaction proceeds so slowly that the time during which the initially formed 4,5-tautomer exists in the acidic-basic medium proves to be sufficient for conversion to 1,4-tautomer IVc isolated as a result of the reaction. Its structure is unambiguously determined by the doublet of quartets of pyridazine proton $H_A$ centered at $\delta$ 4.3 ppm with spin-spin coupling constants (SSCC) $^4J_{H_A-H_{A'}} = 2$ Hz and $^4J_{H_A-CH_3} = 1$ Hz. Thus the primary orientation of the methylene C atom of the exocyclic bond of anhydro base A relative to the $C_{(3)}$ atom of s-tetrazine IIa bonded to the methyl group, the explanation of which is given in [1], also occurs for the addition of the lepidinium anhydro base.

A slight change in the structure of salt Ia, which has already been used to obtain tautomers IIIa and IVa (replacement of methiodide Ia by N-methyllepidinium perchlorate Ib) or a certain increase in the severity of the conditions (heating of the reaction mixture after completion of the cycloaddition, which is readily detected from the disappearance of the red color of the s-tetrazine and cessation of the liberation of molecular nitrogen) leads to an unexpected result. We isolated products Va, b with salt character, since, according to the results of elementary analysis, they contain, respectively, iodide and perchlorate anions. Despite the poor resolution (because of the low solubilities) of the PMR spectra of V recorded from solutions in $d_6$-DMSO, one can establish the 1,4-dihydro structure of the pyridazine fragment and ascertain a contradiction in the structure of the quinoline fragment: the chemical shift (CS) of the protons of the $N-CH_3$ group corresponds to a nonquaternized nitrogen atom, while the heteroring protons are shifted to weak field, which should characterize this ring as aromatic or quaternized. We carried out an x-ray diffraction analysis of Va to unequivocally determine the structure of the products of the reaction of V.

According to the experiment, the reaction product has the structure of a 2,5,6,12-tetraaza tricyclic cation, the formation of which (see below) can be represented by the addition of a proton of the acid to the $\beta$-carbon atom of the enamine fragment of the 1,4-dihydroquinoline ring of IIIa or IVa and subsequent attack by the unshared pair of electrons of the nitrogen atom of the $\alpha$-pyridyl substituent at the positively charged $\alpha$-carbon atom of the quinoline heteroring:




We established the structure of the Va molecule and determined the bond lengths and bond angles (see Fig. 1). The cation is constructed from six six-membered rings, five of which form a rather complex condensed system connected to a sixth pyridine ring C by a $C_{(1)}-C_{(6)}$ single bond with a length of 1.49 Å. While the B, C, and E rings are planar (see Table 2), the planarity of the remaining rings is substantially disrupted. The A and F rings have a twisted boat conformation, while the D ring has a boat conformation [the deviations of the $N_{(2)}$ and $C_{(8)}$ atoms from the plane passing through the four remaining atoms are −0.21 Å and −0.39 Å, respectively]. The torsion angles (see Table 3), which also characterize the conformations of these rings, were determined. The distortions of the bond angles at spiro atom $C_{(8)}$ are small — they vary from 107° to 114°. It is interesting to note that the dihydropyridazine (D) and tetrahydropyridine (A) rings that form the $C_{(8)}$ spiro node do not undergo a change in their initial (in IIIa and IVa) perpendicular orientation during the cyclization. This indicates that substantial rotation of the pyridine ring (E) relative to the dihydropyridazine ring (D) is required for attack by the $sp^2$-hybridized unshared pair of electrons of the nitrogen atom lying in the plane of the pyridyl ring (E) at the positively charged C atom. On the other hand, the other pyridine ring (C) and the dihydropyridazine ring (D) remain almost coplanar [the angle of rotation about the $C_{(1)}-C_{(6)}$ bond is only 15°], while the intramolecular $N_{(1)}-N_{(2)}$ distance, which is 2.61 Å, constitutes evidence for the presence of an $N_{(1)}\cdots H-N_{(2)}$ intramolecular hydrogen bond in the V cation. Thus in the Va molecule the planar $\alpha$-pyridyl C and E rings prove to be turned by their $N_{(1)}$ and $N_{(5)}$ atoms in different directions, being fastened in this state by an intramolecular hydrogen bond and the $C_{(12)}-N_{(5)}^+$ single bond. All of the bond lengths and bond angles are in good agreement with the values previously found in similar polynitrogen heterocyclic systems [7]. In the A, D, and F rings one may note rather distinct alternation of the single and double bonds; the lengths of the $C_{(7)}-N_{(3)}$ (1.30 Å) and $C_{(6)}-C_{(9)}$ (1.37 Å) bonds are comparable to the lengths of standard C=N (1.29 Å) and C=C (1.33 Å) double bonds.

