both the singlet ("pure" hydride transfer [13]) and triplet (a "diradical" pathway that includes a step involving one-electron transfer with the formation of diradical pairs) states of the system. In our opinion, therefore, the "quantum-chemical evidence" for the presence of hydride transfer obtained in a number of studies is not completely convincing.

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# SATURATED NITROGEN-CONTAINING HETEROCYCLES.

# 13.* PERHYDROACRIDINES. SYNTHESIS AND STEREOCHEMISTRY


A. P. Kriven'ko, T. G. Nikolaeva, L. M. Yudovich, N. T. Komyagin, A. I. Yanovskii, Yu. T. Struchkov, and V. G. Kharchenko



UDC 547.835.2:543.422.25:541.634



The configurations of the perhydroacridines formed in the catalytic hydroamination of threo-methylenedicyclohexanone and the product of its cyclization — 2-hydroxy-2,3-tetramethylenebicyclo[3.3.1]nonan-9-one — were established by means of the $^{13}C$ NMR spectra and alternative synthesis. It is shown that isomers with cis-anti-cis and cis-syn-cis configurations are formed as a result of the reactions. The results of x-ray diffraction analysis are presented for cis-syn-cis-N-(2-hydroxyethyl)perhydroacridine.


We have reported the synthesis of perhydroacridines by means of the catalytic reductive amination of methylenedicyclohexanone (I) and the product (II) of its cyclization [2, 3]. The present research was undertaken in order to establish the stereochemical compositions of the resulting heterocyclic bases.

It is known that a mixture of three or four isomeric perhydroacridines is formed in the hydroamination of oxo compounds I and II by means of the Leuckart reaction [4]: isomers with trans-syn-trans and trans-anti-cis configurations are obtained under the conditions of borohydride amination [5].

We have established that the catalytic reductive amination of I and II proceeds stereospecifically with the formation of heterocycles of the cis,cis type:

*See [1] for Communication 12.


N. G. Chernyshevskii Saratov State University, Saratov 410601.


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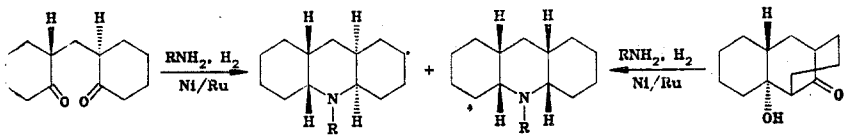
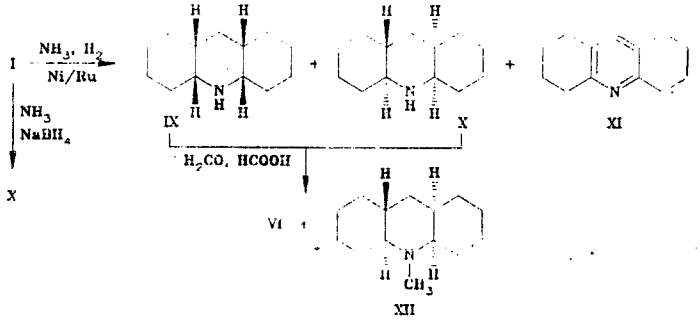



I III—V VI—VIII II

III, VI R=$CH_3$; IV, VII R=$CH_2CH_2OH$; V, VIII R=$C_6H_5$

We isolated new or little-studied isomers — N-substituted cis-anti-cis- (III-V) and cis-syn-cis-perhydroacridines (VI-VIII). The overall yields of bases III and VI and IV and VII, regardless of the structure of the substrate, are 82-92%. N-Phenylperhydroacridines V and VIII are formed in 50% yield in the hydroamination of diketone I. Under the conditions of hydroamination with the use of aniline, β-cycloketol II is converted to 2,3-tetramethylenebicyclo[3.3.1]nonane-2,3-diol.

