

Neutralization-Reionization Mass Spectrometry and Matrix Isolation of Some 9-Silaanthracenes

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Received May 22, 1990

Key Words: 9-Silaanthracene, derivatives / MS, neutralization-reionization / Matrix isolation

Neutralization-reionization mass spectrometry of silaanthracene radical cations, which are generated from the 9,10-dihydro-9-silaanthracenes **1**, **3**, **8** and **11** under electron-impact conditions, indicates that silaanthracenes are stable molecules

in the gas phase. Flash pyrolysis of the starting compounds mentioned above also yields the silaanthracenes **2**, **4**, and **10**, which may be isolated in an argon matrix at 15 K and exhibit characteristic UV spectra.

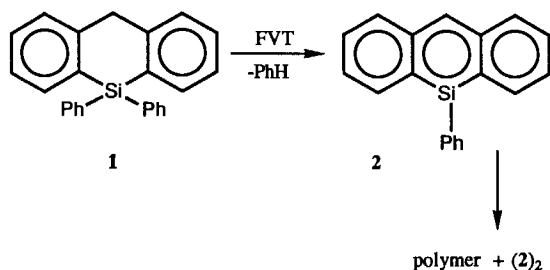
A survey of the recent literature shows an increasing interest in compounds with low coordination states of group-14 and -15 elements, as this type of bonding violates the classical double-bond rule¹. In recent years, a large number of kinetically stabilized compounds, containing a silicon–element double bond, have been reported^{1,2}. Each of these compounds had a more or less isolated, acyclic silicon–element double bond. In marked contrast, stable sila-aromatic compounds, which contain a silicon–element double bond as part of a delocalized system, have not yet been prepared.

In the sila-aromatic series, most synthetic efforts have been directed towards (derivatives of) silabenzene³ and disilabenzene⁴. Only a few attempts to prepare derivatives of 9-silaanthracene are known. Thus, Jutzi⁵ and our group⁶ tried to prepare silaanthracenes by elimination of a hydrogen halide from suitable dihydro precursors, but only dimeric or polymeric material was obtained. Similarly, a thermolytic approach, which had been developed for the synthesis of 10-aryl-9-heteroanthracenes of phosphorus and arsenic, was unsuccessful when applied to silicon⁷. In the course of these investigations, we attempted the elimination

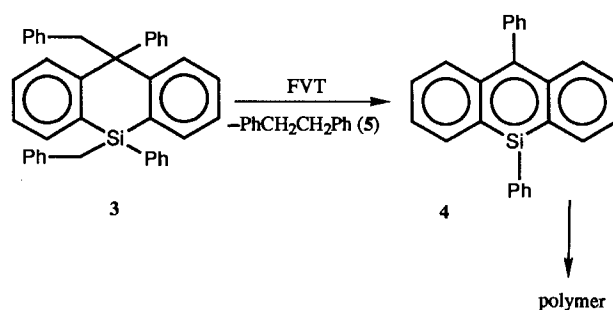
of benzene from 9,10-dihydro-9,9-diphenyl-9-silaanthracene (**1**) under flash vacuum thermolysis (FVT) conditions in order to obtain 9-phenyl-9-silaanthracene (**2**). It was not very surprising that **2** did not survive the thermal reaction conditions, but the results were promising in so far as the dimer of **2** was found as a component of the (mostly polymeric) reaction products.

More recently, we reported on an alternative approach⁸, which seemed to be more promising because on FVT, two benzyl radicals were cleaved from the precursor **3**. Presumably, the substituted 9-silaanthracene **4** was indeed generated, but polymerized under the reaction conditions. Direct evidence for the presence of **4** was not obtained; however, the expected byproduct of this reaction, 1,2-diphenylethane (**5**), was found in considerable yield (> 70%).

Scheme 1



Scheme 2



In this paper, we present two additional pieces of evidence which corroborate that silaanthracenes are indeed molecules which are highly reactive, but capable of existence in the absence of conditions which lead to their polymerization.