The results of x-ray diffraction analysis make it possible to unambiguously interpret the PMR spectra of V. On the basis of the established structure it is evident that the appearance at weak field of the signal of the $\alpha$-H proton of the quinoline heteroring is due not to aromatization or quaternization of the latter but rather to the presence in

direct proximity of a positive charge on the nitrogen atom of the α-pyridyl substituent. In addition, as demonstrated by replacement of $d_6$-DMSO by deuterochloroform as the solvent for recording the spectrum, under the signal of DMSO is hidden the well-resolved (in deuterochloroform) AB part of the ABX system of three protons of the tetrahydroquinoline ring, which is readily decoded by the double-resonance method. The use of the JMODX technique makes it possible to also assign the signals of some carbon nuclei in the $^{13}C$ NMR spectrum

The above-presented mechanism of the formation of V from IIIa or IVa finds definite confirmation in carrying out the reactions of these compounds with triethylammonium perchlorate. Heating alcohol solutions of either of them (IIIa or IVa) with triethylammonium perchlorate gives identical and almost quantitative yields of Vb, i.e., the nucleophilicity of the β-carbon atom of the enamine 1,4-dihydroquinoline fragment of IIIa and IVa (of course, necessarily with the subsequent cyclization process) proves to be sufficiently high to "intercept" the acid away from such a strong base as triethylamine. This sort of behavior of enamine systems has been noted in the synthesis of cyanine dyes [8, 9], and the addition of a proton is always accompanied by major rearrangements of the starting molecules.

Our observed formation of carcass structure V with the direct participation of the components of a spirocyclic system is described for the first time.

## EXPERIMENTAL

The PMR spectra of solutions of the compounds in deuterochloroform (IIIa, b and IVa) and $d_6$-DMSO (IVb, c) were recorded with Perkin—Elmer R-12B (60 MHz) and Bruker WH-90 spectrometers at 40°C with tetramethylsilane (TMS) as the internal standard.

The PMR and $^{13}C$ NMR spectra of V were obtained with Bruker WH-90 (at 90 MHz for the PMR spectra and at 22.62 MHz for the $^{13}C$ NMR spectra) and Bruker 80 WP (at 80.13 MHz for the PMR spectra and at 20.13 MHz for the $^{13}C$ NMR spectra) spectrometers; double-resonance experiments were accomplished with the same spectrometers, and the JMODX method was realized. The $^{13}C$ chemical shifts were measured with respect to the signals of the solvent (δ, in $CDCl_3$, 77.0 ppm). The mass spectra of field desorption of Va, b were recorded with a Varian MAT-311A spectrometer with direct introduction of the samples into the ion source.

X-ray diffraction analysis was carried out with a Syntex-P1 diffractometer ($\lambda_{Mo\ K_\alpha}$) using a graphite monochromator and $\theta/2\theta$ scanning with $2° \leq 2\theta \leq 50°$. The crystals of iodide Va were grown from ethanol in the form of the dihydrate, were monoclinic, and had the following unit cell parameters: a = 12.979(9), b = 8.069(5), c = 22.009(19) Å, β = 101.57(5)°, V = 2249(3) Å$^3$, $d_{calc}$ = 1.57 g/cm$^3$, Z = 4, space group $P2_1/n$. The Va·$2H_2O$ structure was decoded by the heavy-atom method and was refined by the method of least squares within the completely matrix anisotropically (I)-isotropic approximation up to a final divergence factor R = 0.064 ($R_w$ = 0.0691) for 2240 reflections with $F^2 \geq 3\sigma$. The coordinates of the atoms and their temperature factors can be obtained from the authors. In the crystal the heterocyclic cations, the $I^-$ anions,a nd the solvate water molecules are interlinked by hydrogen bonds and interionic forces. Since the only active proton of the heterocyclic cation that is capable of forming a hydrogen bond participates in the $N_{(1)}\cdots H—N_{(2)}$ intramolecular bond (see the scheme and Fig. 1), the cation does not participate in the formation of interionic hydrogen bonds. However, the water molecules and the iodide anion form hydrogen bonds [$I^-\cdots O_{(2)}$ 3.73 Å and $I^-\cdots O_{(1)}$ (1/2 − x, 1/2 + y, 1/2 − z) 3.61 Å], and, in addition, the water molecules form hydrogen bonds with one another [$O_{(1)}\cdots O_{(2)}$ 2.81 Å].