The nature of the nucleophilic reagent has a significant effect on the isomeric composition and the direction of the process. Perhydroacridine in the form of a mixture of two isomers IX and X and sym-octahydroacridine (XI) were obtained when ammonia was used as the amine component. Methylation of the mixture of bases IX and X leads to N-methylperhydroacridines VI and XII. To ascertain the structures of the isomers obtained we carried out alternative synthesis under the conditions of the Leuckart reaction [4] and borohydride amination [5]. As a result of many recrystallizations we obtained trans-syn-trans- and trans-anti-cis-perhydroacridines XIII and X, respectively, in pure form.




The three-dimensional structures of the saturated azaheterocycles were established by means of $^{13}C$ NMR spectroscopy (Table 1). trans-syn-trans-Perhydroacridine (XIII) and its N-methyl homolog (XIV) were previously characterized [6]. The spectrum of X contains 13 resonance lines; this constitutes evidence for its unsymmetrical structure. The close chemical shifts of the $C_{(10a)}$ atoms in the spectra of X and trans-syn-trans isomer XIII, as well as the presence of a strong-field signal of a $C_{(9)}$ atom at 20.72 ppm, confirm the trans-anti-cis

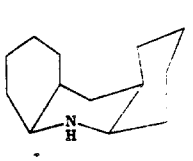
TABLE 1. $^{13}C$ Chemical Shifts of the Perhydroacridines (δ, ppm $CDCl_3$)

| Compound | $C_{(1)}$, $C_{(8)}$ | $C_{(2)}$, $C_{(7)}$ | $C_{(3)}$, $C_{(6)}$ | $C_{(4)}$, $C_{(5)}$ | $C_{(9)}$ | $C_{(8a)}$, $C_{(9a)}$ | $C_{(4a)}$, $C_{(10a)}$ | R |
|---|---|---|---|---|---|---|---|---|
| IV* | 28,39 | 22,35 | 22,35 | 23,34 | 30,24 | 33,87 | 55,38 | 59,64, 50,44 |
| V | 29,87 | 22,06** | 23,79** | 25,72** | 27,07 | 32,29 | 55,71 | 148,34, 128,42, 119,43, 118,39 |
| VI | 32,26 | 22,70 | 25,89 | 25,89 | 26,89 | 37,58 | 60,95 | 39,00 |
| VII | 32,34 | 22,06 | 26,57** | 26,77** | 26,29 | 37,71 | 58,80 | 57,29, 51,93 |
| VIII | 32,46 | 21,62 | 26,11 | 26,11 | 26,02 | 37,49 | 53,53 | 147,31, 129,17, 115,00, 111,60 |
| IX | 30,54 | 27,22 | 21,81 | 33,83 | 36,21 | 35,91 | 57,15 | — |
| X | 26,93, 33,83 | 26,40, 26,47 | 20,72, 25,76 | 32,69, 33,15 | 38,98 | 36,70** 37,63** | 55,37, 63,19 | — |
| XII | 27,47, 33,81 | 27,07, 25,89 | 19,80, 26,15 | 30,70, 30,97 | 39,47 | 37,08** 37,76** | 63,55, 70,19 | 36,41 |
| XIII [6] | 32,34 | 26,21 | 25,57 | 33,66 | 39,91 | 43,25 | 62,10 | — |
| XIV [6] | 33,46 | 25,83 | 26,10 | 31,03 | 40,69 | 40,99 | 69,28 | 36,07 |

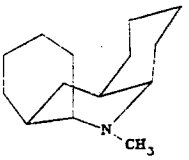
*In DMSO at 100°C; the signal of the solvent (39.60 ppm) was used as the standard.