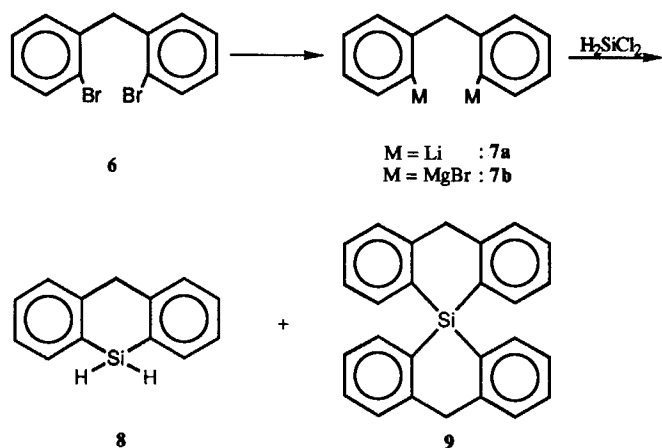
In the first place, in continuation of our previous mass-spectrometric identification of the radical cations of silaanthracenes⁸, we here present proof that the neutral molecules are formed too and identified under the conditions of mass spectrometry by neutralization of ionized, mass-selected silaanthracenes.

Secondly, an even more direct and convincing identification of silaanthracenes was achieved by matrix isolation and measurement of their characteristic anthracene-like UV spectra.

Synthesis of Starting Materials

The synthesis of the dihydro precursors has been described^{8,9}. As reported earlier⁸, we encountered some difficulties when trying to prepare the parent dihydro compound **8** from the dilithio compound **7a** and dichlorodimethylsilane; while **8** was formed indeed, the spiro compound **9** turned out to be the main product. These problems were avoided by applying the di-Grignard reagent **7b** instead of **7a**; the desired **8** was thus obtained in 85% yield after crystallization from pentane.

Scheme 3



NRMS of 9-Silaanthracenes

Neutralization-reionization mass spectrometry (NRMS) can provide a proof for the stability of 9-silaanthracenes in the gas phase, if the corresponding radical cations can be

generated under electron-ionization (EI) conditions. In our earlier work⁸, we found that the EI mass spectra of (substituted) 9,10-dihydro-9-silaanthracenes indeed show moderate to strong signals for the derived silaanthracene radical cations. These silaanthracene radical cations are potentially suitable for neutralization experiments.

NRMS has proven to provide access to otherwise inaccessible neutral molecules, e. g. $X-C\equiv C-Y$ with $X = H, NH_2, OH$ and $Y = NH_2, OH$ ¹⁰. The technique of NRMS has recently been reviewed¹¹; therefore, only the principle of a typical NRMS experiment is presented (Figure 1) for compound **1** as an example.

The ions of interest are mass-selected by the first mass analyzer, the magnet. A major fraction of the mass-selected ions is then neutralized inside the first gas cell, by collision with target gas or with metal-vapor atoms. The beam of ions and neutrals which emanates from the first gas cell passes a deflector electrode which bends the ions out of the beam; the path of flight of the neutrals remains unaffected. The beam of neutrals then enters a second gas cell where part of all neutrals is reionized by collision with a reionization gas. Fragment ions, which result from dissociative reionization, and reionized neutrals (survivor ions) are subsequently mass-analyzed by an electrostatic analyzer and detected.

In the experiments described here, potassium vapor is used as the neutralization agent and oxygen for reionization. An attempt to perform neutralization with the experimentally easier to handle xenon has failed; this is indicative of the expected non-resonant charge-exchange conditions^{11,12}; the ionization energy (I.E.) of silaanthracenes is estimated to be ca. 6.5 eV (compare: anthracene: 7.5 eV¹³; benzene: 9.2 eV¹³; silabenzene: 8.1 eV³⁸), whereas the I.E. of xenon is 12.1 eV, thus making the neutralization with xenon endothermic by ca. 5 eV. Neutralization with potassium (I.E. = 4.3 eV¹⁴) is exothermic by ca. 2.7 eV and therefore efficient; subsequently, survivor ion signals are produced in a satisfactory yield. This is in line with earlier findings on the dependence of neutralization efficiency on the ionization energy of the neutralization agent^{11,12}.

