nitrosamine VIII. The filtrate from the separation of the mixture of VIII and IIIa was evaporated, and the residue was separated with a column as described above to give 0.16 g (3.5%) of IIIb, 0.23 g (5%) of IIIa, and 0.25 g (5.5%) of IVb.

N-Nitroso-11,14-dicyanoperhydroacridine (VIII). A solution of 2.8 g (0.04 mole) of NaNO₂ in 10 ml of water was added with stirring and cooling (to 15°) in the course of 15 min to a suspension Of 2.43 g (0.01 mole) of 11,14-dicyanoperhydroacridine in 40 ml of CH₃COOH, after which the mixture was stirred for another 3 h. The solid material was removed by filtration, washed with water, and dried to give 2.4 g (88%) of nitrosamine VIII (identical to a sample obtained by oxidation of IIa with respect to a mixed-melting-point determination and its IR spectrum).

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AZOMETHINES OF NITROGEN-CONTAINING HETEROCYCLES.

I. SYNTHESIS AND STUDY OF THE STRUCTURES OF SCHIFF BASES

FROM 3-METHYL-2-AZAFLUORENONE AND ARYLAMINES

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UDC 547.574.4:547.553:547.298.1:542.952.1

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In an investigation of the conditions for the formation of Schiff bases from 3-methyl-2-azafluorenone and arylamines it was shown that the use of boron trifluoride etherate as the catalyst insures the highest yields. The fundamental possibility of the preparation of Schiff bases by condensation of 3-methyl-2-azafluorene with p-nitrosodimethylaniline and subsequent reduction of the resulting oxazirane structure is demonstrated. The ratio of the cis and trans isomers of the resulting azomethines was established on the basis of PMR spectral data.

At present there are no data available on the synthesis of Schiff bases with the participation of azafluorene systems, and this has been responsible for the inaccessibility of the latter. Continuing our research on the chemistry of azomethines that we have used in the syntheses of complex heterocyclic systems (azaphenanthrenes and naphthyridines) [1], we turned to the preparation of Schiff bases from 3-methyl-2-azafluorenone (I) and 3-methyl-2azafluorene (II) [2]).

Patrice Lumumba International-Friendship University, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 109-115, January, 1976. Original article submitted December 11, 1974.

This material is protected by copyright registered in the name of Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$7.50. The previously unknown N-(3-methy1-2-aza-9-fluorenylidene) ary lamines (III-VII) were obtained by condensation of I with aniline, o-, m-, and p-toluidines, and mesidine.



III $R^1 = R^2 = R^3 = R^4 = R^5 = H$; IV $R^1 = CH_3$, $R^2 = R^3 = R^4 = R^5 = H$; V $R^2 = CH_3$, $R^1 = R^3 = R^4 = R^5 = H$; VI $R^3 = CH_3$, $R^1 = R^2 = R^4 = R^5 = H$; VII $R^1 = R^3 = R^5 = CH_3$, $R^2 = R^4 = H$

The condensation of azafluorenone I with aniline and the isomeric toluidines was realized under various conditions: by heating at $170-210^{\circ}C$ without a catalyst and by heating at $150-160^{\circ}$ in the presence of anhydrous zinc chloride, and also in the presence of boron trifluoride etherate. The yields of bases III-VI obtained by the first two methods range from 20 to 60%, whereas VII was obtained in 70% yield by the third method. The third method was previously used in the synthesis of N-(9-fluorenylidene)arylamines, which were obtained in almost quantitative yields [3]. We also accomplished the condensation of 3-methyl-2-azafluorene (II) with p-nitrosodimethylaniline in alcohol, which leads to N-(3-methyl-2-aza-9-fluorenylidene)-p-dimethylaminoaniline N-oxide, which, according to its IR spectrum, has an oxazirane structure (VIII), in agreement with the data in [4].