**Equally probable assignments.

configuration of base X. The assignment of the signals in this and other cases was made on the basis of the off-resonance spectra and with allowance for the increment taken from [7]. In the spectrum of the hydrogenation product obtained when ammonia was used as the nitrogenous agent, in addition to signals corresponding to sym-octahydroacridine (XI) and X, we isolated seven signals of isomer IX. The presence of a strong-field signal at 21.81 ppm and the small chemical shift of the $C_{(4a)}$ and $C_{(10a)}$ atoms (57.15 ppm) made it possible to determine the configuration of this compound as being cis-syn-cis. The position of the resonance signal of the $C_{(9)}$ atom, the intensity of which is half the intensities of the remaining signals, at 39.21 ppm constitutes evidence that, in contrast to its carbon analog, cis-syn-cis-perhydroacridine (IX) is stabilized in one conformation. In the spectrum of the conformationally labile cis-syn-cis-perhydroanthracene the averaged signal of the $C_{(9)}$ and $C_{(10)}$ atoms is located at 33.90 ppm at room temperature [8]. In the low-temperature spectrum of this compound the signals of the $C_{(9)}$ and $C_{(10)}$ atoms are found at 38.37 and 26.94 ppm [8]. The significant difference in these signals can be used as a unique conformational marker for heterocycles that are similar to the investigated compounds. Thus for cis-syn-cis-perhydroacridine (IX) the most preferred conformer is that in which the axial C–C bonds are β-oriented with respect to the nitrogen atom. In analogy with cis-decahydroquinolines it can be called the A conformer [7]. The reason for this stabilization is the decrease in the lengths of the C–N bonds as compared with the C–C bonds; this is manifested in the case of cis-decahydroquinolines. At –68°C the ratio of the conformers A:B = 9:1 [7]. Taking into account the fact that methylation of cis-decahydroquinoline leads to a shift in the conformational equilibrium (A:B = 7:3) [7], destabilization of the A form also should have been expected for N-methylperhydroacridine (VI). In fact, in the spectrum of VI, obtained by methylation of base IX, the resonance signal of the $C_{(9)}$ atom is located at 26.89 ppm; this constitutes evidence for the preferableness of the B conformer for N-methyl-cis-syn-cis-perhydroacridine (VI).



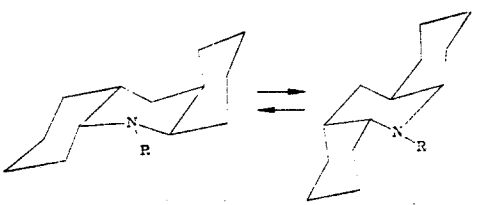

A IX




B VI

It is apparent from Table 1 that other cis-syn-cis isomers (VII and VIII) are also stabilized in the B form. The small values of the resonance signals of the $C_{(4a)}$ and $C_{(10a)}$ atoms for VIII are explained by the shielding effect of the phenyl substituent.

In addition to signals of N-substituted cis-syn-cis-perhydroacridines VI-VIII, signals of another isomer are present in the spectra of the hydrogenation products obtained in the hydroamination of I and II. Two narrow signals at 31.08 and 39.78 ppm, which belong to the $C_{(9)}$ atom and the N-methyl group, are observed for III. The remaining signals are broadened. Three narrow signals at 30.70, 58.66, and 49.04 ppm, which are related to the $C_{(9)}$ atom and the carbon atoms of the hydroxyethyl group, are present in the spectrum in the case of base IV, which was isolated in pure form. The spectrum of this compound in DMSO at 100°C is compressed and has eight lines. Judging from the intensities, the signals of the $C_{(2)}$, $C_{(3)}$, $C_{(6)}$, and $C_{(7)}$ atoms are superimposed. This sort of behavior of III and IV indicates conformational lability and makes it possible to assign them to isomers with a cis-anti-cis configuration. A comparison of the spectrum of base V with the high-temperature spectrum of IV provides evidence for the identical character of the configurations of these azaheterocycles. The fact that 11 narrow resonance lines are observed at room temperature in the spectrum of isomer V is explained by the high rate of the conformational conversion of isomer V as compared with III and IV.