The NR and collision-induced dissociation (CID) mass spectra of 9-phenyl-9-silaanthracene (**2**), generated from **1** under EI conditions, are shown in Figure 2. As all the primary ions have been deflected under neutralization condi-

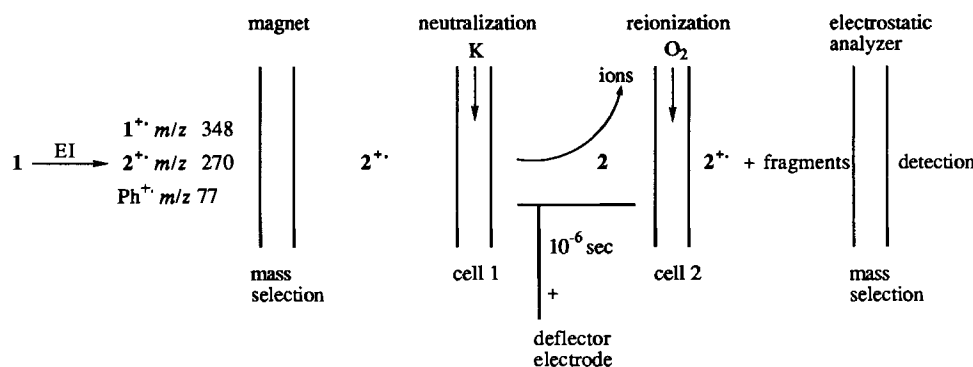


Figure 1. Principle of an NRMS experiment; generation of **2** from $2^{+\bullet}$ as an example

tions, the signal at $m/z = 270$ is a measure of the neutral molecules **2** which have survived both the neutralization and the reionization processes. The survivor ion region of the NR mass spectra of **2**, **4**, and **10** is given in Figure 3.

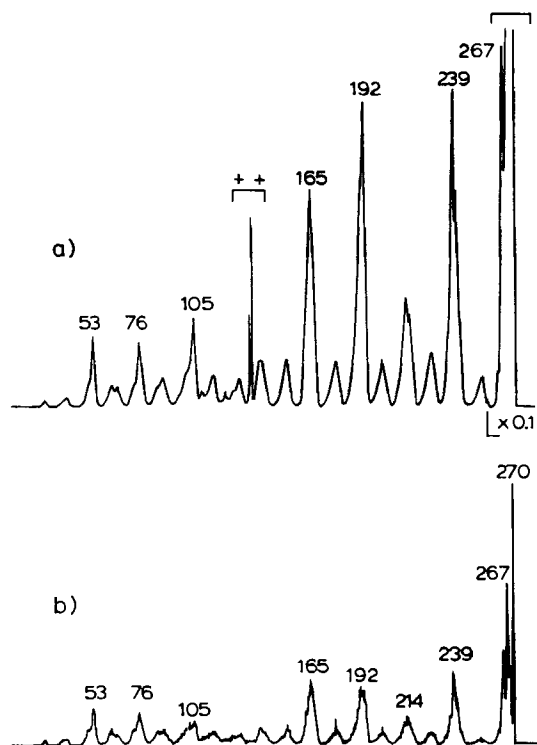


Figure 2. CID mass spectrum (a) and NR mass spectrum (b) of 2^{+o}

The mass resolution of both the NR and CID mass spectra is poor, because peak broadening occurs from the kinetic energy which is released in the fragmentation processes. The energy resolution of the spectra permits mass assignment with sufficient accuracy for **2** and **10**, but in the case of **4**, mass assignment of fragment ions is obscured by peak broadening. Because in general, no kinetic energy release is observed for ions which only undergo neutralization and reionization, the survivor-ion signal in the NR mass spectrum is relatively narrow and can be clearly distinguished.