The IR spectrum of VIII contains intense bands at 1268 and 1183 cm⁻¹ due to stretching vibrations of N-O and C-O bonds in the oxazirane system, and bands of stretching vibrations of a C=N bond are absent. Reduction of VIII with zinc in alcohol gives N-(3-methyl-2-aza-9-fluorenylidene)-p-dimethylaminoaniline (IX), whereas reduction of azomethine III with lithium aluminum hydride gives N-(3-methyl-2-aza-9-fluorenyl)aniline (X), acylation of which with acetic anhydride gives N-phenyl-N-(3-methyl-2-aza-9-fluorenyl)acetamide (XI).



Two singlets at 2.47 ppm (3 H), which correspond to the protons of the α -methyl group of the pyridine ring, and at 8.57 ppm, which is due to the 8-H proton, are observed in the PMR spectrum (CDCl₃) of X. The broad singlet at 5.67 ppm (1 H) is related to the 9-H proton, whereas the signal at 3.50-4.24 ppm belongs to the proton of the amino group. The assignment of the latter two signals is confirmed by measurements of the PMR spectrum of a solution of X containing CF₃COOH. In this case the signal of the labile proton at 3.50-4.24 ppm vanishes, whereas the singlet of the 9-H proton coupling with it (5.35 ppm) becomes sharp, and its position remains practically unchanged.

Picrate	N. %	l calc.		2 14,0	3 14,0) 14,0	2 2 2 2 3 2 3 0 0 2 3 0 0 2 3 0 0 2 3 0 0 2 3 0 0 2 3 0 0 2 3 0 0 2 3 0 0 1 3 0 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 1 3 0 0 0 0
			tounc	.14,2	14,3	14,0	ដូ ដូ ដូ
	Emp irical formula			C25H17N5O7	C25H17N5O7	$\mathrm{C}_{25}\mathrm{H}_{17}\mathrm{N}_{5}\mathrm{O}_{7}$	C26H19N6O7 C26H19N6O7 C26H19N5O7 C26H19N5O7 C28H23N6O7 C27H22N6O7
	mp, °C (from methanol)			202-204	224-225,5	202	212-213 214-215 211-212 229-231
	Yield.	d'o		30	46	6	80,5 20,5 30,5 30,5 30,5 30,5 30,5 30,5 30,5 3
	nol. vt.			270	270	270	284 284 312 313
ت			z	10,4	10,4	10,4	0,00,00 0,00 0,00 0,00
Cal	č	<u>0</u>	H	5,2	5,2	5,2	0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0 0,0
			v	84,4	84,4	84,4	84,5 84,5 84,5 80,5 5,5 5 5,5 5 5 5 5 5 5 5 5 5 5 5 5 5
		mol.	wt.	270	270	270	284 284 312 312 313 313
pu			z	10,3	10,3	10,4	9,9 9,7 13,7
Fou	i	°8	H	5,3	5,5	5,5	6,5 6,5 7
			υ	84,3	84,4	84,2	84,8 84,8 84,5 84,5 80,3 90,3 90,3 90,3 90,3 90,3 90,3 90,3 9
	Em pirical formula				$\mathrm{C}_{19}\mathrm{H}_{14}\mathrm{N}_2$	C ₁₉ H ₁₄ N ₂	C ₂₀ H ₁₆ N ₂ C ₂₀ H ₁₆ N ₂ C ₂₀ H ₁₆ N ₂ C ₂₂ H ₂₀ N ₂ C ₃₁ H ₁₅ N ₃
		Rf		0,75	0,75	0,75	0,85 0,8 0,76 0,84 0,57
	<u>.</u>	mp, °C	1	129-130	129	130	88—89 114—115,5 147—148 118,5—120 160—162
		R		H	Н	Н	нн СН
	÷.				Н	Н	тити
		R³		Н	H	Н	H H CH ₃ CH ₃
		R²		H	Η	Η	ннсн
		R		H	н	Н	сн, сн,
Compound				Red crystals	Yellow crystals	Brown crystals	VV VV XI XI

TABLE 1. N-(3-Methyl-2-aza-9-fluorenylidene)arylamines (III-VII, IX)