III $R=CH_3$; IV $R=CH_2CH_2OH$; V $R=C_6H_5$

To the best of our knowledge, perhydroacridines have not been previously subjected to x-ray diffraction study. In this connection, one of the first-obtained perhydroacridines of

TABLE 2. Bond Angles (ω)

| Angle | ω° | Angle | ω° | Angle | ω° |
|---|---|---|---|---|---|
| $C_{(4a)}NC_{(10a)}$ | 116,82(8) | $C_{(4)}C_{(4a)}C_{(9a)}$ | 111,21(9) | $C_{(1)}C_{(9a)}C_{(9)}$ | 114,2(1) |
| $C_{(4a)}NC_{(11)}$ | 111,66(8) | $C_{(6)}C_{(5)}C_{(10a)}$ | 110,9(1) | $C_{(1)}C_{(9a)}C_{(4a)}$ | 110,8(1) |
| $C_{(10a)}NC_{(11)}$ | 114,04(8) | $C_{(5)}C_{(6)}C_{(7)}$ | 110,5(1) | $C_{(9)}C_{(9a)}C_{(4a)}$ | 111,21(9) |
| $C_{(2)}C_{(1)}C_{(9a)}$ | 110,9(1) | $C_{(6)}C_{(7)}C_{(8)}$ | 110,4(1) | $NC_{(10a)}C_{(5)}$ | 117,0(1) |
| $C_{(1)}C_{(2)}C_{(3)}$ | 110,6(1) | $C_{(7)}C_{(8)}C_{(8a)}$ | 113,8(1) | $NC_{(10a)}C_{(8a)}$ | 109,9(1) |
| $C_{(2)}C_{(3)}C_{(4)}$ | 110,7(1) | $C_{(8)}C_{(8a)}C_{(9)}$ | 114,3(1) | $C_{(5)}C_{(10a)}C_{(8a)}$ | 112,0(1) |
| $C_{(3)}C_{(4)}C_{(4a)}$ | 110,8(1) | $C_{(8)}C_{(8a)}C_{(10a)}$ | 111,1(1) | $NC_{(11)}C_{(12)}$ | 113,39(9) |
| $NC_{(4a)}C_{(4)}$ | 112,61(9) | $C_{(9)}C_{(8a)}C_{(10a)}$ | 110,9(1) | $C_{(11)}C_{(12)}O$ | 112,1(1) |
| $NC_{(4a)}C_{(9a)}$ | 109,58(9) | $C_{(8a)}C_{(9)}C_{(9a)}$ | 109,6(1) | | |

TABLE 3. Principal Torsion Angles (τ) in Structure VII

| Endocyclic angles | | | | | |
|---|---|---|---|---|---|
| ring A | | ring B | | ring C | |
| angle | τ° | angle | τ° | angle | τ° |
| $NC_{(4a)}C_{(9a)}C_{(9)}$ | 54,0(1) | $C_{(4a)}C_{(4)}C_{(3)}C_{(2)}$ | 57,7(1) | $C_{(10a)}C_{(5)}C_{(6)}C_{(7)}$ | −58,8(1) |
| $C_{(4a)}C_{(9a)}C_{(9)}C_{(8a)}$ | −58,4(1) | $C_{(4)}C_{(3)}C_{(2)}C_{(1)}$ | −57,6(1) | $C_{(5)}C_{(6)}C_{(7)}C_{(8)}$ | 57,9(1) |
| $C_{(9a)}C_{(9)}C_{(8a)}C_{(10a)}$ | 58,2(1) | $C_{(3)}C_{(2)}C_{(1)}C_{(9a)}$ | 55,0(1) | $C_{(6)}C_{(7)}C_{(8)}C_{(8a)}$ | −54,8(1) |
| $C_{(9)}C_{(8a)}C_{(10a)}N$ | −54,0(1) | $C_{(2)}C_{(1)}C_{(9a)}C_{(4a)}$ | −51,1(1) | $C_{(7)}C_{(8)}C_{(8a)}C_{(10a)}$ | 50,9(1) |
| $C_{(8a)}C_{(10a)}NC_{(4a)}$ | 52,8(1) | $C_{(1)}C_{(9a)}C_{(4a)}C_{(4)}$ | 50,6(1) | $C_{(8)}C_{(8a)}C_{(10a)}C_{(5)}$ | −50,5(1) |
| $C_{(10a)}NC_{(4a)}C_{(9a)}$ | −52,6(1) | $C_{(9a)}C_{(4a)}C_{(4)}C_{(3)}$ | −54,6(1) | $C_{(8a)}C_{(10a)}C_{(5)}C_{(6)}$ | 55,2(1) |
| $NC_{(11)}C_{(12)}O$ | 173.6(2) | | | | |

