The production of compounds I-III was described in [1]. 2-Amino-4-thiazolinone hydrochloride was produced by the method of [18].

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MASS SPECTROMETRIC STUDY OF 9-SUBSTITUTED 10-SILA-2-AZAANTHRACENES

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UDC 543.51:547.682

The dissociative ionization of 10 derivatives of 10-sila-2-azaanthracene, containing cyanoethyl (I-III), aminopropyl (IV), amino (V, VI), and amide (VII-X) groups at the $C_{(9)}$ atom, was investigated. It was shown that for all the compounds the general direction of decomposition is elimination of substituents from the silicon and carbon $C_{(9)}$ atoms. The stability of the compounds to electron impact is determined chiefly by the nature of the substituent at the $C_{(9)}$ atoms and depends weakly on the type of substituent at the silicon atom. In the case of amino-derivatives V-X, fragmentation of the molecular ions is determined by the method of localization of the positive charge in the molecular ion. This determines the occurrence of specific decompositions, which permits reliable identification of the compounds studied according to their mass spectra.

An investigation of the dissociative ionization of a new type of heterocyclic compounds, dihydrosilaazaanthracenes and their derivatives, was begun in [1, 2]. It was shown that the main directions of the decomposition of these substances under electron impact are determined primarily by the nature of the substituents in the central hydrogenated ring of the molecule. In this work we studied the mass spectrometric behavior of new derivatives of 10-sila-2-azaanthracene, containing cyanoethyl (I-III), aminopropyl (IV), amino (V, VI), and amide (VII-X)

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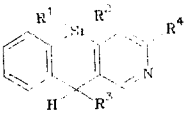
groups at the $C_{(9)}$ atom was studied. The mass spectra of the investigated compounds are cited in Table 1.

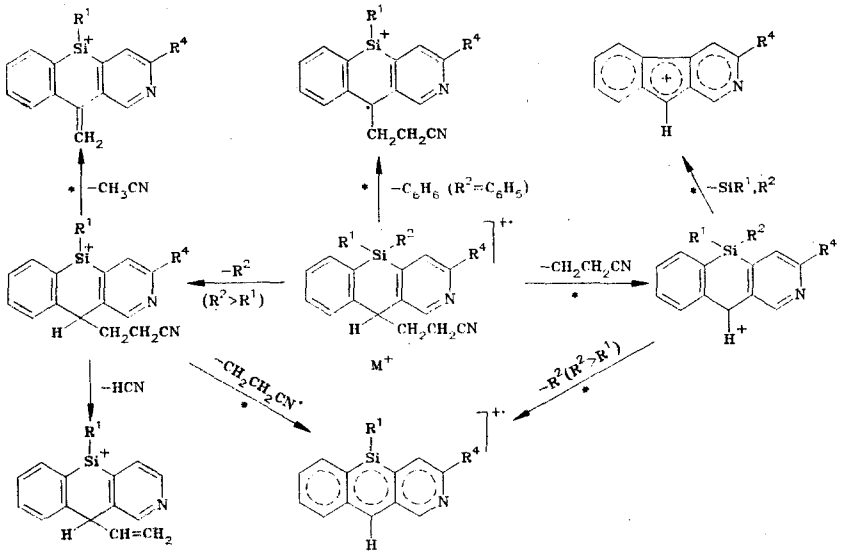


I–X

I $R^1=R^2=CH_3$, $R^3=CH_2CH_2CN$, $R^4=H$; II $R^1=CH_3$, $R^2=C_6H_5$, $R^3=CH_2CH_2CN$, $R^4=H$; III $R^1=R^2=C_6H_5$, $R^3=CH_2CH_2CN$, $R^4=CH_3$; IV $R^1=R^2=CH_3$, $R^3=CH_2CH_2CH_2NH_2$, $R^4=H$; V $R^1=R^2=CH_3$, $R^3=NH_2$, $R^4=H$; VI $R^1=R^2=C_6H_5$, $R^3=NH_2$, $R^4=CH_3$; VII $R^1=R^2=CH_3$, $R^3=NHCOOCH_3$, $R^4=H$; VIII $R^1=R^2=CH_3$; $R^3=NHCO(CH_2)_2Cl$, $R^4=H$; IX $R^1=R^2=CH_3$, $R^3=NHCO(CH_2)_4Cl$, $R^4=H$; X $R^1=R^2=CH_3$, $R^3=NHCO(CH_2)_4N(C_2H_5)_2$, $R^4=H$

