was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.6 g (85%) of VI, which was crystallized from dichloroethane and sublimed at 188-190°C to give a product with R_f 0.8 (system A). Found: Cl 30.2; N 10.6%. $C_6Cl_2N_2O_2S$. Calculated: Cl 30.2; N 10.9%.

B) A 0.2-g (1.6 mmole) sample of iodine was added to a solution of 0.25 g (1.1 mmole) of VII in 5 ml of glacial acetic acid heated to 90°C, and bubbling of chlorine into the mixture was begun immediately. Bubbling of chlorine through the refluxing mixture was continued for 1 h, after which the mixture was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.23 g (65%) of VI, which was crystallized from dichloroethane and sublimed at 189-190°C. The R_f value of 0.8 (system A) was in agreement with the R_f value of VI obtained by method A.

5,6-Dichloro-4,7-dihydroxybenzo-2,1,3-thiadiazole (VIII). A) Sulfur dioxide was bubbled into a mixture of 0.71 g (3 mmole) of thiadiazole VI in 7 ml of methanol and 1.5 ml of water heated to the boiling point for 30 min, after which the mixture was cooled and treated with 10 ml of water. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.6 g (84%) of VIII with mp 245-247°C and R_f 0.48 (system A). Found: N 11.3; S 13.1%. $C_6H_2Cl_2N_2O_2S$. Calculated: N 11.8; S 13.5%.

B) A solution of 1.7 g (10 mmole) of sodium hydrosulfite in 17 ml of water was added to a hot solution of 0.41 g (1.7 mmole) of thiadiazole VI in 12 ml of ethylene glycol and 3 ml of ethyl acetate, and the mixture was stirred for 3 min. It was then cooled and extracted with chloroform. The chloroform extracts were filtered, and the solvent was removed to give 0.22 g (53%) of VIII with mp 245-247°C. The R_f value of 0.48 (system A) was in agreement with the R_f value of VIII obtained by method A.

LITERATURE CITED

1. V. G. Pesin and I. A. Belen'kaya-Lotsmanenko, Khim. Geterotsikl. Soedin., No. 3, 354 (1965).
2. I. A. Belen'kaya, N. S. Tsepova, Ya. L. Kostyukovskii, and V. G. Pesin, Khim. Geterotsikl. Soedin., No. 7, 926 (1973).

INVESTIGATION OF THE STRUCTURE OF SUBSTITUTED 3H,6H-6-SILA-3-AZAACEANTHRYLENES BY PMR SPECTROSCOPY

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The structure of substituted 3H,6H-6-sila-3-azaaceanthrylenes was confirmed as a result of an analysis of the PMR spectra and by the spectra at 360 MHz. Computer analysis of the ABCD spectrum of the phenylene protons demonstrated the characteristic nature of the spin—spin coupling constants (SSCC) in the indicated series.

The preparation of compounds that belong to the previously unknown heterocyclic system of one of the isomeric dihydrosilaazaaceanthrylenes, the molecules of which contain a 1H-pyridine (pseudoazulene) fragment, was described in [1, 2]. In the present paper we present a detailed analysis of the PMR spectra in order to confirm the structure of the following compounds of this series: 3H,6H-6,6-dimethyl-3-benzyl-1,2-dicarbomethoxy-, 3H,6H-6,6-dimethyl-3-benzyl-2-cyano-, 3H,6H-3,6,6-trimethyl-2-cyano-, and -1,2-dicarbomethoxy-6-sila-3-azaaceanthrylenes (I-IV):

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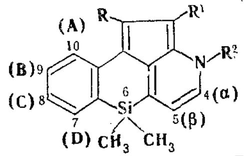
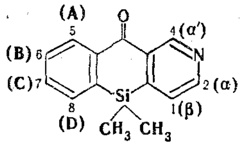


I $R=R^1=COOCH_3$, $R^2=CH_2C_6H_5$; II $R=H$, $R^1=CN$, $R^2=CH_2C_6H_5$; III $R=H$, $R^1=CN$, $R^2=CH_3$; IV $R=R^1=COOH_3$, $R^2=CH_3$

The PMR spectra of I-IV in the weak-field region of the aromatic protons at 80 MHz proved to be complex, so that we were unable to make a complete assignment of the lines. Special difficulties arose in the case of I and II, which contain an N-benzyl substituent.