In our earlier work⁸⁾ we have pointed out that 2^{+o} and 10^{+o} are generated by a transannular 1,4-elimination of benzene from ionized **1** and **11**, respectively, and that 4^{+o} is generated by the consecutive loss of two benzyl radicals from ionized **3**. Further proof for the product-ion structure is obtained from the CID mass spectra of the aromatic product ions 2^{+o} , 4^{+o} , and 10^{+o} presented here. Only few heteroaromatic or fused ring aromatic systems have been investigated by CID¹⁵⁾. Comparison of our CID mass spectra with these literature spectra confirms that a fused aromatic ring system is present: in all cases the ions exhibit a typical fragmentation pattern, in which $m/z = 165$ (fluorenyl cation) is indicative of the two benzene rings joined by one carbon atom. Other signals are attributed to the loss of fragments typical of aromatics such as C_2H_2 , C_3H_3 , C_4H_3 , and C_5H_4 ^{15c)}. Thus, the CID mass spectra are in line with our earlier

proposals based on the metastable ion mass spectra of the precursor ions⁸⁾.

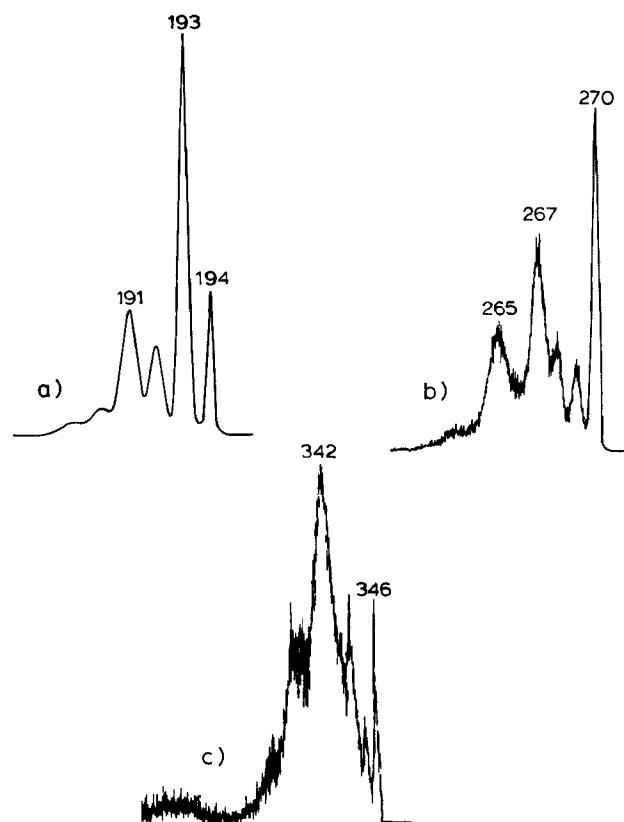


Figure 3. Partial NR mass spectra of a) **10**, b) **2**, and c) **4**, showing the survivor-ion region only

Only for 2^{+o} , the complete spectra are given in Figure 2. But for all three silaanthracenes, the relative intensity distribution for the fragment ion signals in the NR and CID mass spectra is almost identical, although the absolute intensity in CID is larger by two to three orders of magnitude. Only in the case of 10^{+o} ($m/z = 194$), a significant isotopic contribution of ^{29}Si and ^{13}C ($m/z = 193$ ["M-1"]) to the survivor ion signal is experimentally observed; however, this contribution makes up less than ten percent of the survivor-ion signal. We note that metastable ion signals do not contribute to any of the CID mass spectra, because metastable ion fragmentation of the aromatic ions 2^{+o} , 4^{+o} , and 10^{+o} is of very low abundance. Furthermore, the NR mass spectrum does not show any signals for doubly charged ions, in contrast to the relatively abundant charge-stripping signals in the CID mass spectrum. For anthracene, it is known that the second ionization energy is 13.6 eV ($M^{+o} \rightarrow M^{++}$; $M \rightarrow M^{++}$: 21.1 eV¹³⁾, which makes it likely that double (re)ionization of **2**, **4**, and **10** is hardly important under the conditions of NRMS. Considering that the minor differences between CID and NR mass spectra can thus be accounted for, the similarity of these types of spectra of 2^{+o} , 4^{+o} , and 10^{+o} shows that the ions are neutralized without loss of their structural identity. Hence, we conclude that the sur-

vivor-ion signals in the NR mass spectra prove that neutral **2**, **4**, and **10** are stable species in the dilute gas phase.

