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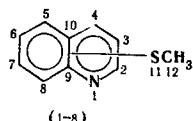
¹³C NMR SPECTRA OF S-METHYLQUINOLINES

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UDC 543.422.25:547.831.78

The ¹³C chemical shifts and the increments ($\Delta\delta$) of the SCH_3 group in the NMR spectra of S-methylquinolines were measured. It is shown that the chemical shifts of S-methylquinolines correlate satisfactorily with the total charges on the carbon atoms calculated within the CNDO/2 approximation. The coupling of the SCH_3 group with the quinoline ring was examined on the basis of the $\Delta\delta$ values.

In the present research we examined the ¹³C NMR spectra of quinoline (1), 2-methylthio- (2), 3-methylthio- (3), 4-methylthio- (4), 5-methylthio- (5), 6-methylthio- (6), 7-methylthio- (7), and 8-methylthioquinoline (8) in order to ascertain the electronic structures of these compounds, the nature of the coupling of the SCH_3 group with the quinoline ring, and the effect of this group on the chemical shifts of the ring carbon atoms.



The literature contains very little information regarding the ¹³C chemical shifts of quinoline derivatives, viz., communications dealing with the spectra of quinoline [1-7], 5-aminoquinoline [3], methylquinolines [5, 8, 9], 8-hydroxyquinoline [10], and 6-methoxy-quinoline [8]. The effect of the SCH_3 group on the ¹³C chemical shifts of aromatic compounds has been studied for thioanisole [11, 12] and S-methyl derivatives of purine [13]. The literature data show that the $\Delta\delta_R$ ¹³C substituent increments measured in the spectra of monosubstituted benzenes can be applied to polycyclic aromatic derivatives with a great deal of caution [3, 4, 14].

The ¹³C NMR spectra with decoupling of the protons and without it (with the Overhauser nuclear effect) and the spectra with extraresonance suppression of the ¹³C-¹H spin-spin coupling (SSC) were obtained for 1-8 (Fig. 1). The parameters of the signals in the ¹³C NMR spectra of 1-8, for the assignment of which we used the increments of the SCH_3 group in thioanisole and the ¹³C-¹H spin-spin coupling constants (SSCC), are presented in Tables 1-3.

In the literature the ¹³C chemical shifts are often correlated with the chemical shifts calculated within the CNDO/2 approximation [1, 15, 16]. Good correlation is observed for this approach only for the carbon atoms of the aromatic ring that are bonded to hydrogen atoms. The chemical shifts are much too high for the nodal and α -carbon atoms [1]. In this connection, the discussion of the ¹³C chemical shifts and their changes of the spectra in 2-8 (relative to 1) was carried out on the basis of the total charges q calculated within the CNDO/2 approximation.

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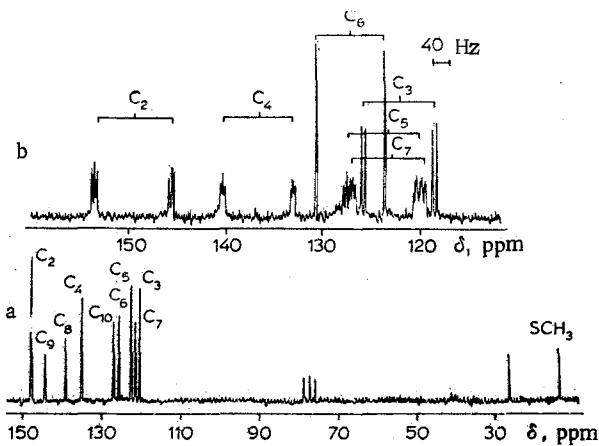


Fig. 1. ^{13}C NMR spectra of 8-methylthio-quinoline: a) with noise decoupling of the protons, b) without decoupling of the protons.

It follows from the dependence of $\delta^{13}\text{C}$ on q presented in Fig. 2 that the ^{13}C chemical shifts in the spectra of 1-8 are satisfactorily described by the total charges on the carbon atoms:

$$\delta^{13}\text{C} = 207.2q + 128.5 \quad (r=0.96),$$

whereas the sensitivity of the chemical shifts to a change in the charge, viz., $\Delta\delta/\Delta q = 207.2$ ppm/electron, is close to the value obtained for aromatic hydrocarbons [17].