The chief problem was the isolation and analysis of the complex spectrum of the ABCD type of the 7-H, 8-H, 9-H, and 10-H phenylene protons in all four compounds. We obtained a first approximation for the spin–spin coupling constants (SSCC) of these protons from an analysis of the PMR spectrum of 9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthrone (V), which was selected as a model compound. The results of a calculation of the spectrum of silaazaanthrone V at 80 MHz by means of the ITRCAL program are presented in Fig. 1. Preliminary assignment of the signals was made by comparing the spectra obtained in various solvents ($CDCl_3$, C_6D_6, d_6-acetone, CD_3OD, and d_6-DMSO).



The shift in the A multiplet, which reaches 0.4 ppm on passing from $CDCl_3$ to d_6-DMSO and is synchronous with the shift of the signals from the 4-H proton, made it possible to assign this multiplet to the phenylene ring 5-H proton attached to the carbon atom adjacent to the carbonyl group. The assignment of the chemical shifts of the remaining protons after this, was established automatically by computer analysis of the spectrum of the phenylene protons according to the ABCD type (Fig. 1). During this analysis we uncovered the signals of the 1-H proton of the pyridine ring that lie in the same region; this proton, in addition to J_{ortho}= 4.8 Hz, displays a relatively large J_{para} value of 1.0 Hz (Fig. 1). The results of further analysis of the spectra of I-IV showed that for the phenylene protons the set of SSCC is extremely characteristic in the spectra of all five compounds (Table 1), and the J values of the phenylene protons of silaazaanthrone V therefore served as a basis for the assignment of the chemical shifts and computer analysis of the spectra of silaazaaceanthrylenes I-IV. The very weak (as compared with the A proton) change in the chemical shift of the D proton that is observed upon examination of the calculated shifts (Table 2) on passing from I to IV is an additional confirmation of the correctness of the assignment. This also had to be expected for the proton that is most remote from the labile pseudoazulene fragment of I-IV.

In the case of benzyl derivatives I and II superimposition of the spectrum of the phenyl protons of the N substituent on the spectrum of the phenylene protons (Fig. 2a) made analysis of the 80 MHz spectrum virtually impossible, and the spectra of I and II were therefore recorded at a working frequency of 360 MHz (Fig. 2b). However, in the case of I it is apparent that even this did not lead to a first-order spectrum, and computer analysis of the spectrum is also necessary. Measurement of the J values from the corresponding splittings here would also result in substantial errors. It should be noted that the strong spin–spin coupling in the spectrum of the phenylene protons of I was also retained at 360 MHz except at the expense of partial overlapping of the multiplets of the A and D protons, despite the fact that J_{AD} is only 0.6 Hz when $\Delta\nu_{AD}$ = 5.2 Hz (formally, $J/\Delta\nu$ 0.12!).

Isomeric (with respect to the position of the nitrile group) dihydrosilaazaaceanthrylenes could have been formed in the synthesis of II and III. However, experimentally in both cases we isolated only one isomer; this was confirmed by data from thin-layer chromatography (TLC) and the PMR spectra, in which only one signal from the proton of the five-membered ring in both II and III is observed. Considering the polarization of the double bond in acrylonitrile, the formation of a dihydrosilaazaaceanthrylene with a nitrile group in the 2 position should be considered to be preferable, and we therefore assigned precisely this structure to the isolated isomers. From the double-resonance spectra at 360 MHz we were able to show that the splitting of the signals from the 1-H proton observed in the spectra of II and III is associated with long-range spin–spin coupling with the 4-H proton ($^6J_{HCCCNCH}$ = 0.4 Hz), whereas