the cis-syn-cis type — N-(2-hydroxyethyl)perhydroacridine (VII) — was subjected to x-ray diffraction analysis. The structure of the VII molecule with the bond lengths is shown in Fig. 1; the bond and torsion angles are presented in Tables 2 and 3. The central piperidine ring has a chair conformation. The N and $C_{(9)}$ atoms deviate from the $C_{(4a)}C_{(9a)}C_{(8a)}C_{(10a)}$ (A) plane, realized with an accuracy of 0.001 Å, by −0.583(1) and 0.699(1) Å, respectively. The dihedral angles between plane A and the planes of angles $C_{(4a)}NC_{(10a)}$ and $C_{(8a)}C_{(9)}C_{(9a)}$ are 48.5(1)° and 52.6(1)°, i.e., the heteroring is somewhat flattened at the nitrogen atom. The $N-C_{(11)}$, $C_{(1)}-C_{(9a)}$, and $C_{(8)}-C_{(8a)}$ bonds are equatorial with respect to the piperidine ring, whereas the $C_{(4)}-C_{(4a)}$ and $C_{(5)}-C_{(10a)}$ bonds are axial; this is in agreement with the $^{13}C$ NMR spectroscopic data on the cis-syn-cis fusion of the rings in this compound. The carbocycles, like the central heterocycle, have a chair conformation that is close to that found by x-ray diffraction analysis in cyclohexane [9]; the $C_{(1)}C_{(2)}C_{(4)}C_{(4a)}$ (B) and $C_{(8)}C_{(7)}C_{(5)}C_{(10a)}$ (C) planes are realized with an accuracy of 0.001 Å and 0.004 Å, respectively. The dihedral angles formed by plane B with angles $C_{(2)}C_{(3)}C_{(4)}$ and $C_{(1)}C_{(9a)}C_{(4a)}$ are 52.2(1)° and 45.5(1)°, whereas plane C forms angles of 52.9(1)° and 45.6(1)° with angles $C_{(5)}C_{(6)}C_{(7)}$ and $C_{(8)}C_{(8a)}C_{(10a)}$. In other words, both carbocycles are somewhat flattened; in fact, torsion angles $C_{(5)}C_{(10a)}C_{(8a)}C_{(8)}$ [50.5(1)°] and $C_{(7)}C_{(8)}C_{(8a)}C_{(10a)}$ [50.9(1)°] and, correspondingly, $C_{(4)}C_{(4a)}C_{(9a)}C_{(1)}$ [50.6(1)°] and $C_{(2)}C_{(1)}C_{(9a)}C_{(4a)}$ [51.1(1)°] are smaller than in cyclo-

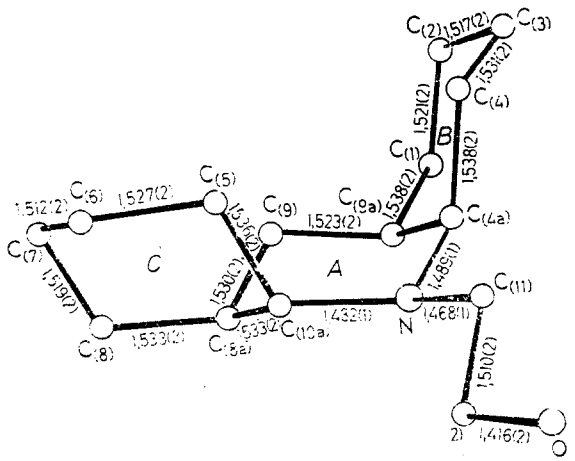



Fig. 1. Structure of the N-(2-hydroxyethyl)-cis-syn-cis-perhydroacridine molecule (VII).