The changes in the chemical shifts of the α -carbon atoms as a result of replacement of the protons of 1 by an SCH_3 group are comparable to those observed for thioanisole ($\Delta\delta_\alpha = 9.9$ ppm) and, depending on the site of ring substitution, range from 9.1 to 12.0 ppm (Table 4).

The decrease in $\Delta\delta_\alpha$ in the case of 5 as compared with, for example, the $\Delta\delta_\alpha$ value observed for 6 is evidently associated with the steric strain in the molecule. The latter in the case of 5 also leads to a strong-field shift of the C_4 signal relative to 1 (the γ effect of the substituent). However, differences of this type in the $\Delta\delta_\alpha$ values are not observed in the case of a similar comparison of compounds that are substituted in the pyridine ring (4 and 3) (Table 4). The $\Delta\delta_\alpha$ ratio in the latter case is close, e.g., to that observed for 3- and 4-methoxypyridines, in which such steric hindrance is absent [18]. The $\Delta\delta_\alpha$ values are also reduced appreciably in the spectrum of 5 as compared with 4 (and also with 3, 6, and 7, in which steric hindrance is known to be absent), whereas the $\Delta\delta_p$ values are smaller than the value in the spectrum of the 8 molecule (a comparison with the $\Delta\delta_p$ values in the spectra of the 3, 6, and 7 molecules is impossible, since the para carbon atoms are nodal atoms, the $\Delta\delta$ and Δq values of which are less sensitive to exocyclic substitution, whereas a nitrogen atom occupies the para position in 4). These differences in the increment in the spectra of the 4 and 5 molecules are evidently due to the fact that in the latter molecule the steric hindrance leads to weakening of the conjugation of the SCH_3 group with the ring (a similar effect is observed in 5-amino quinoline [3]). It may be assumed that the C-S bond in 4 is stronger than the C-S bond in 5, i.e., the contribution of structure I is greater than that of II in the ground states of these molecules. The latter is in agreement, e.g., with the increase in the basic properties of 4 ($\text{pK}_{\text{NH}^+} = 5.81$) relative to 5 ($\text{pK}_{\text{NH}^+} = 4.50$). This is evidently the reason for the higher sensitivity of the SCH_3 group in 5 to distortions in the sterically strained fragment of the molecule. The observed large γ effect of the substituent in 4 (Table 1) is also in agreement with this.

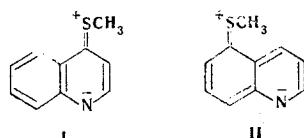


TABLE 1. Total Charges (q) and π Charges (q^π) on the Atoms and ^{13}C Chemical Shifts (δ^* , ppm) in Compounds 1-8

Atom No.	Compound 1						Compound 2						Compound 3						Compound 4					
	q	q^π	6	δ^\dagger	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6					
2	0,099	0,046	150,7	150,2	0,155	0,078	160,4	0,076	0,010	150,1	0,112	0,069	149,8											
3	-0,026	-0,029	121,6	120,9	-0,049	-0,064	121,1	0,035	0,005	133,3	-0,065	-0,086	115,1											
4	0,034	0,048	136,4	135,7	0,046	0,066	135,5	0,007	-0,012	131,2	0,092	0,079	147,6											
5	-0,001	-0,002	128,4	127,6	0,005	0,005	128,1	-0,008	-0,014	127,1	0,002	0,003	123,8											
6	0,002	-0,004	127,0	126,4	-0,005	0,016	125,6	0,007	0,003	127,5	-0,003	-0,012	126,5											
7	0,017	0,013	129,9	129,2	0,021	0,019	130,1	0,008	-0,002	128,9	0,020	0,018	130,0											
8	-0,022	-0,016	129,9	129,4	-0,028	-0,025	128,5	-0,016	-0,007	129,7	-0,026	-0,020	130,4											
9	0,101	0,024	148,8	148,3	0,109	0,044	148,9	0,086	-0,002	146,2	0,109	0,041	149,0											
10	0,012	-0,002	128,8	128,2	-0,002	-0,022	126,3	0,023	0,016	128,7	-0,011	-0,033	126,5											
11	-0,162	-0,078			-0,204	-0,152		-0,150	-0,053		-0,187	-0,126												
12					-0,026	-0,085		-0,025	-0,072		-0,011	0,084							14,1					
							13,3				15,9													
Atom No.	Compound 5						Compound 6						Compound 7						Compound 8					
	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6	q	q^π	6			
2	0,102	0,052	151,1	151,3	-0,092	0,034	149,8	0,104	0,054	151,2	0,094	0,038	149,4											
3	-0,031	-0,038	121,3	133,0	-0,021	-0,021	122,1	-0,035	-0,043	120,7	-0,022	-0,022	122,2											
4	0,037	0,053	133,0	133,0	0,027	0,037	135,0	0,040	0,056	136,1	0,030	0,042	136,7											
5	0,060	0,033	137,5	137,5	-0,044	-0,066	122,7	0,012	0,019	128,2	-0,023	-0,040	123,9											
6	-0,040	-0,066	124,5	124,5	0,062	0,026	138,1	-0,023	-0,036	126,4	0,015	0,016	127,2											
7	0,030	0,033	129,7	129,7	-0,004	-0,018	129,2	0,077	0,044	141,9	-0,023	-0,050	123,2											
8	-0,044	-0,052	127,7	127,7	-0,021	0,003	130,1	-0,061	-0,079	123,8	0,042	0,020	140,6											
9	0,110	0,038	149,0	149,0	0,088	0,004	146,9	0,111	0,041	149,4	0,081	0,006	145,8											
10	-0,009	-0,030	127,7	127,7	0,021	0,014	129,2	-0,002	-0,002	126,4	0,022	0,011	128,5											
11	1	-0,167	-0,086	-0,158	-0,069	-0,023	0,073	-0,020	-0,094	-0,171	-0,159	-0,070												
12		-0,018	0,078	16,7						15,9		0,075										14,6		