Matrix Isolation of 9-Silaanthracenes

As expected, the starting compound **1** eliminates benzene on flash pyrolysis at 800 °C; this can be seen from the IR spectrum of the matrix-isolated products. The UV spectrum, measured under the same conditions, exhibits characteristic absorptions between $\lambda = 350$ und 510 nm. These bands disappear when the matrix is not protected against irradiation. Even daylight causes the fading of the UV spectrum. If one irradiates into the maximum at $\lambda = 502$ nm, all bands shown in the spectrum (Figure 4, curve b; Table 1) disappear within 5 minutes. We suppose that this spectrum originates from silaanthracene **2**. The pattern, including vibrational structure, resembles that of the electron spectrum of anthracene. The characteristic feature is a shift of both bands of anthracene to longer wavelengths; we have previously observed the same behavior in the case of silabenzene^{3a)} and disilabenzene^{4d)}.

Scheme 4

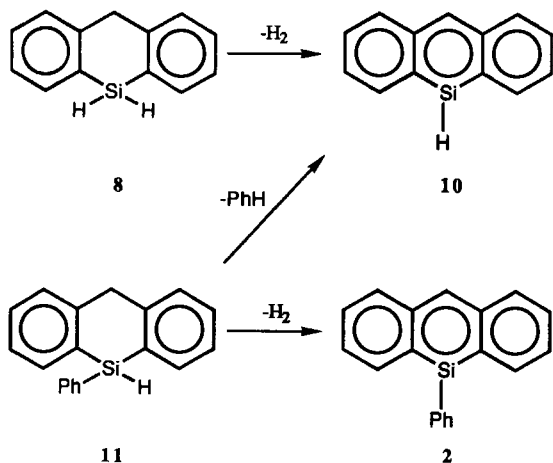


Table 1. UV absorptions [nm] of 9-silaanthracene (**10**), 9-phenyl-9-silaanthracene (**2**), and 9,10-diphenyl-9-silaanthracene (**4**)

10	2	4
362	364 ^{a)}	362 ^{b)}
380	384	382
400	404	404
420	420	420
444	444	444
468	470	468
494	502	500

^{a)} Pyrolysis of **1**. — ^{b)} Pyrolysis of **11**.

The disappearance of the characteristic absorptions on irradiation — an observation, which allows to measure the difference spectra shown in Figure 4 — is probably due to the photoisomerization of the silaanthracene to the corresponding Dewar valence isomer^{3a)}.

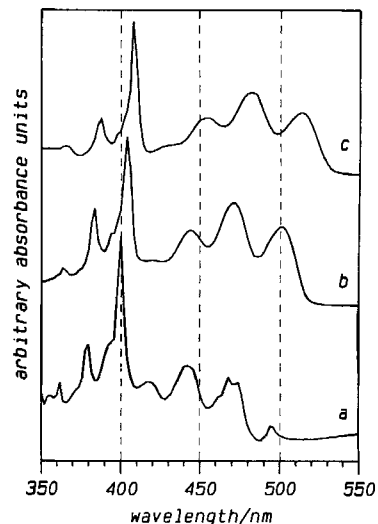


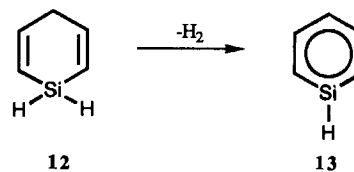
Figure 4. Difference spectra (nonirradiated minus irradiated sample) of 9-silaanthracene (**10**) (curve a), 9-phenyl-9-silaanthracene (**2**) (curve b, pyrolysis of **1**), and 9,10-diphenyl-9-silaanthracene (**4**) (curve c)

As long as the argon is present ($T < 40$ K) and **2** is matrix-isolated, it turns out to be quite stable. But the spectrum of **2** cannot be measured in the condensed phase, when the fragments are directly frozen at 15 K in the absence of argon.