TABLE 4. Coordinates of the Nonhydrogen Atoms ($\cdot 10^4$) in the VII Structure*

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| O | −1627(2) | 2563(1) | 3800(1) | $C_{(6)}$ | −3601(2) | 4660(1) | 3031(2) |
| $O_w$ | 1002(1) | 2710(1) | 1938(1) | $C_{(7)}$ | −5677(3) | 4955(1) | 2525(1) |
| N | −5970(1) | 3382(1) | 1244(1) | $C_{(8)}$ | −7547(2) | 4637(1) | 2655(2) |
| $C_{(1)}$ | −10273(2) | 3702(1) | −2766(2) | $C_{(8a)}$ | −7799(2) | 4147(1) | 1708(1) |
| $C_{(2)}$ | −8833(3) | 3871(1) | −3763(2) | $C_{(9)}$ | −8777(2) | 4204(1) | −132(2) |
| $C_{(3)}$ | −6813(3) | 3553(1) | −3385(2) | $C_{(9a)}$ | −9124(2) | 3693(1) | −927(1) |
| $C_{(4)}$ | −5572(2) | 3575(1) | −1573(1) | $C_{(11)}$ | −4056(2) | 3061(1) | 1682(1) |
| $C_{(4a)}$ | −7002(2) | 3402(1) | −545(1) | $C_{(12)}$ | −3323(2) | 2915(1) | 3452(1) |
| $C_{(5)}$ | −3798(2) | 4194(1) | 1985(1) | | | | |

*The coordinates of the hydrogen atoms and the temperature factors can be obtained from the authors.

hexane (56°) [9]. The lengths of the endocyclic and exocyclic N—C bonds are the usual values for piperidine derivatives [10, 11]. The length of the $O—C_{(12)}$ bond actually coincides with the standard value (1.426 Å) for the $C_{sp^3}—OH$ bond [12].

Chains along helical axes are formed through hydrogen bonds of three types of the VII molecule and crystallization water: 1) O—H...$O_w$ [O...$O_w$ 2.708(1) Å, H...$O_w$ 1.88(2) Å, OH 0.85(2) Å, angle O—H...$O_w$ 165(2)°]; 2) $O_w—H(O_w1)...O'$ (x, $\frac{1}{2}$ − y, $-\frac{1}{2}$ + z) [$O_w$...O' 2.831(1) Å, H...O' 2.00(2) Å, $O_w—H$ 0.84(2) Å, angle $O_w—H...O'$ 171(2)°]; 3) $O_w—H(O_w2)...N''$ (1 + x, y, z) [$O_w$...N'' 2.867(1) Å, H...N'' 2.1(2) Å, $O_w—H$ 0.81(2) Å, angle $O_w—H...N''$ 167(2)°]. Thus the hydroxy group is a donor in the hydrogen bond with one $H_2O$ molecule and an acceptor in the hydrogen bond with another. The $H_2O$ molecule also fulfills the same function by participating as a donor in two hydrogen bonds and as an acceptor in one.

## EXPERIMENTAL

The $^{13}C$ NMR spectra of solutions in deuterochloroform were recorded with a Varian FT-80A spectrometer with tetramethylsilane (TMS) as the internal standard.