*Relative to tetramethylsilane.

†Data from [5] (50% solutions in CDCl_3).

TABLE 2. $^{13}\text{C}-\text{H}$ Spin-Spin Coupling Constants in the Spectra of 1-8

Com- ound	SSCC ^1J , Hz						
	C ₂ H ₂	C ₃ H ₃	C ₄ H ₄	C ₅ H ₅	C ₆ H ₆	C ₇ H ₇	C ₈ H ₈
1	175,4	163,6	160,8	159,4	160,0	161,4	161,0
1*	178,0	165,0	162,0	160,0	161,0	162,0	161,0
2		165,2	161,6	159,8	160,4	159,6	162,0
3	180,7		161,2	161,0	161,2	159,4	162,7
4	175,8	163,2		159,4	160,0	159,1	161,0
5	178,2	164,2	161,8		163,6	161,8	164,4
6	176,8	164,3	161,3	161,4		161,0	162,8
7	175,3	163,5	161,4	160,4	160,7		162,1
8	178,8	165,1	162,0	162,0	161,6	161,2	

*Data from [5].

TABLE 3. Long-Range $^{13}\text{C}-\text{H}$ Spin-Spin Coupling Constants in the Spectra of 1-8

Com- ound	SSCC, J, Hz									
	$^2J_{\text{C}2\text{H}3}$	$^3J_{\text{C}2\text{H}7}$	$^2J_{\text{C}3\text{H}2}$	$^3J_{\text{C}4\text{H}2}$	$^3J_{\text{C}4\text{H}5}$	$^3J_{\text{C}5\text{H}4}$	$^3J_{\text{C}5\text{H}7}$	$^3J_{\text{C}6\text{H}8}$	$^3J_{\text{C}7\text{H}5}$	$^3J_{\text{C}8\text{H}6}$
1	3,8	8,1	9,0	5,6	5,6	5,2	6,8	8,6	8,8	6,9
1*	3,7	7,9	9,6	5,4	5,4	5,2	7,3	8,6	8,9	6,6
2	—	—	—	—	4,4	4,8	7,0	8,4	8,4	6,6
3	—	6,2	—	4,8	4,8	5,0	7,6	8,5	8,4	6,4
4	2,3	—	9,8	—	—	—	7,5	8,6	8,6	6,2
5	3,6	8,1	9,4	5,6	—	—	—	8,4	6,8	6,8
6	3,7	8,0	9,1	5,5	5,5	5,6	5,6	—	7,3	—
7	4,0	7,8	9,1	5,5	5,5	5,2	—	7,3	—	5,1
8	3,7	9,2	9,2	5,4	5,4	4,8	7,0	—	7,7	—

*Data from [5].