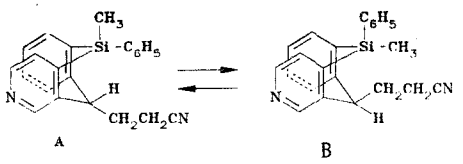
In contrast to the previously studied dihydrosilaazaanthracenes unsubstituted in the 9-position [1], in the decomposition of their cyanoethyl derivatives I-III the intensity of the peak of the molecular ion is negligible and is virtually independent of the nature of the substituent at the silicon atom (Table 1). This result is due to the introduction of a cyanoethyl group into the molecule, which lowers the stability of the compounds to electron impact on account of the appearance of new energetically profitable channels of the decomposition [3]. The main direction of fragmentation of substances I-III is determined by elimination of the cyanoethyl substituent by the molecular ions (M^+) (scheme 1), with the formation of the fragment $[M-CH_2CH_2CN]^+$, the peak of which has a maximum intensity in the mass spectra (Tables 1 and 2). The second direction of decomposition of the molecular ions of azaanthracenes I-III is due to elimination of the hydrocarbon radical from the silicon atom (Scheme 1); moreover, the probability of this process is determined by the nature of the particle eliminated (Table 2, compounds I and II). In the case of replacement of one of the methyl substituents at the silicon atom by a phenyl, the intensity of the peak of the ion $[M-CH_3]^+$ is sharply decreased, while in the mass spectrum of the diphenyl-substituted compound II, together with the $[M-C_6H_5]^+$ ion, an intense peak of an odd-numbered electron fragment $[M-78]^{+\bullet}$ is observed. The formation of this ion can be explained by splitting out of a hydrogen atom and a phenyl radical in different sequences or elimination of the molecule C_6H_6 by M^+.

Scheme 1



In the mass spectra of compounds II and III there are metastable ions (m^*), indicating that M^+ lose a C_6H_6 molecule in one step, and m*, confirming the successive splitting out of $H^\bullet$ and $C_6H_5^+$ radicals, are absent. These data agree with the premise of energetic unprofitability of the elimination of a phenyl radical and a hydrogen atom from the even-numbered electron ions $[M-H]^+$ and $[M-C_6H_5]^+$, respectively [3]. It should be noted that the formation of the ions was noted earlier in a study of the fragmentation of dihydrosilaanthracenes [4] – nitrogen-free analogs of the compounds studied in this work, which contain a phenyl group at the silicon atom. The indicated facts suggest that the formation of the fragment $[M-78]^{+\bullet}$

is associated primarily with the splitting out of a benzene molecule from the $M^{+\bullet}$ ion, while the intensity of the peaks of the ions $[M-78]^{+\bullet}$ formed in two steps, should be negligible. In [1] it was suggested that the stripping of a benzene molecule is preceded by migration of a hydrogen atom from the $C_{(9)}$ atom to the phenyl radical enriched by π-electrons. It is essential that in the case of decomposition of compound II the splitting out of a $C_6H_5^{\bullet}$ radical and a C_6H_6 molecule occurs with equal probability, whereas in the mass spectrum of compound III, diphenyl-substituted at the silicon atom, the intensity of the peak of the ion $[M-C_6H_5]^+$ is 3.1 times lower than that of the ion $[M-C_6H_5]^{+\bullet}$ (Table 2). One of the explanations for this result may be the assumption of the existence of M^+ of compound II in the form of two conformers with cis-diaxial (A) and cis-diequatorial (B) arrangement of the hydrogen atom at the $C_{(9)}$ atom and of the phenyl radical at the silicon atom:



