products were extracted with ether. The residue after driving off the ether from the extract was crystallized. In the IR spectra of the amines (in KBr), bands of stretching vibrations of the bound NH_2 group were observed in the 3200-3450 cm^{-1} region.

LITERATURE CITED

1. C. Eaborn and R. A. Shaw, J. Chem. Soc., 1420 (1955).
2. F. B. Deans and C. Eaborn, J. Chem. Soc., 498 (1957).
3. V. F. Traven', V. B. Knyazhevskaya, M. F. Éismont, A. B. Kudryavtseva, and B. I. Stepanov, Zh. Org. Khim., 51, 99 (1981).
4. N. S. Prostakov, Saksena Navin, A. V. Varlamov, and A. M. Klochkov, Khim. Geterotsik. Soedin., No. 2, 240 (1981).
5. R. A. Benkeser and H. Landesman, J. Am. Chem. Soc., 76, 904 (1954).
6. N. S. Prostakov, A. A. Fomichev, N. I. Golovtsov, A. V. Varlamov, Islam Nazrul, and V. Polosin, Khim. Geterotsikl. Soedin., No. 11, 1532 (1985).
7. V. K. Shevtsov, A. V. Varlamov, Islam Nazrul, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 4, 534 (1985).

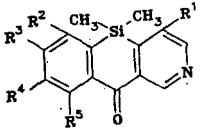
DETERMINATION AND PROOF OF STRUCTURE OF MONOSUBSTITUTED DIHYDROSILAAZANTHRONES ON THE BASIS OF PMR SPECTRA

N. S. Prostakov, A. A. Fomichev,
N. I. Golovtsov, A. V. Varlamov,
Islam Nazrul, and V. M. Polosin

UDC 543.422.25:547.823'819

PMR spectra have been used in establishing the structure of ten bromo-, nitro-, and amino-substituted 10,10-dimethyl-10-sila-2-azaanthrones. Anomalous effects of NO_2 and NH_2 groups adjacent to the carbonyl carbon have been observed and explained; these effects are related to the specific geometry of these molecules.

One of the areas in studying silaazaanthrones that we have synthesized [1] is the determination of relationships in their substitution. The geometry of the planar molecules, which is determined by the substantially different lengths of the C–C and C–Si bonds [2] (Fig. 1), may influence the orientation of substituent entry and the chemical properties of the resulting compounds.



I–XII

I, III–VI, VIII–XII $R^1=H$; II $R^1=NO_2$; VII $R^1=Br$; I, II, IV–VII, IX, XI, XII $R^2=H$; III $R^2=NO_2$; VIII $R^2=Br$; X $R^2=NH_2$; I–III, V–XII $R^3=H$; IV $R^3=NO_2$; I–IV, VI–VIII, X, XII $R^4=H$; V $R^4=NO_2$; IX $R^4=Br$; XI $R^4=NH_2$; I–V, VII–XI $R^5=H$: VI $R^5=NO_2$; XII $R^5=NH_2$

Upon nitration of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene and the corresponding silaazanthrone I in our laboratory, we obtained 10,10-dimethyl-4- (II), -5- (III), -6- (IV), -7- (V), and -8- (VI) -nitro-10-sila-2-azaanthrone. We isolated as the bromine derivatives 10,10-dimethyl-4- (VII), -5- (VIII), and -7- (IX) -bromo-10-sila-2-azaanthrone. The nitro derivatives III, V, and VI were reduced to the corresponding amino derivatives X, XI, and XII.

The position of the substituents in compounds II-XII was determined from an analysis of PMR spectra (Tables 1-3). Any ambiguity in such structural analysis was eliminated by performing a comparative investigation of increments in chemical shift and SSCC in relation

---

P. Lumumba Peoples' Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1532-1535, November, 1985. Original article submitted September 29, 1984.

0009-3122/85/2111-1264 $09.50

TABLE 1. Chemical Shifts of Protons in Monosubstituted Silaazaanthrones (pom, $CDCl_3$, TMS internal standard)

Comp.	Substituent	1-H	3-H	4-H	5-H	6-H	7-H	8-H	$Si(CH_3)_2$	NH_2
I	—	9,53	8,72	7,56	7,69	7,64	7,61	8,42	0,53	—
II	4-NO_2	9,81	9,59	—	7,72	7,70	7,61	8,36	0,67	—
III	5-NO_2	9,50	8,80	7,60	7,60	5,58	7,84	8,87	0,66	—
IV*	6-NO_2	9,53	8,80	7,60	8,53	—	8,39	8,60	0,66	—
V	7-NO_2	9,54	8,82	7,60	7,91	8,42	—	9,19	0,62	—
VI	8-NO_2	9,31	8,79	7,56	7,65	7,72	7,83	—	0,60	—
VII	4-Br	9,48	8,82	—	7,69	7,65	7,60	8,38	0,73	—
VIII	5-Br	9,52	8,80	7,58	—	7,81	7,49	8,48	0,72	—
IX	7-Br	9,52	8,78	7,42	7,44	7,67	—	8,54	0,52	—
X	5-NH_2	9,51	8,78	7,57	—	6,95	7,43	7,97	0,63	3,94
XI	7-NH_2	9,50	8,75	7,55	7,48	6,97	—	7,72	0,47	4,05
XII	8-NH_2	9,51	8,70	7,49	6,89	7,32	6,77	—	0,48	7,35and7,53†

*Parameters were taken from [3].