	Spectrum of the Schiff base								
Assignment	III	IV	v	VI	VII	IX			
Stretching vibrations, ν	Band, cm ⁻¹								
C—H (aromatic)	3078 w 3062 w 3028 w	3070 w 3020 w	3052 w 3025 w	3055 w 3020 w	3018 w	3055 w			
bonds C—H group CH ₃	2925 W	2930 W	2920 W 2860 W	2925 W 2872 W	2920 w 2855 w	2895 w			
Č=N	1655 1661 m	1660 m	1660 m	1662 m	1660s	1650 m			
C=C (aromatic)	1601 vs 1483 m	1611 vs 1485 m	1610 vs 1483 m	1610 vs. 1506 m	1612 vs 1560 m 1480 m	1610 s 1557 m			
$\delta_{as} \operatorname{CH}_3$	1448 121	1460 m 1450 m	1452 m	1450 s	1451 m	1450 s			
Out-of-plane deformation vibrations of adjacent	*741s	*770 s 741 s 720 s	*742s	*745s	*746 s	*744 s			
	†775s 700 s	-	‡790s 704 m	*820s	_	*815s			

TABLE 2. Data from the IR Spectra of Schiff Bases III-VII and IX $% \left({{{\rm{TABLE}}} \right)$

*Four adjacent C-H bonds. +Five adjacent C-H bonds.

+Three adjacent C-H bonds.

****Two adjacent C-H bonds.** The stretching vibrations of the C-H bonds of the CH_3 group in the spectrum of base IX appear as a weak band at 2815 cm⁻¹.

Schiff bases III-VII and IX are colored. Compound III was obtained as crystals that differed in color (Table 1) but were identical to one another with respect to melting points and principal spectral characteristics (UV, IR, and PMR); this indicates the identical character of their chemical structures. The difference in color is apparently explained by the existence of polymorphic modifications. A similar phenomenon was previously noted in the case of N-(2,5-dinitro-9-fluorenylidene)-p-fluoroaniline, for a mixture of the red and yellow samples of which no melting-point depression was noted [5].

The stretching vibrations of the C=N bonds of the azomethine obtained in this study appear as bands of medium intensity at 1650-1662 cm⁻¹ (Table 2). In the IR spectrum of the model compounds N-(9-fluorenylidene)aniline this band is found at 1647 cm⁻¹.

Three groups of bands with clearly expressed absorption maxima at 256-258, 291-306, and 380-390 nm (Fig. 1) are observed in the UV spectra (in ethanol) of azomethines III-VII and IX, and the overall character of the spectra and the positions of the absorption maxima are similar to the spectrum of N-(9-fluorenylidene)aniline [λ_{max} , nm (log ϵ): 258 (4.8), 291 (3.98), 302 (4.02), and 390 (3.45)].

The molecular weights of bases III-VII and IX determined by mass spectrometry are in conformity with their empirical formulas.

It is evident from a comparison of Stuart-Briegleb molecular models of imines III-VII and IX that they are noncoplanar, that rotation of the phenyl ring about the C-N bond is sterically hindered, and that this hindrance is intensified even more when methyl groups are introduced into the ortho position of the phenyl ring.

The fluorescence spectrum of azafluorenone I is similar to the spectrum of fluorenone with respect to the form of the band and the intensity and position of the maximum. The luminescence spectra of bases III-VII and IX are of extremely low intensity and structure-less, and this indicates the noncoplanarity of these molecules [6].

The existence of configurational isomers of the cis-trans type is possible for Schiff bases III-VII and IX.

Signals of protons of two methyl groups at 2.50 and 2.64 ppm are present in the PMR spectrum (CC14) of base III (Fig. 2). If it is assumed that these signals are due to the



Fig. 1. UV spectra (in ethanol): 1) N-(3-methyl-2-aza-9-fluorenylidene)aniline (III); 2) N-(3-methyl-2-aza-9-fluorenylidene)-o-toluidine (IV); 3) N-(3-methyl-2-aza-9-fluorenylidene)-m-toluidine (V); 4) N-(3-methyl-2-aza-9-fluorenylidene)p-toluidine (VI); 5) N-3(methyl-2-aza-9fluorenylidene)mesidine (VII); 6) N-(3methyl-2-aza-9-fluorenylidene)-p-dimethylaniline (IX).



standard).

protons of the methyl groups of the cis and trans isomers, in this case one should expect the presence of two signals also for the aromatic protons, in particular 8-H and 1-H. The integral intensities of the signals at 8.94 ppm (singlet), 6.68 ppm (broad doublet), and 2.64 ppm (singlet) are in a ratio of 1:1:3.