TABLE 4. Increments of the SCH_3 Group in the Spectra of Compounds 2-8

Com- ound	$\Delta\delta_\alpha$	$\Delta\delta_\alpha'$	$\Delta\delta_\alpha''$	$\Delta\delta_m'$	$\Delta\delta_m''$	$\Delta\delta_p$
2	9,7		-0,5	-0,9	0,1	-2,5
3	11,7	-5,2	-0,6	-0,9	-0,1	-2,6
4	11,2	-6,5	-2,3	-0,9	0,2	
5	9,1	-2,5	-1,1	-0,2	0,2	-2,2
6	11,1	-5,7	-0,7	0,2	0,4	-1,9
7	12,0	-6,1	-0,6	-0,2	0,6	-2,4
8	10,7	-6,7	-3,0	-0,3	0,2	-4,5

In this case of 8, in which one may also assume the presence of steric strain, it may be assumed on the basis of a comparison of the increments of the SCH_3 group that steric hindrance on the part of the unshared electron pair of the nitrogen atom does not have a substantial effect on the conjugation of the SCH_3 group with the ring. This may be associated with the fact that only the readily polarizable electron cloud of the unshared pair evidently undergoes deformation under the influence of electrostatic repulsion. The certain decrease in the $\Delta\delta_\alpha$ value of the SCH_3 group in the 8 molecule is associated with polarization of the C-S bond as a consequence of an electron-electron interaction.

The $\Delta\delta_\alpha$ value in the spectrum of 2 is smaller than the $\Delta\delta_\alpha$ values in the spectra of 3, 4, 6, 7, and 8 and differs little from the $\Delta\delta_\alpha$ value in the spectrum of 5, although steric strain is absent in this part of the molecule. In the case of substituted diazines and 2-substituted pyridines, e.g., it is assumed that the decrease in the $\Delta\delta_\alpha$ value of the substituent (relative to substituted benzenes) is due to the competitive effect of the nitrogen atom [19]. However, according to the results of the calculation of the quinolines that we studied, it may be assumed that this effect is due to partial compensation of

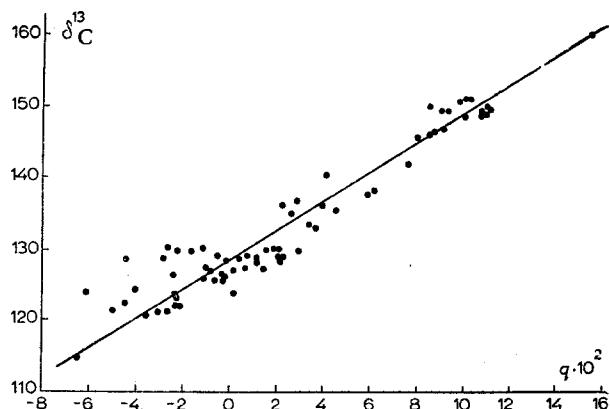


Fig. 2. Dependence of the $\delta^{13}\text{C}$ values of methylthioquinolines on the total charge q on the ring carbon atoms.

the positive charge on the C_2 atom as a consequence of withdrawal of the σ electrons from the closely located nitrogen atom (the $-I$ effect of the sulfur atom). This effect masks the effect of the SCH_3 group on the chemical shift of the C_2 atom in 2. The σ charge on the nitrogen atom also decreases in the 4 molecule but to a lesser extent. The C_4 atom is farther away from the nitrogen atom than the C_2 atom, as a consequence of which the influence of this effect on the $\Delta\delta_\alpha$ value of the SCH_3 group in the 4 molecule is substantially smaller.

The chemical shift of the carbon atom of the SCH_3 group changes ($\Delta\delta_{\text{SCH}_3}$) as a function of the substitution in the quinoline ring. The signal of the carbon atom of the SCH_3 group in 5, in which, according to the substituent increments, the coupling of the SCH_3 group with the ring is disrupted, is observed at weakest field. The signal of the SCH_3 group of 4 is shifted to strong field relative to the signal of this group in 5. The latter is in good agreement with the assumption of the smaller effect of the steric strain on the coupling of the SCH_3 group with the aromatic ring in the 4 molecule. The C_4 atom is also deshielded substantially in the latter (the $-I$ effect of the sulfur atom) and, correspondingly, the carbon atom of the SCH_3 group is deshielded to a lesser extent relative to 5.