TABLE 1. Spin–Spin Coupling Constants (SSCC) of the Phenylene Protons

Compound	J of the phenylene protons, Hz						Root-mean-square (rms) deviation, ITRCAL	Other J, Hz
	AB	AC	AD	BC	BD	CD		
I	8,19	1,03	0,63	7,29	1,60	7,22	0,07	$^3J_{\alpha\beta}=5{,}9,\ ^4J\,(H_\alpha,\ CH_2)=0{,}4$
II	8,01	1,06	0,70	7,49	1,49	7,47	0,02[a]	$^3J_{\alpha\beta}=5{,}8,\ ^4J\,(H_\alpha,\ CH_2)\approx{}^6J_{\alpha,\ H_1}=0{,}4$
III	7,93	1,21	0,57	7,21	1,52	7,28	0,07	$^3J_{\alpha\beta}=5{,}7,\ ^4J\,(H_\alpha,\ CH_3)\simeq{}^6J_{\alpha,\ H_1}=0{,}4$
IV	8,09	0,92	0,59	7,31	1,59	7,38	0,09	$^3J_{\alpha\beta}=5{,}9,\ ^4J\,(H_\alpha,\ CH_3)=0{,}5$
V	8,29	1,28	0,62	7,29	1,43	7,27	0,07	$^3J_{\alpha\beta}=4{,}7,\ ^5J_{\beta\alpha'}=1{,}0$

[a] In this case, because of overlapping of the signals, a smaller (than in the case of I and III-V) number of lines was assigned, and the sharp decrease in the rms deviation is associated with the smaller number of degrees of freedom in calculations by the method of least squares, which constitutes the basis of the ITRCAL iteration program.

TABLE 2. Chemical Shifts of the Protons in the Investigated Compounds for Solutions in Deuteroacetone

Compound	Spectrometer	δ, ppm (relative to tetramethylsilane as the internal standard)							
		A	B	C	D	H_α	H_β	$H_{\alpha'}$	$(CH_3)_2$
Ia	WH-360	7,662	7,338	7,143	7,645	8,180	7,381	—	0,492
IIb	WH-360	7,893	7,333	7,097	7,577	8,132	7,358	—	0,503
IIIc	WP-80	7,889	7,339	7,104	7,576	7,950	7,273	—	0,465
IVd	WP-80	7,632	7,285	7,094	7,587	7,987	7,274	—	0,521
V	WP-80	8.376	7,683	7,730	7,900	8,191	7,842	9,402	0,593

[a] δ_{COOCH_3} 3,64, 3,90; δ_{NCH_2} 6,12. [b] δ_{NCH_2} 6,04, $\delta_{1\text{-}H}$ 7,860. [c] δ_{NCH_3} 4,44, $\delta_{1\text{-}H}$ 7,838. [d] δ_{COOCH_3} 3,76, 3,86, δ_{NCH_2} 4,38.