This makes it possible to conclude that the corresponding protons enter into the composition of one and the same molecule. An examination of the Stuart-Briegleb molecular models of the isomers of this imine shows that the indicated signals should be assigned to the trans isomer. In fact, the 8-H proton experiences substantial shielding by the phenyl ring attached to the C=N bond, as a consequence of which its signal should be shifted to strong field; this is actually observed in the spectrum (broad doublet at 6.68 ppm). The α -H signal of the pyridine ring at 8.94 ppm does not experience the anisotropic effect of the phenyl ring, and its shift to weak field as compared with the position of the α proton at 8.54 ppm in the spectrum of 3-methyl-2-azafluorene II is due to the anisotropic effect of the azomethine bond. In the cis isomer of III the shielding effect of the phenyl ring should be experienced by α -H, whereas the signal of the 8-H proton is shifted to weak field because of the absence of the anisotropic effect of the phenyl group. Because of the indicated effects these signals are shifted to the region of the remaining aromatic protons at 7.0-7.6 ppm. The integral intensity of the multiplet at 7.97 ppm is one third the intensity of the singlet at 2.50 ppm, as a consequence of which both of these signals can be assigned to the cis isomer. The signal at 2.50 ppm is due to the protons of the $3-CH_3$ group. The assignment of the multiplet at 7.97 raises some difficulty. It may be assumed that this signal belongs to 8-H of the cis isomer. However, the signals at 6.68 ppm (8-H of the trans isomer) and 7.97 ppm have different multiplicities, in connection with which one cannot exclude the alternative possibility of assignment of the latter to the 5-H proton of the cis isomer. It follows from the PMR spectrum that the ratio of the cis and trans isomers of base III is ${\sim}2{:}1$. The formation of picrates of this base with different melting points evidently is also explained by the presence of cis and trans isomers. Approximately the same ratio of cis and trans isomers was also established for bases IV-VII and IX, and the difference between the positions of the signals of the protons of the $3-CH_3$ groups of the cis and trans isomers is 0.13 to 0.15 ppm.

Our study of the structure of azomethines III-VII and IX by PMR spectroscopy with the application of a paramagnetic shift reagent — bis(pivaloylmethanato)europium — confirmed the conclusion regarding the existence in solution of an equilibrium mixture of cis and trans isomers for the imines obtained in this research.

EXPERIMENTAL

Column and thin-layer chromatography (TLC) were carried out on activity II aluminum oxide (elution by ether). The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The electronic spectra were measured with a Hitachi spectrophotometer. The PMR spectra of CCl₄ and CDCl₃ solutions of the compounds were recorded with an HA-100 spectrometer with hexamethyldisiloxane as the internal standard. The molecular weights were determined with an MKh-1303 mass spectrometer.

<u>N-(3-Methyl-2-aza-9-fluorenylidene)aniline (III).</u> A) A mixture of 2.77 g (0.014 mole) of I and 3 g (0.033 mole) of aniline was stirred vigorously at 170-200° for 2 h and at 200-210° for 5 h, after which it was extracted with 50 ml of ether. The ether and excess aniline were removed by diltillation, and the residue was dissolved in hexane (the residue did not dissolve completely). The hexane solution was passed through a 29 by 2 cm chromatographic column filled with 75 g of Al_2O_3 with elution by hexane. A total of 1000 ml of eluate was collected, evaporated to 50 ml, and cooled to yield 0.67 g (20%) of bright-red crystals of base III with mp 129-130°.