The decrease in the charge of the nitrogen atom under the influence of the $-I$ effect of the SCH_3 group is evidently the reason for the smaller degree of deshielding of the carbon atom of the SCH_3 group in 2 and 4 as compared with 3, 6, 7, and 8; this is expressed more strongly in the 2 molecule because of the closeness of the nitrogen atom.

The ortho, meta, and para increments ($\Delta\delta_o$, $\Delta\delta_m$, and $\Delta\delta_p$) of the SCH_3 group in 2-8 differ substantially from those in thioanisole. First, the $\Delta\delta_o$ values in the same compound differ markedly in magnitude. Second, $\Delta\delta_o > \Delta\delta_p$ for the same ortho carbons, whereas $\Delta\delta_o < \Delta\delta_p$ for the others ($\Delta\delta_o < \Delta\delta_p$ in thioanisole). The $\Delta\delta_m$ value of the SCH_3 group is considerably smaller than the $\Delta\delta_o$ values, while their differences in the compounds are not so clearly expressed. The $\Delta\delta_p$ value of the SCH_3 group in 4 and the $\Delta\delta_o$ value of the SCH_3 group in 2 remain undetermined (the chemical shift of the nitrogen atom was not measured). Only $\Delta\delta_o''$ of the SCH_3 group appears in the ^{13}C spectrum of 2 and, with allowance for the fact that $\Delta\delta_o'' > \Delta\delta_p$, the nitrogen atom in this compound is assumed to be more shielded as compared with the nitrogen atom in the 4 molecule. The latter is in good agreement with the calculated charge on the nitrogen atom (Table 1).

From a comparison of the $\Delta\delta_o$ values of the SCH_3 group in the 2-8 molecules with the chemical shifts of the corresponding carbon atoms of 1 it may be noted that in the case of exocyclic substitution precisely the ortho carbon atom whose signal, in the case of the 1 molecule, is found at stronger field (the 7 molecule constitutes an exception) undergoes the strongest-field shift. This sort of effect of the substituent on the ^{13}C chemical shift of 1 is also observed in the case of 5-amino- and 6-methoxyquinoline [3, 8].

To explain the observed differences in the ortho increments of the SCH_3 group in 2-8 we compared them with the Δq values on the carbon atoms. The $\Delta\delta_o$ value and the corresponding increase in the negative charge Δq are greater in the case of that o-carbon atom which has

*The ortho increments will subsequently be designated as $\Delta\delta_o'$ and $\Delta\delta_o''$ respectively.

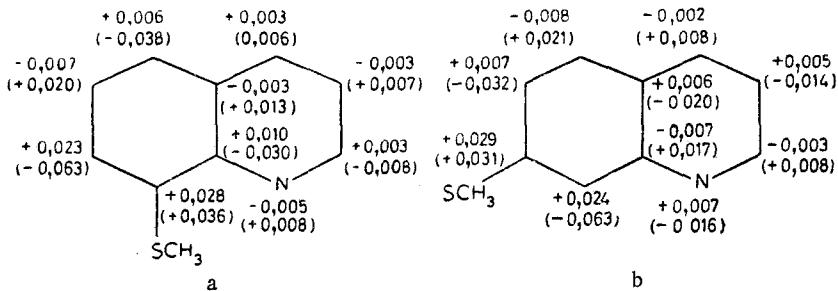


Fig. 3. Changes in the $\sigma(\pi)$ -electron density of quinoline in the case of substitution by the SCH_3 group in the 8 (a) and 7 (b) positions.

the highest negative charge in the case of 1. According to the changes in the σ - and π -electron densities in the 1 molecule in the case of exocyclic substitution (Fig. 3a for 8), Δq^π makes the most substantial contribution to Δq ($\Delta\delta$). In the case of substitution this value is determined to a first approximation by polarization of the σ skeleton of 1 (the $-I$ effect of the SCH_3 group). With respect to the σ system, those σ -carbon atoms on which the σ -charge in the 1 molecule is higher are deshielded more markedly and, as a consequence of the corresponding polarization of the π -electron cloud, these carbon atoms are shielded to a greater degree.

We noted above that in the case of 7 the $\Delta\delta_0'$ value of the SCH_3 group was assigned to the $\sigma\text{-C}_8$ atom, the signal of which in the ^{13}C spectrum of 1 is found at weaker field as compared with the signal of the $\sigma\text{-C}_6$ atom (Tables 1 and 3). However, according to the results of the calculation, the C_8 atom in the 1 molecule is shielded to a greater extent than the C_6 atom (Table 1). The $\Delta\delta_0$ and Δq values are in good agreement with the latter (the Δq^π and Δq^σ values are presented in Fig. 3b).