†Protons of NH_2 give two broad signals.

TABLE 2. Increments of Chemical Shifts of Protons in Substituted Silaazaanthrones

Comp.	1-H	3-H	4-H	5-H	6-H	7-H	8-H	$Si(CH_3)_2$
II	+0,28	+0,87	—	+0,03	+0,06	0	−0,06	+0,14
III	−0,03	+0,08	+0,04	—	+0,94	+0,23	+0,45	+0,13
IV	0	+0,08	+0,04	+0,84	—	+0,78	+0,18	+0,13
V	+0,01	+0,10	+0,04	+0,22	+0,78	—	+0,77	+0,09
VI	−0,22	+0,07	0	−0,04	+0,08	+0,22	—	+0,07
VII	−0,05	+0,10	—	0	+0,01	−0,01	−0,04	+0,20
VIII	+0,01	+0,08	+0,02	—	+0,17	−0,12	+0,06	+0,19
IX	−0,01	+0,01	−0,14	−0,15	+0,02	—	+0,10	−0,01
X	−0,02	+0,06	+0,01	—	−0,69	−0,18	−0,45	+0,1
XI	−0,03	+0,03	−0,01	−0,21	−0,67	—	−0,70	−0,06
XII	−0,02	−0,02	−0,07	−0,8	−0,32	−0,84	—	−0,05

TABLE 3. SSCC J_{HH} in Monosubstituted Silaazaanthrones, Hz

Comp.	1—4	3—4	5—6	5—7	5—8	6—7	6—8	7—8
I	1,0	4,7	7,57	1,14	0,83	7,43	1,29	7,83
II	—	—	7,7	1,3	0,8	7,3	1,0	7,8
III	0,7	4,7	—	—	—	8,3	1,2	7,9
IV	0,9	4,8	—	2,4	0,5	—	—	8,8
V	0,5	4,7	8,0	—	0,40	—	2,5	—
VI	0,7	4,7	7,8	1,6	—	7,2	—	—
VII	—	—	7,46	1,36	0,62	7,19	1,29	8,06
VIII	0,0	4,7	—	—	—	7,9	1,1	8,1
IX	0,0	4,7	7,8	—	0,4	—	2,0	—
X	0,7	5,0	—	—	—	8,0	0,7	8,0
XI	0,7	5,0	8,0	—	0,0	—	2,5	—
XII	1,0	4,8	7,0	1,3	0,0	8,5	—	—

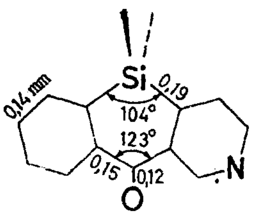


Fig. 1

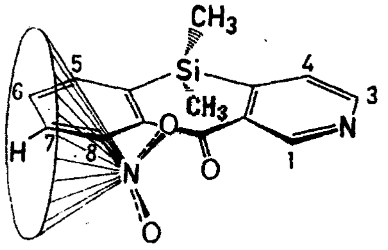


Fig. 2

Fig. 1. Geometry of planar skeleton of dihydrosilaazanthrone, according to x-ray spectrometry [1].

Fig. 2. Nonplanar conformation of nitro group in 8-nitro derivative; the 7-H proton falls into the cone of magnetic sheilding.

to the unsubstituted silaazaanthrone I, and also by using the PMR spectral parameters of the 6-nitro derivative IV that we had found previously [3]. These compounds were used as models in determining the position of the nitro group in the other nitro derivatives. The increments in chemical shift upon substitution in the phenylene ring, as expected, proved to be similar to the corresponding increments for monosubstituted benzenes [4] in all cases other than compounds VI and XII (Table 2). Also identical with the characteristics of substituted benzenes were the changes in SSCC under the influence of the substituents (Table 3). For example, we found increases in $^3J_{HH}$ of the ortho-protons ($J_{6,7}$ in III, VIII, X, and XII, and $J_{7,8}$ in IV, Table 3) and $^4J_{HH}$ of protons separated by a substituted carbon atom ($J_{5,7}$ in IV, and $J_{6,8}$ in V, IX, and XI). According to the PMR spectral data, in the example of the nitro derivative II and the bromo derivative VII (Tables 1-3), we established a case that is rare for such systems, in which the nitro group and the bromine atom are attached to the pyridine ring upon electrophilic substitution.