In the cis-conformer A the phenyl radical and hydrogen atom at the $C_{(9)}$ atom are in steric proximity, which facilitates migration of hydrogen to the phenyl group and subsequent stripping of a benzene molecule. When the trans-form is realized in the molecular ion, analogous migration of hydrogen at the $C_{(9)}$ atom to the phenyl radical is sterically hindered, and in this case the predominating process is splitting out of a $C_6H_5^{\bullet}$ radical. In the decomposition of substances I and II, which contain a methyl substituent at the silicon atom, elimination of the methane molecule, analogous to the stripping of a benzene molecule, is not observed, which agrees with the data of [1].

The decomposition of M^+ of the β-cyanoethyl derivatives I-III, at its profound stages, permits establishment of a relationship between the structure of these compounds and the nature of their mass spectra. Thus, the ion $[M-CH_2CH_2CN]^+$ then loses the substituent R^2 from the silicon atom (scheme 1), forming a stable fragment that evidently has the structure of the silaazaanthracene cation. Further decomposition of the ions $[M-R^2]^+$ is characterized by elimination of the acetonitrile molecule and hydrocyanic acid as a result of breaking of bonds in the cyanoethyl substituent. The elimination of the particle SiR^1R^2 characteristic of fragmentation of organosilicon compounds [1, 4] occurs at the second stage of decomposition of the molecular ion (scheme 1). The high probability of this process is evidently due to the formation of a stable azafluorene cation.

When cyanoethyl group is replaced by a γ-aminopropyl group (compound IV), the intensity of the peak of the molecular ion increases sharply (Table 1), while the nature of the fragmentation of this compound is determined by the site of localization of the positive charge in M^+. The main directions of the decomposition of compound IV, just as in the case of cyanoethyl derivatives I-III, are associated with elimination of the substituent R^3 (Tables 1, 2, ion 224*) and elimination of a methyl group from the silicon atom (ion 267); moreover, the probability of occurrence of the latter reaction is significantly lower than in the fragmentation of compounds I and II. The formation of other characteristic fragments at the first stage of decomposition is due to localization of the charge on the nitrogen atom of the aminopropyl group [5]. Thus, the ion 265 corresponds to elimination of an ammonia molecule, while the fragment 252, $[M-CH_2NH_2]^+$, is formed as a result of cleavage of the α − β C–C bond in the aminopropyl radical. The peaks of the ions formed in the cleavage of the β − γ C–C bond of the aminopropyl radical (ion 238), as well as in the elimination of a γ-aminopropyl group in the form of an allylamine molecule (ion 225), are even more intense. In all cases of decomposition due to the presence of an amino group in the molecule, the charge is localized on the tricyclic fragment. The secondary stages of fragmentation are characterized by elimination of a methyl substituent (transitions 225 → 210, 224 → 209) and a $Si(CH_3)_2$ particle (transitions 238 → 180, 225 → 167). All the processes of decomposition discussed are confirmed by the corresponding metastable peaks.

As we go to amino-derivatives V and VI, the nature of the fragmentation of the molecular ion is sharply changed. The substantial intensity of the peaks of M^+ in the mass spectra of

*The numbers characterizing an ion define the value of m/z.