EXPERIMENTAL

The ^{13}C NMR spectra of 20% solutions of the compounds in CDCl_3 containing cyclohexane (as the internal standard) at room temperature were obtained with a Brucker WH-90 spectrometer (22.63 MHz). The spectra were recorded under pulse conditions with a pulse length of 5 μsec . The error in the shift on the δ scale from tetramethylsilane (in the case of a computer memory of 4 kilobytes and a 6000 Hz degree of sweep) was ± 0.1 ppm. The spin-spin coupling constants were measured in the spectra with a degree of sweep of 1200 Hz, the error in the determination was ± 0.1 Hz..

The methylthioquinolines were synthesized by the method described in [20].

The authors thank E. E. Liepin' for his discussion of the results.

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RESEARCH ON PHENANTHRIDONE AND TETRAHYDRODIAZAPYRENE.

2.* SYNTHESIS OF 2,7-DIAMINO-5,10-DIOXO-4,5,9,10-

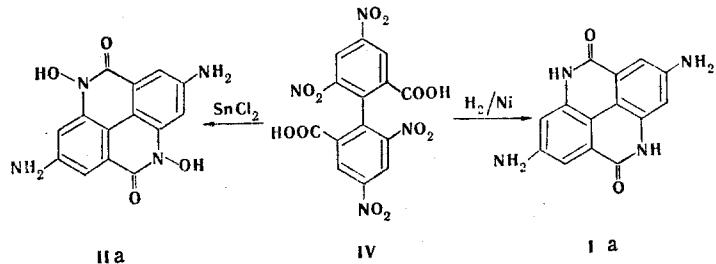
TETRAHYDRO-4,9-DIAZAPYRENE AND ITS DERIVATIVES

G. I. Migachev, A. M. Terent'ev,
and V. I. Lisoded

UDC 547.677+547.624

The synthesis of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (Ia) and its 4,9-dihydroxy derivative (IIa) from diphenic acid (III) is described. 4,4',6,6'-Tetranitrodiphenic acid (IV) was obtained by nitration of III. Reduction of IV with iron or with hydrogen over Raney nickel gave Ia, while reduction with stannous chloride gave IIa. Diacetyl and tetraacetyl derivatives of Ia and IIa were obtained. The amino groups in Ia and IIa were replaced by H, Cl, Br, I, CN, NO₂, and OH through diazotization. It is shown that II and its derivatives can be reduced with iron or with hydrogen over a nickel catalyst to compounds of the 5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene series.

The synthesis of 2,7-diamino-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (Ia) and its 4,9-dihydroxy derivative (IIa) from diphenic acid (III) is proposed in the present paper. Treatment of acid III with a nitrating mixture gave 4,4',6,6'-tetranitrodiphenic acid (IV) in up to 90% yield; acid IV was previously obtained by the Ullmann reaction [1] or through nitro-substituted phenanthrenequinones [2]. The reduction of tetranitro compound IV with stannous chloride was described in [3]. The Ia structure was erroneously assigned to the reaction product. In a preliminary communication [4] we demonstrated that the structure of the product of the reduction of IV with stannous chloride is described by structural formula IIa.



When diamine IIa is heated with acetic anhydride, it undergoes both N acylation and O acylation to give 2,7-diacetamido-4,9-diacetoxy-5,10-dioxo-4,5,9,10-tetrahydro-4,9-diazapyprene (V). A solution of diamine IIa in dimethylformamide (DMF) takes on the intensely red coloration that is characteristic for N(OH) groups in the ortho position relative to a carbonyl group [5] when trivalent iron salts are added. The deamination of diamine IIa through diazotization and subsequent reduction gives IIb, the IR spectrum of which is identical to the spectrum of the compound obtained by the reduction of 6,6'-dinitrodiphenic acid with zinc in a neutral medium [6]. Compound IIa cannot be reduced further even with excess stannous chloride.

*See [4] for communication 1.

Scientific-Research Institute of Plastics, Moscow 111112. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 12, pp. 1672-1677, December, 1979. Original article submitted August 31, 1978; revision submitted June 27, 1979.