The 8-substituted silaazaanthrones VI and XII merit special attention; in these compounds, anomalous effects of the substituents are manifested, both in the chemical shifts and in the SSCC (Tables 2 and 3). The source of these anomalies is the closeness of the substitutent in the $C_{(8)}$ position to the carbonyl oxygen, characteristic for silaazaanthrone molecules (Fig. 1). In the case of the 8-nitro derivative VI, this creates a major steric hindrance to the usual, most favorable planar orientation of the nitro group bonded to the aromatic ring. Another important factor here may be electrostatic repulsion of the oxygen atoms of the carbonyl and nitro group. In the nonplanar conformation (Fig. 2), which in this case proves to be the preferred conformation, the influence of the nitro group with respect to the mesomeric mechanism is eliminated; and as a consequence, there is no downfield increment of the chemical shift of the 5-H proton for compound VI (−0.04 ppm, Table 2). The increment of chemical shift of the ortho-proton 7-H in the nitro derivative VI is also very small, 0.22 ppm in contrast to 0.8-9 ppm for the ortho-protons in the 5- and 7-nitro derivatives III and V (Table 2) and nitrobenzenes [5], in spite of the fact that the nonplanar conformation does not eliminate the influence of the nitro group with respect to the inductive mechanism. Such a deshielding effect is apparently compensated to a large degree by the influence of the magnetically anisotropic nitro group (Fig. 2), which gives an upfield contribution to the chemical shift of the 7-H proton in the nonplanar conformation, since this proton falls into the "shielding cone." This effect was examined in detail in the example of ortho-methyl-substituted nitrobenzenes [5], where it was noted that the shielding of the methyl protons increases with increasing angle of rotation of the nitro group relative to the plane of the benzene ring, which was determined independently from UV spectra. The absence of mesomeric interaction of the nitro group with the phenylene ring in the 8-nitro-substituted silaazaanthrone VI is also supported by the unusual change in the SSCC $^3J_{6,7}$ of the protons adjacent to the substituent. This constant proves to be smaller in comparison with its value in the unsubstituted silaazaanthrone I, not larger as is the case in the 5-, 6-, and 7-nitro-substituted compounds III, IV, and V (Table 3) and nitro-substituted benzenes [5]. The smaller value of $J_{6,7}$ in compound VI can be explained only by the inductive effect of the electronegative substituent.

The structural features of the 8-aminosilaazaanthrone XII are reflected in the PMR parameters in a completely different manner. Here, in contrast, the intramolecular hydrogen bond of the amino proton with the carbonyl oxygen fixes the planar conformation of the amino group relative to the aromatic ring, in which mesomeric interaction is facilitated. Hydrogen bond formation is indicated by the anomalously large shift of the amino group protons in compound XII (more than 7 ppm) in comparison with the values for the 5- and 7-substituted compounds (4.05 and 3.94 ppm), and also the broadening and splitting of their signal. The extremely large increment of chemical shift of the para-proton 5-H (−0.08 ppm, Table 2), along with the increment of $^3J_{HH}$ of the ortho-proton 7-H, which is larger than in other amino derivatives or aniline (1.07 Hz as shown in Table 3; 0.48 Hz for aniline [4]), confirms the greater +M effect of the amino group, which can be explained by its planar conformation.

Thus, on the basis of PMR spectra, we have established the positions of the nitro group, the bromine atom, and the amino group in seven monosubstituted 10,10-dimethyl-10-silaazaanthrones, and the nature of the anomalous effects of nitro and amino substituents in the $C_{(8)}$ position has been investigated.

EXPERIMENTAL

The synthesis of compounds II-XII was described in [6]. The PMR spectra of the solutions of these compounds in deuterochloroform were obtained in a WP-80 spectrometer. Calculations of the PMR spectra, according to the ABC and ABCD type, were performed by the use of the ITRCAL program that is available in the software of the BNC-28X minicomputer in combination with a WP-80 Fourier-NMR spectrometer.

LITERATURE CITED

1. Y. A. Sokolova, O. A. D'yachenko, L. O. Atovmyan, N. S. Prostakov, A. V. Varlamov, and N. Saxena, J. Organomet. Chem., 202, 149 (1980).
2. N. S. Prostakov, A. V. Varlamov, I. V. Shendrik, B. N. Anisimov, A. P. Krapivko, S. Lavani-Édogiaverie, and A. A. Fomichev, Khim. Geterotsik. Soedin., No. 10, 1384 (1983).
3. S. Lavani-Édogiaverie, Candidate's Dissertation, Moscow (1982).
4. L. M. Jackman and S. Sternhell, Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, Oxford (1969), p. 456.
5. I. Yamaguchi, J. Mol. Phys., 6, 105 (1963).
6. V. K. Shevtsov, A. V. Varlamov, Islam Nazrul, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 4, 534 (1985).