Lepidine methiodide (Ia) was obtained by the standard quaternization method (in benzene with a small excess of methyl iodide), and perchlorate Ib was obtained from it by an exchange reaction with saturated sodium perchlorate solution. Citations to methods for obtaining s-tetrazines were presented in [1].

The results of elementary analysis for C, H, and N were in agreement with the calculated values.

**3,6-Di(2-pyridyl)-4,5,1′,4′-tetrahydro-1′-methylspiro(pyridazino-4,4′-quinoline) (IIIa). A.** A mixture of 1 g (4.2 mmole) of IIa and 1.3 g (4.6 mmole) of lepidine methiodide (Ia) was suspended in 3.5 ml of DMF, after which the mixture was cooled to −20°C, and 1.3 ml of triethylamine was added with stirring. After 1-2 min, IIIa began to precipitate. After gas liberation had ceased, the mixture was allowed to stand for 5-10 min at −20°C. The precipitate was removed by filtration, washed with 5 ml of ethanol, and dried in vacuo at room temperature. The yield was 1.2 g (78%).

**B.** A freshly prepared benzene extract of lepidinium anhydro base A [obtained by shaking a mixture of 3 g (10.5 mmole) of lepidine methiodide (Ia), 15 ml of 20% NaOH solution, and 30 ml of benzene for 1-2 min] was added dropwise with stirring and cooling with cold water to a suspension of 1.5 g (6.4 mmole) of tetrazine IIa in 20 ml of benzene. The addition of the anhydro base caused the vigorous evolution of a gas. After all of the benzene solution had been added, the mixture was stirred for another 5-10 min, and the benzene was removed by distillation in vacuo at no higher than 20°C. The residue was washed with ethanol to give orange-colored IIIa. The yield was 2 g (85.5%).

Compound IIIb was obtained in 69% by method A and in 81% yield by method B.

**3,6-Diphenyl-1,4,1′,4′-tetrahydro-1′-methylspiro(pyridazino-4,4′-quinoline) (IVb).** Triethylamine (2 ml) was added to a suspension of 1.5 g (6.4 mmole) of 3,6-diphenyl-s-tetrazine (IIb) and 2.5 g (8.8 mmole) of lepidine methiodide (Ia) in 15 ml of DMF. The reaction was complete after 10 min. The reaction mixture was then heated for a few minutes on a boiling-water bath, and the resulting yellow solution was poured into 50 ml of water. The light-yellow precipitate of IVb was removed by filtration and crystallized from ethanol to give a product with mp 177-179°C. The yield was 1.9 g (81%).

**3,6-Di(2-pyridyl)-1,4,1′,4′-tetrahydro-1′-methylspiro(pyridazino-4,4′-quinoline) (IVa).** A suspension of 1 g (2.7 mmole) of spiro compound IIIa was stirred in a mixture of 10 ml of isopropyl alcohol and 10 ml of 20% NaOH solution. After ≈15 min, the solid material dissolved. The reaction mixture was diluted with 50 ml of water, and the resulting yellow precipitate was removed by filtration and dried to give a product with mp 127-130°C. The yield was 0.7 g (70%).

**3-Methyl-6-phenyl-1,4,1′,4′-tetrahydro-1′-methylspiro(pyridazino-4,4′-quinoline) (IVc).** A 0.5-g (2.9 mmole) sample of s-tetrazine IIc and 0.9 g (3.1 mmole) of quaternary salt Ia were suspended in 6 ml of ethanol, and 0.5 ml of triethylamine was added. After 24 h, gas evolution ceased, and the resulting precipitate was removed by filtration and washed with ethanol to give a product with mp 133-135°C (from n-heptane). The yield was 0.5 g (57%).