If one pyrolyzes the dibenzyl derivative **3** at 900 °C, it is again possible to detect the matrix-isolated silaanthracene **4** by its characteristic UV spectrum (Figure 4, curve c; Table 1). The spectrum is very similar to the one observed for **2**. On irradiation ($\lambda > 360$ nm) the absorptions again slowly disappear, but not completely.

The parent silaanthracene **10** is obviously formed if dihydro-silaanthracene **8** is treated under identical conditions (900 °C). In this case the UV spectrum, which should be attributed to **10**, has the same appearance (Figure 4, curve a, Table 1), but the positions of the bands are at shorter wavelengths than in the spectra of **2** and **4**. On irradiation with wavelengths $\lambda > 570$ nm, the bands of **10** again diminish to a certain extent, and with light of $\lambda > 360$ nm, they disappear completely. So we assume that (transannular) dehydrogenation of **8** gives **10**; this finding is in accordance with the formation of silabenzene (**13**) from silacyclohexadiene **12**^{3d)}. On photoexcitation, **10** can probably be slowly transformed into Dewar 9-silaanthracene.

Scheme 5



The monophenylated precursor **11** should also be a good candidate for the preparation of the parent silaanthracene **10**. Indeed, pyrolysis of **11** at 1000 °C yields some benzene, which can be seen in the IR spectrum of the matrix-isolated

fragments. But the corresponding UV spectrum is practically superimposable with the one observed in the pyrolysis of the starting compound **1**. In other words, in the case of **11**, the elimination of hydrogen is preferred over that of benzene, and 9-phenyl-9-silaanthracene (**2**) seems to be the main product.

Conclusions

Silaanthracene **10** and its phenyl derivatives **2** and **4** are capable of existence under specific conditions (in the gas phase of a mass spectrometer or in an argon matrix at 15 K). But benzoannulation of the central silabenzene ring is not conducive to stabilize compounds of this type; on the contrary, a destabilization is observed analogous to that of the couple benzene/anthracene. Even the two phenyl rings in **2** do not furnish sufficient steric protection, in contrast to the phospha- and arsaanthracene analogs¹⁷.

This investigation was supported by the *Netherlands Foundation for Chemical Research* (SON) with financial aid (Y.v.d.W.) from the *Netherlands Organization for Scientific Research* (NWO).

Experimental

General: Reactions were carried out in flame-dried glassware under nitrogen. THF was distilled from LiAlH₄. The NMR spectra were recorded with a Bruker WM-250 NMR spectrometer at 250 MHz (¹H), 62.89 MHz (¹³C), or 49.49 MHz (²⁹Si). Chemical shifts were measured relative to external Me₄Si. The purity was checked by GC/MS, using a Hewlett-Packard 5970 mass-selective detector connected to a HP 5890 gas chromatograph, equipped with a 25-m CPsil 5 CB capillary column. Direct inlet mass spectrometry and exact mass measurements were performed with a Finnigan MAT 90 instrument (Finnigan MAT, San José, California, USA).