B) A mixture of 5.5 g (0.03 mole) of I, 40 g (0.43 mole) of aniline, and 5 g (0.3 mole) of zinc chloride was stirred at $150-160^{\circ}$ for 2 h, after which 100 ml of water was added to the reaction mixture, and the resulting mixture was made alkaline with solid potassium hydroxide. The orange bases were extracted with ether and dried with sodium sulfate. The

residue (6 g) remaining after removal of the ether and excess aniline by distillation was dissolved in 50 ml of hot ligroin. When the solution was cooled, crystals precipitated and a brown oil separated. The crystals were separated and recrystallized five times from ligroin to give 3 g of yellow crystals of base III with mp 129°. The hydrochloride of III had mp 233-234° (from alcohol). Found: N 9.4%. $C_{19}H_{14}N_2$ ·HCl. Calculated: N 9.1%. The mother liquors remaining after isolation of the yellow crystals of base III were evaporated to 70 ml and refluxed with activated charcoal. Cooling of the solution to 20° yielded an additional 0.5 g of III (for an overall yield of 46%). Crystals were isolated from the residual mother liquor by cooling to -10° and were recrystallized five times from ligroin to give 0.7 g (9.3%) of brown crystals of base III with mp 130°. The same hydrochloride (mp 233-234°) obtained from the brown crystals was the same as that obtained from the yellow crystals.

Schiff bases IV-VI (Tables 1 and 2) were obtained by method A. Hydrolysis of base V with 18% hydrochloric acid gave azafluorenone I in 73% yield.

<u>N-(3-Methyl-2-aza-9-fluorenylidene)mesidine (VII)</u>. A mixture of 1.7 g (0.01 mole) of I, 3 g (0.02 mole) of mesidine, and 0.6 ml of boron trifluoride etherate was heated rapidly to 120-130° and stirred at this temperature for 15 min. It was then cooled, treated with 30 ml of hexane, heated to the boiling point, and filtered. Cooling of the solution gave 1.9 g (70%) of azomethine VII.

<u>N-(3-Methyl-2-aza-9-fluorenylidene)-p-dimethylaniline Epoxide (VIII)</u>. A solution of 3 g (0.017 mole) of azafluorene II in 16 ml of ethanol was added to a solution of 2.5 g (0.017 mole) of p-nitrosodimethylaniline in 16 ml of ethanol, after which the mixture was heated to the boiling point, 0.16 ml of 33% sodium hydroxide solution was added, and the mixture was stirred and refluxed for 4 h. It was then cooled, and the precipitated brown crystals were recrystallized from n-propylalcohol to give 3.6 g (80%) of VIII with mp 200° and R_f 0.4. UV spectrum λ_{max} , nm (log ε): 244 (4.57), 262 (4.54), 360 (4.28), and 446 (3.84). IR spectrum, cm⁻¹: 3070 vw, 3035 vw, 2912 w, 2870 w, 2818 w (N-CH₃), 1612 vs, 1540 sh, 1519 s (C=C_{arom}), and 1453 m (δ_{as} CH₃), 1366 m (δ_{s} CH₃), 1268 s (N-O), 1183 s (C-O), 948 s, 813 s, and 738 s. Found: N 12.8%. C₂₁H₁₉N₃O. Calculated: N 12.8%.

<u>N-(3-Methyl-2-aza-9-fluorenylidene)-p-dimethylaniline (IX)</u>. A mixture of 8 g (0.024 mole) of VIII, 15 g of zinc dust, and 200 ml of ethanol was stirred and refluxed for 11 h, after which 0.95 g of crystalline ammonium chloride was added, and the mixture was stirred and refluxed for 3 h (1 h after the addition of the ammonium chloride the dark-red color of the reaction mixture changed to a greenish hue). The zinc dust was removed by filtration and washed with hot alcohol (50 ml), and the filtrate was evaporated to 50 ml and cooled. The resulting black-violet crystals (4.1 g) were dissolved in boiling hexane, and the solution was passed through a column filled with aluminum oxide (elution with hexane) to give 400 ml of eluate, which was evaporated to 100 ml and cooled to give 2.2 g (3%) of IX.

The physical characteristics of Schiff bases III-VII and IX are presented in Table 1.