TABLE 1. Mass Spectra of Compounds I-X

Compound	Name	Values of m/z (peaks with intensity >5% of the maximum)
I	10,10-Dimethyl-9-(β-cyanoethyl)-9,10-dihydro-10-sila-2-azaanthracene	278 (0,5), 264 (20), 263 (81), 236 (7), 225 (23), 224 (100), 222 (6), 210 (12), 209 (30), 208 (6), 206 (7), 197 (7), 196 (11), 182 (8), 181 (9), 180 (15), 179 (12), 167 (15), 166 (7), 165 (5), 155 (7), 154 (6), 153 (6)
II	10-Methyl-10-phenyl-9-(β-cyanoethyl)-9,10-dihydro-10-sila-2-azaanthracene	341 (0,2), 340 (0,8), 326 (16), 325 (51), 287 (28), 286 (100), 285 (7), 284 (12), 272 (8), 271 (19), 270 (13), 269 (8), 263 (17), 262 (16), 259 (5), 242 (7), 241 (7), 222 (17), 215 (8), 209 (9), 181 (6), 179 (7), 178 (6), 166 (9), 164 (7), 149 (7), 83 (6), 81 (6), 71 (9), 69 (11), 57 (13), 56 (6), 55 (10), 53 (6)
III	3-Methyl-10,10-diphenyl-9-(β-cyanoethyl)-9,10-dihydro-10-sila-2-azaanthracene	416 (0,3), 363 (28), 362 (100), 339 (13), 338 (40), 298 (9), 297 (29), 285 (6), 284 (20), 283 (16), 240 (6), 214 (7), 164 (9), 151 (6), 78 (7), 77 (7), 53 (11), 51 (7)
IV	10,10-Dimethyl-9-(γ-aminopropyl)-9,10-dihydro-10-sila-2-azaanthracene	283 (4), 282 (27), 266 (5), 265 (21), 240 (6), 239 (8), 238 (27), 226 (19), 225 (44), 224 (100), 210 (15), 209 (27), 197 (8), 181 (6), 180 (13), 179 (8), 167 (10)
V	9-Amino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene	241 (22), 240 (85), 239 (100), 226 (10), 225 (29), 224 (27), 223 (27), 211 (7), 210 (32), 209 (20), 208 (17), 197 (10), 196 (12), 195 (6), 183 (6), 182 (14), 181 (16), 180 (14), 179 (8), 167 (17), 166 (13), 163 (9), 162 (11), 161 (13), 155 (8), 152 (6), 139 (7), 132 (6), 102 (7)
VI	3-Methyl-9-amino-10-diphenyl-9,10-dihydro-10-sila-2-azaanthracene	379 (3), 378 (10), 377 (23), 376 (9), 364 (6), 363 (20), 362 (19), 361 (7), 301 (50), 300 (100), 299 (10), 286 (12), 285 (29), 284 (10), 283 (6), 196 (13), 181 (6), 115 (6)
VII	9-Methoxycarbonylamino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene	299 (18), 298 (62), 284 (15), 283 (65), 266 (8), 253 (7), 252 (18), 251 (78), 241 (10), 240 (33), 239 (100), 238 (15), 237 (13), 225 (17), 224 (7), 223 (17), 211 (12), 210 (47), 209 (25), 208 (8), 196 (12), 195 (7), 182 (10), 181 (12), 180 (12), 179 (8), 167 (13), 166 (13), 161 (7), 156 (7), 149 (27), 139 (8), 112 (10), 105 (10)
VIII	9-(γ-Chlorobutyrylamino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene	346 (37), 345 (26), 344 (96), 343 (6), 331 (36), 330 (24), 329 (100), 314 (6), 308 (10), 281 (7), 279 (7), 278 (6), 270 (9), 241 (9), 240 (25), 239 (93), 227 (6), 225 (24), 224 (81), 223 (12), 226 (25), 222 (6), 211 (16), 210 (15), 209 (30), 208 (16), 207 (30), 206 (6), 196 (11), 182 (10) 181 (15), 180 (12), 179 (10), 167 (16), 166 (18)
IX	9-(δ Chlorovaleryl-amino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene	360 (39), 359 (30), 358 (100), 357 (7), 345 (41), 344 (27), 343 (97), 323 (5), 284 (12), 282 (12), 282 (11), 268 (8), 241 (8), 240 (25), 239 (99), 226 (22), 225 (20), 224 (60), 223 (11), 211 (14), 210 (11), 209 (27), 208 (17), 207 (22), 196 (10), 182 (9), 181 (15), 180 (11), 179 (8), 167 (13), 166 (12), 69 (7), 55 (13)
X	9-(γ-Diethylamino-valeryamino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene	396 (7), 395 (23), 380 (7), 366 (17), 358 (10), 324 (7), 240 (6), 239 (22), 226 (11), 225 (33), 224 (61), 210 (7), 209 (14), 87 (10), 86 (100)