9,10-Dihydro-9-silaanthracene (8): The di-Grignard reagent^{9a} was prepared from 2,2'-dibromodiphenylmethane (**6**) (5.5 g, 17 mmol) and double-sublimed magnesium (1.0 g, 42 mmol) in THF (5 ml). The solution of the Grignard reagent was separated from the residual magnesium by siphoning into a dropping funnel and added slowly to a solution of H₂SiCl₂ (2.0 g, 20 mmol) in THF (75 ml) at -70°C (**Caution:** extreme care must be taken in the handling of H₂SiCl₂; for details of handling and hazards see ref.^{9b}). The reaction mixture was allowed to warm to room temp. over ca. 12 h, and was then poured onto ice. After the addition of pentane, the organic layer was separated and the aqueous layer extracted twice with pentane. The combined organic layers were dried with MgSO₄. After filtration and evaporation of the solvent, the residue was recrystallized from pentane, yielding **8** as colorless crystals (2.8 g, 85%), m. p. 74–75°C (ref.^{9a} 74–76°C). — ¹H NMR (CDCl₃): δ = 4.12 (s, 2H, CH₂), 4.83 (s, 2H, SiH₂), 7.22–7.78 (m, 8H, aryl-H). — ¹³C NMR (CDCl₃): δ = 41.95 [t, ¹J(CH) = 126.5 Hz], 125.74 [d, ¹J(CH) = 159.5 Hz], 128.14 [d, ¹J(CH) = 155.9 Hz], 128.54 (s), 129.73 [d, ¹J(CH) = 159.4 Hz], 134.97 [d, ¹J(CH) = 158.5 Hz], 146.57 (s). — ²⁹Si NMR (CDCl₃): δ = -52.23 [t, ¹J(SiH) = 203.0 Hz]. — MS (70 eV): *m/z* (%) = 196 (100) [M⁺], 195 (87), 194 (20), 193 (32), 165 (62).

C₁₃H₁₂Si (196.3) Calcd. 196.0708 Found 196.068 (MS)

Mass Spectrometry of 9-Silaanthracenes: Electron impact and metastable ion mass spectra were obtained with a reversed geometry magnetic sector MAT 90 instrument (Finnigan MAT, San José, California, USA). Collision-induced dissociation (CID) and neu-

tralization reionization (NR) mass spectra were obtained from EI-generated ions with a VG ZAB-2F reversed geometry magnetic sector instrument, equipped with a metal-vapor collision gas cell, a deflector electrode and a common collision gas cell in the second field-free region (as described elsewhere¹⁶). Potassium was used for neutralization and oxygen for reionization, at ca. 50% overall main beam reduction; the deflector electrode was operated at 300 V. Isotopic contributions in NRMS were only significant in the case of 9-silaanthracene itself (<10% of the survivor ion signal at *m/z* = 194 consists of ²⁹Si and ¹³C contribution by *m/z* = 193). CID mass spectra were recorded under the same gas cell conditions, but with the deflector electrode switched off.

Matrix Isolation of 9-Silaanthracenes. — Pyrolysis: The dihydro-silaanthracenes were sublimed at 10⁻⁶ Torr and at different temperatures (**1**: 200°C; **3**: 300°C; **8**: 40°C; **11**: 40°C), and the vapor was transferred through an oven at 800–1000°C. The products were immediately condensed together with argon (ratio ca. 1:500) on an optical window at 15 K. In all cases the fragmentation of the starting material was not complete. Therefore, the spectra were recorded by subtraction (original minus irradiated sample).

Matrix Isolation Equipment: Cryostat: Displex-Closed-Cycle-Refrigerator CSA 202 (Air Products) with CsI (IR) and BaF₂ (UV/VIS) windows. — **Spectrometers:** FT-IR spectrometer IFS 85 (Bruker) UV/VIS Diode Array Spectrometer 8452 A (Hewlett-Packard). — **Light Sources:** Mercury light-pressure lamp HBO 200 (Osram) with a monochromator (Bausch & Lomb) for λ = 502 nm or with filters for λ > 570 or > 360 nm. — **Flash Pyrolysis / Matrix Isolation:** Home-made oven with an inner quartz tube (i. d. 15 mm, length of heated zone 4 cm), which could be heated with a heating wire up to 1000°C, surrounded by a water-cooled metal jacket. The oven was directly flanged to the cryostat.

CAS Registry Numbers

1: 123335-03-5 / **2:** 128328-90-5 / **3:** 128328-91-6 / **4:** 123335-00-2 / **6:** 61592-89-0 / **8:** 38948-57-1 / **10:** 23636-28-4 / **11:** 21993-96-4 / H₂SiCl₂: 4109-96-0

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