The VII ($C_{15}H_{27}NO \cdot H_2O$) crystals were monoclinic and had the following parameters at 20°C: a = 6.505(1), b = 26.899(1), c = 8.639(1) Å, β = 107.60(1)°, V = 1440.5(2) Å$^3$, z = 4, $d_{calc}$ = 1.095 g/cm$^3$, and space group $P2_1/c$. The cell parameters and the intensities of 2629 independent reflections with $F^2 \geq 5\sigma$ were measured with a Hilger Watts Y/290 automatic four-circle diffractometer (20°C, $\lambda_{MoK_\alpha}$, graphite monochromator, θ/2θ scanning, θ ≤ 30°). The structure was decoded by the direct method by means of the MULTAN program and was refined by the total-matrix method of least squares, initially within the isotropic approximation and then within the anisotropic approximation; one molecule of crystallization water was detected. All of the H atoms were exposed objectively in differential synthesis and were included in refinement within the isotropic approximation. The final R factor was 0.040 ($R_w$ = 0.060). All of the calculations were made with an Eclipse S/200 computer by means of the INEXTL program [14]. The coordinates of the atoms and their temperature factors are presented in Table 4.

Thin-layer chromatography was carried out on Silufol UV-254 plates by elution with hexane—ether—chloroform (3:1:1).

The catalytic hydroamination of I and II was carried out by the methods in [2, 3] in the presence of Raney nickel modified with ruthenium. Bases IV [mp 107-108°C (from ethanol)], V [mp 124-126°C (from ethanol)], VI [mp 57-59°C (from acetone)], and XI [mp 68-69°C (from ethanol)] precipitated in pure form when the hydrogenation products were evaporated to approximately one fifth of their original volumes and cooled. Complete evaporation of the hydrogenation products led to mixtures of isomers III and VI, IV and VII, V and VIII, and IX and X. The mixture of isomers IV and VII was separated by fractional recrystallization from ethanol; pure isomer VII (mp 89-91°C) was obtained in the form of the monohydrate. Pure isomer X [mp 47-48°C (from a mixture of alcohol with acetone)] was isolated by chromatography of the mixture of IX and X with a column packed with α-$SiO_2$ with a length of 50 cm by elution with hexane—chloroform—ether (2:2:1). Base X was also obtained by the method in [5]. trans-syn-trans-Perhydroacridine XIII was synthesized by the method in [4] and was isolated from a mixture of isomers by means of many recrystallizations from ethanol (mp 89-90°C). Bases III, VIII, IX, and XII were identified on the basis of the $^{13}C$ NMR spectra.

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# SPECTRAL-LUMINESCENCE CHARACTERISTICS OF 1,3-DIARYL-4,7-PHENANTHROLINES

N. S. Kozlov, K. N. Gusak,
V. A. Serzhanina, L. F. Gladchenko,
and N. A. Krot

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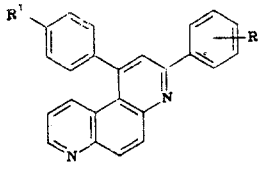
The effect of the nature of the substituents and the solvent on the absorption and fluorescence spectra and the fluorescence quantum yields of 1,3-diaryl-4,7-phenanthrolines was studied. Electron-donor groups in the para position of the phenyl ring cause a bathochromic shift of the absorption and fluorescence spectra and an increase in the fluorescence quantum yields. A change in the polarity of the solvent leads to a significant shift of the fluorescence spectra of hydroxy and dialkylamino derivatives of 4,7-phenanthroline.

The spectral-luminescence properties of 4,7-phenanthroline derivatives have not been adequately studied. The fluorescence spectra of unsubstituted phenanthroline in the frozen state were described in [1-3], and the luminescence intensities of toluene solutions of unsubstituted 4,7-phenanthroline and three monoaryl-4,7-phenanthrolines were presented in only one communication [4]. Wiley and co-workers [4] state the fact of the decrease in the luminescence activity of these compounds as compared with a standard (p-terphenyl) without explaining the reasons for this phenomenon. No information regarding the spectral-luminescence properties of 1,3-disubstituted 4,7-phenanthrolines is available in the literature. In this connection the aim of the present research was to study the absorption and fluorescence spectra and the fluorescence quantum yields of 1,3-diaryl-4,7-phenanthrolines I-XX. The bases of the 4,7-phenanthroline series were obtained by the reaction of 6-(R-benzylideneamino)quinolines with acetophenone or its p-substituted derivatives (with acetone in the case of XX) in the presence of a proton catalyst, as previously described in [5].

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