N-(3-Methyl-2-aza-9-fluorenyl)aniline (X). A solution of 5.4 g (0.02 mole) of azomethine III in 200 ml of dry ether was added with stirring in the course of 2.5 h to a suspension of 6 g (0.16 mole) of lithium aluminum hydride in 200 ml of dry ether, after which the mixture was stirred and refluxed for 6 h. It was then treated successively with 150 ml of ethyl acetate, 150 ml of water, and saturated potassium hydroxide solution until it was strongly alkaline. The ether-extracted reaction products were dried with magnesium sulfate, and the residue (5 g) remaining after removal of the ether by distillation was washed with ether and recrystallized from 200 ml of ligroin to give 1 g (18%) of yellowish-green needles of X with mp 168-170° and Rf 0.6. IR spectrum, cm⁻¹: 3298 m (N-H), 3028 vs (C-H_{arom}), 1603 vs. 1568 m and 1560 s (C=C_{arom}), 1525 s (δ N-H), 1452 m (δ_{as} CH_a), 1323 m, 870 m, 773-m, and 695 s (monosubstituted benzene ring), and 753 vs (δ, four adjacent C-H aromatic bonds of the azafluorene system). Found: C 83.8; H 5.9; N 10.0%, M 272 (mass spectrum). C₁₉H₁₆N₂. Calculated: C 83.8); H 5.9; N 10.3%; M 272. The picrate of X had mp 198-199° (from alcohol). Found: N 13.7%. C₁₉H₁₆N₂·C₉H₉O₇. Calculated: N 13.9%.

The ether solution yielded 3.4 gof a mixture of III and X (R_f 0.7 and 0.6).

 $\frac{N-Pheny1-N-(3-methy1-2-aza-9-fluoreny1)acetamide (XI). A mixture of 0.35 g (1.2 mmole)}{and 9.9 g (0.09 mole) of acetic anhydride was refluxed for 5 h, after which the excess$

anhydride was removed by distillation, 20 ml of water was added, and the mixture was saturated with sodium carbonate. The reaction products were extracted with ether, the extracts were dried with magnesium sulfate, and the solvent was removed by distillation. Crystallization of the residue from hexane gave 0.2 g (50%) of amide XI as pale rose granular crystals with mp 114.5-130° and R_f 0.75. IR spectrum, cm⁻¹: 3015 w (C-H_{arom}), 2978 w, 2938 w and 2885 w (ν of CH bonds of the CH₃ group), 1722 m (C = 0),1602 m and 1542 s (C=C_{arom}), 1465 m (δ_{as} CH₃), 1365 m (δ_{s} CH₃), and 682 s (monosubstituted benzene ring). Found: N 8.7%. C₂₁H₁₈N₂O. Calculated: N 8.9%.

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF SOME

SUBSTITUTED 1, 3-DIARYLBENZO[f]QUINOLINES

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Amino derivatives of 1,3-diarylbenzo[f]quinoline were synthesized and subjected to reaction with methyl vinyl ketone in the presence of catalytic amounts of concentrated HCl to give the corresponding (3'-oxobutyl)aminophenyl derivatives. The electronic absorption and fluorescence spectra were studied, and the absolute fluorescence quantum yields of the synthesized compounds were determined. A relationship between the position and intensity of the absorption bands and the electron-donor substituents was uncovered, and a substantial effect of the nature of the solvent on the fluorescent spectra was established.

The available data on the luminescence properties of benzo[f]quinoline and its derivatives are limited [1, 2]. In the present paper we describe the synthesis and electronicabsorption and emission spectra of some amines and amino ketones of 1,3-diarylbenzo[f]quinoline (V-XII) (Table 1). Amines V-VIII were obtained by reduction of the corresponding nitro $derivatives (I-IV), which were synthesized by catalytic condensation of arylidene-<math>\beta$ -naphthylamines with aliphatic-aromatic ketones [3, 4]. Amino ketones IX-XII were obtained by reaction of amines V-VIII with methyl vinyl ketone in the presence of a catalyst.



Institute of Physical-Organic Chemistry, Academy of Sciences of the Belorussian SSR. Institute of Physics, Academy of Sciences of the Belorussian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 116-120, January, 1976. Original article submitted February 10, 1975.

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UDC 547.832:0.7:535.372