TABLE 2. Stability of Molecular Ions (W_M) and Relative Intensity of the Peaks of the Characteristic Fragments (in % of total ionic current) in the Mass Spectra of Silaazaanthracenes I-X

Compound	W_M	$[M-H]^+$	$[M-CH_3]^+$	$[M-C_6H_5]^+$	$[M-C_6H_6]^+$	$[M-R^3]^+$
I	0,1	0,11	12,6	—	—	15,6
II	0,1	0,11	6,1	2,0	2,0	11,9
III	0,05	0,08	—	1,8	5,6	13,9
IV	6,4	0,35	0,9	—	—	23,8
V	11,0	14,2	3,8	—	18,8	—
VI	1,9	4,3	3,7	9,4	—	—
VII*	6,2	—	6,5	—	—	4,5
VIII*	11,9	0,5	12,1	—	—	9,4
IX	12,9	0,6	12,8	—	—	7,6
X	3,6	0,2	1,1	—	—	9,7

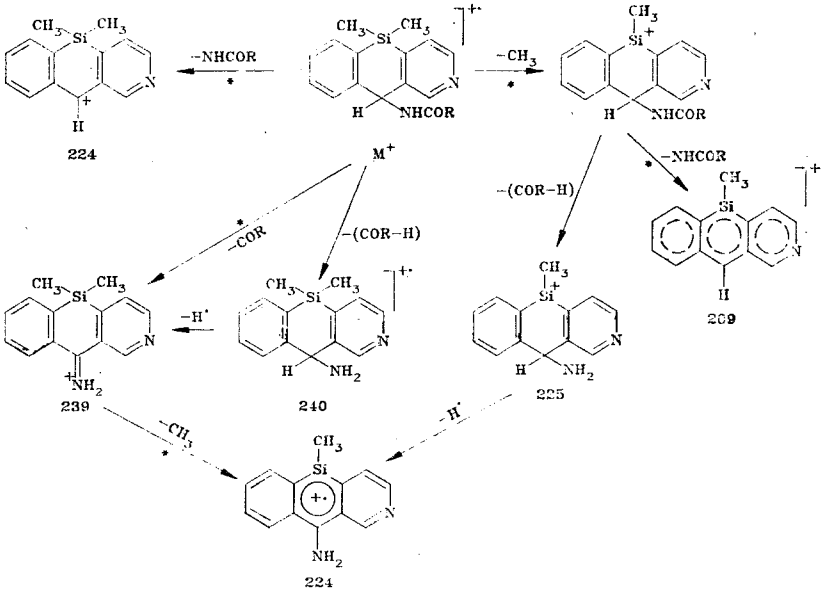
*For chlorine-containing ions the values of m/z are given calculated for the isotope ^{35}Cl.

these compounds (Table 2) is due to the presence of a strong electron donor group in the molecules [3]. One of the main directions of decomposition of the amines V and VI is elimination of a hydrogen atom by M^+ (Tables 1 and 2). The high probability of formation of the ions $[M - H]^+$ in this case can be explained by the possibility of splitting out of a hydrogen atom both from the sp^3-hybridized carbon atom $C_{(9)}$, analogously to the decomposition of dihydrosilaazaanthracenes [1], and from the amino group, as in the fragmentation of aromatic amines [6]. In the latter case the high stability of the $[M - H]^+$ ion can be explained by incorporation of the NH group into the ring and the formation of a fragment with a silaazepine structure [7]. The second direction of decomposition of the amines V and VI is due to elimination of a substituent from the silicon atom (Tables 1 and 2). In the case of fragmentation of compound VI, which contains two phenyl groups at the silicon atom, the dominant process is stripping of a benzene molecule (Table 2), and the intensity of the peak of the ion $[M - H]^+$ is significantly lower than in the decomposition of compound V. In the mass spectra of the amines V and VI, in contrast to compounds I-IV, peaks of the ions corresponding to stripping of a particle SiR^1R^2 are already present at the first stage of decomposition (ions 182 and 196, respectively, Table 1).