**12-Methyl-7-(2-pyridyl)benzo[j]pyrido[1,2-b]-5,6,12-triaza-2-azoniatricyclo[7.3.1.$^{1,9}$.0$^{4,9}$]trideca-2,4,7,10-tetraene (Va).** Triethylamine [0.3 ml (2.2 mmole)] was added to a stirred suspension of 0.5 g (2.1 mmole) of s-tetrazine IIa and 0.6 g (2.1 mmole) of lepidine methiodide (Ia) in 20 ml of dioxane and 10 ml of ethanol. After gas evolution had ceased, the solvent was removed by distillation in vacuo, the residue was refluxed with 80 ml of dioxane, and the hot suspension was filtered. The orange-yellow precipitate was washed with water and crystallized from ethanol to give a product with mp 225-230°C. UV spectrum (ethanol), $\lambda_{max}$, nm ($\log \varepsilon$): 211 (4.61), 287 (4.36), 425 (4.07). [$M^+ - HI^-$] (field desorption) 365. PMR spectrum ($CDCl_3$, see the scheme for the designation of the protons): 5.78 (1H, d, $^4J$ = 2.2 Hz, $H_A$), 10.23 (1H, d, $^4J$ = 2.2 Hz, $H_{A'}$), 3.5 (3H, s, N—$CH_3$), 2.39-2.91 (2H, AB part of an ABX system, $\delta_{\beta\text{-H}}$ = 2.78, $\delta_{\beta'\text{-H}}$ = 2.52 ppm, $^3J_{\beta\text{-H}\alpha\text{-H}}$ = 3.61, $^3J_{\beta'\text{-H}\alpha\text{-H}}$ = 2.10, $^2J_{\beta\text{-H}\beta'\text{-H}}$ = 13.63 Hz), 7.44-7.51 ppm (1H, X part of an ABX system, $\alpha$-H). $^{13}C$ NMR spectrum ($CDCl_3$, see Fig. 1 for the numbering of the atoms): 30.47 [$C_{(8)}$], 31.23 [$C_{(13)}$], 37.59 [$C_{(23)}$], 78.82 [$C_{(12)}$], 102.51 [$C_{(9)}$], 148.13 [$C_{(18)}$], 148.76 ppm [$C_{(22)}$].

**Synthesis of Perchlorate Vb. A.** Triethylamine [1.3 ml (9.3 mmole)] was added with stirring to a suspension of 2 g (8.5 mmole) of tetrazine IIa and 2.4 g (9.3 mmole) of N-methyllepidinium perchlorate (Ib) in 25 ml of ethanol. A gas evolved, the reaction mixture darkened, the starting compounds dissolved, and a dark-yellow crystalline reaction product gradually began to precipitate. The reaction was complete after 30 min, and the precipitate was removed by filtration, washed with ethanol and water, and dried to give a product with mp 235-237°C. UV spectrum (acetonitrile), $\lambda_{max}$, nm ($\log \varepsilon$): 288 (4.38), 417 (4.06). [$M^+ - HClO_4$] (field desorption) 365. The yield was 3.3 g (83%).

**B.** A 1.2-ml sample of a solution obtained by neutralization of 70% perchloric acid with triethylamine was added to a suspension of 0.5 g (1.4 mmole) of spiro hetarene IIIa (or IVa) in 10 ml of ethanol. After heating to 40-60°C, a precipitate began to form. After 1 h, the precipitate was removed by filtration and washed with ethanol. The yield was 0.6 g (94%).

## LITERATURE CITED


1. E. G. Kovalev, G. L. Rusinov, V. A. Anufriev, and L. G. Egorova, Khim. Geterotsikl. Soedin., No. 9, 1244 (1990).
2. M. Dewar, Molecular Orbital Theory in Organic Chemistry [Russian translation], Mir, Moscow (1972), p. 236.
3. E. G. Kovalev, I. Ya. Postovskii, G. L. Rusinov, and I. L. Shegal, Khim. Geterotsikl. Soedin., No. 11, 1462 (1981).
4. R. Bramley and M. D. Johnson, J. Am. Chem. Soc., **87**, 1372 (1965).
5. G. Seitz and T. Kaemppchen, Arch. Pharm., **308**, 237 (1975).
6. J. Kolc and R. S. Becker, J. Am. Chem. Soc., **91**, 6513 (1969).
7. L. E. Sutton, Tables of Interatomic Distances and Configurations in Molecules and Ions: Special Publication, Chem. Soc., London (1965), No. 18.
8. J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, and C. Gaurat, Bull. Soc. Chim. France, No. 11, 2857 (1964).
9. J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, and C. Gaurat, Bull. Soc. Chim. France, No. 1, 40 (1967).