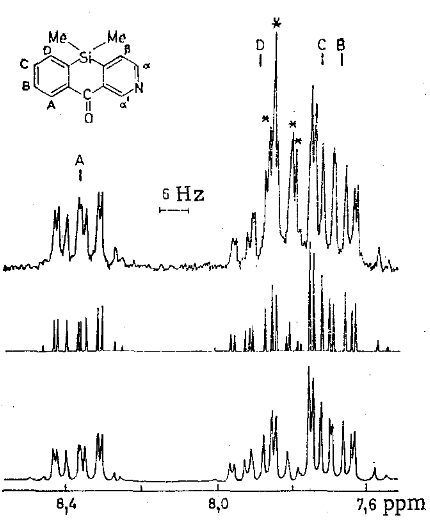


Fig. 1

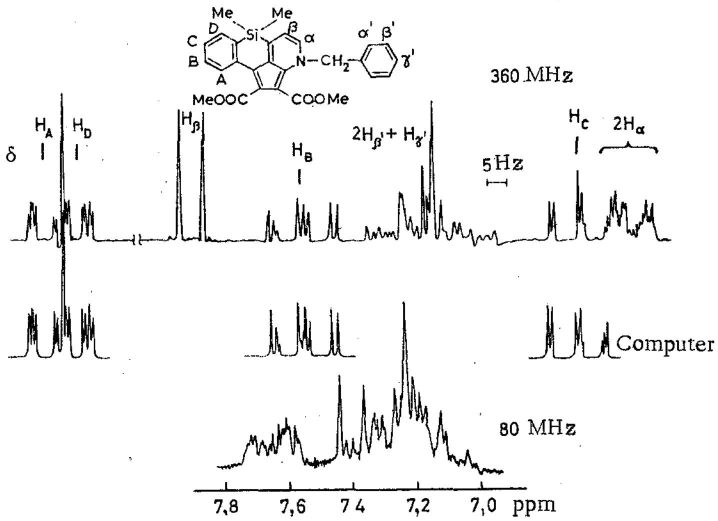


Fig. 2

Fig. 1. Analysis of the ABCD spectrum of the phenylene protons of 9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthrone: the experimental spectrum at 80 MHz is presented at the top, while the theoretical spectra calculated by means of the ITRCAL program (line spectrum and spectrum with a Lorentzian form of the line) are presented below it. The lines from the H_β proton of the pyridine ring are denoted by asterisks.

Fig. 2. Analysis of the PMR spectrum of 3H,6H-6,6-dimethyl-3-benzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrylene: the weak-field section of the spectrum (the doublet from the α proton is not shown) at 80 and 360 MHz, as well as computer calculations for the ABCD system of phenylene ring protons by means of the ITRCAL program.

$^5J_{cis,cis}$ of the 1-H and 10-H protons does not show up in the spectra of II and III, i.e., this constant proves to be less than 0.2 Hz. This situation can be explained within the framework of the known concepts regarding transmission of long-range spin—spin coupling in unsaturated conjugated systems [3].

Thus the results of a detailed analysis of the PMR spectra of I-IV as compared with the spectra of V (Tables 1 and 2) constituted a complete confirmation of the structure of the new heterocyclic system.

EXPERIMENTAL

The PMR spectra were obtained with Bruker Physik WP-80 and WH-360 spectrometers under pulse conditions with Fourier transformation. The conditions for storage of the signals in the computer were selected in such a way as to ensure a resolution of no less than 0.05 Hz. A Lorentz—Gauss filter for contraction of the spectral lines was used prior to Fourier transformation. Iteration analysis of the spectra was carried out by means of the ITRCAL program with a BNC-28X computer equipped with a WP-80 spectrometer.

LITERATURE CITED

1. N. S. Prostakov, A. V. Varlamov, Navin Saksena, and A. A. Fomichev, Khim. Geterotsikl. Soedin., No. 1, 123 (1980).
2. N. S. Prostakov, N. Saxena, A. V. Varlamov, and A. A. Fomichev (Fomichov), J. Organomet. Chem., 218, 17 (1981).
3. H. Günter, NMR Spectroscopy — An Introduction, Wiley, New York (1980), p. 116.

PYRROLES FROM KETOXIMES AND ACETYLENE.

23.* 2-(1-NAPHTHYL)- AND 2-(2-NAPHTHYL)PYRROLES AND THEIR 1-VINYL DERIVATIVES

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2-(1-Naphthyl)- and 2-(2-naphthyl)pyrroles and their 1-vinyl derivatives were synthesized in 22-64% yields by the reaction of 1- and 2-acetylnaphthalene oximes with acetylene at both atmospheric pressure and elevated pressures in an alkali metal hydroxide—dimethyl sulfoxide system.

The available information regarding naphthylpyrroles is limited [2-7], and their 1-vinyl derivatives are not known at all, although they are of great interest as monomers and starting substances for the production of biologically active compounds.

In a systematic study of the reaction of ketoximes with acetylene, which leads to pyrroles and 1-vinylpyrroles [8], we found that it can also be successfully extended to oximes of condensed aromatic ketones such as 1- and 2-acetylnaphthalenes Ia, b.

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*See [1] for communication 22.

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