The amides VII-X are characterized by the presence of several heteroatomic groups in the exocyclic substituent in the molecule, which also determines the variety of pathways of fragmentation of these substances. The peaks of M^+ have high intensity (Table 2); moreover, the stability of compounds VII-X to decomposition (the values of W_M, Table 2) depends on the nature of the substituent at the exocyclic nitrogen: the value of W_M increases when the methoxycarbonyl group (compound VII) is replaced by ω-chloroacyl (compounds VIII, IX) and it decreases when chlorine in the acyl radical is replaced by a diethylamine group (compound X). In the latter case, just as we should have expected [8], the peak of the ion in the mass spectrum of maximum intensity corresponds to the amine fragment $CH_2{=}\overset{+}{N}(C_2H_5)_2$. In the mass spectra of the amides VII-X, in contrast to the amines V and VI, the peaks of the ions $[M - H]^+$ have low intensity.

One of the main directions of decomposition of M^+ of compounds VII-X is associated with the elimination of a methyl substituent from the silicon atom (Scheme 2, Table 2). In the case of decomposition of substances VII-IX this process is dominant, while the introduction of an amino group into the acyl radical (compound X) leads to a sharp drop in the intensity of the peak of the ion $[M - CH_3]^+$. The second direction of decomposition of the amides VII-X is due to elimination of an acyl group by M^+ (ion 239, scheme 2). As can be seen from Table 1, the probability of this process depends weakly on the nature of the substituent at the amide nitrogen, and the charge in all cases is entirely localized on the fragment with greater mass, which agrees with the fragmentation of cycloalkylamides [8].

Scheme 2



The peculiarities of the dissociative ionization of the amides VIII-X include elimination of a ketone molecule by M^+, leading to the formation of ions 240. In the case of urethane VII, the appearance of the ion 240 may be due to elimination both of a $Si(CH_3)_2$ particle and of a $COOCH_2$ group from the M^+ ion. The occurrence of the latter process is supported by the absence of the ions $[M-Si(CH_3)_2]^+$ at the first stage of decomposition of compounds VIII-X. Even more intense peaks correspond to the elimination of the ketene fragment from even-numbered electron ions at the second stage of dissociative ionization of amides (transition $M^{+\bullet} \longrightarrow [M - CH_3]^+ \xrightarrow{-(COR-H)^+} 225$, scheme 2).

In the decomposition of the amides VII-X, just as in the case of compounds I-IV, elimination of a substituent from the $C_{(9)}$ atom is observed; however, in amides the probability of this process is significantly lower (Table 2). In the mass spectra of compounds VIII and IX, peaks of ions corresponding to the elimination of a chlorine atom and a HCl molecule by M^+ are also present (Table 1).

Thus, for the decomposition of dihydrosilazaanthracenes containing an aliphatic substituent at the $C_{(9)}$ atom, the general processes are reactions of elimination of the substituent from the silicon atom and from the $C_{(9)}$ atom. The probability of these processes depends on the nature of the particle to be eliminated.

EXPERIMENTAL

The mass spectra of compounds I-X were obtained on a series-produced MX-1303 instrument using a system of direct introduction of the sample into the ion source at an ionizing voltage of 70 V and a temperature of admission of the sample 30-40°C. Compounds I-X were synthesized by the method of [9]; their purity and individuality were monitored by thin-layer chromatography and by the data of the IR, UV, and PMR spectra.

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