Low-Temperature Isolation of a Labile Silylated Hydrazinium-yl Radical Cation, \([\text{(Me}_3\text{Si)}_2\text{N–N(H)SiMe}_3]^*\)

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Dedicated to Prof. Dr. Wolfgang Beck on the occasion of his 90th birthday.

Abstract: The oxidation of silylated hydrazine, \((\text{Me}_3\text{Si})_2\text{N–N(H)SiMe}_3\) with silver salts led to the formation of a highly labile hydrazinium-yl radical cation, \([(\text{Me}_3\text{Si})_2\text{N–N(H)SiMe}_3]^*\), at very low temperatures (decomposition > -40 °C). EPR, NMR, DFT and Raman studies revealed the formation of a nitrogen-centered radical cation along the N–N unit of the hydrazine. In the presence of the weakly coordinating anion \([\text{Al(OCH(CF}_3)}_2\text{J}]^3\), crystallization and structural characterization in the solid state were achieved. The hydrazinium-yl radical cation has a significantly shortened N–N bond and a nearly planar N$_3$Si$_3$ framework, in contrast to the starting material. According to DFT calculations, the shortened N–N bond has a total bond order of 1.5 with a π-bond order of 0.5. The π bond can be regarded as a three-π-electron, two-center bond.

As early as 1875,[12] Fischer first described aromatic-substituted hydrazines and proposed the name hydrazine for this class of compounds, although the parent compound, N$_2$H$_4$, was not isolated until 1898 by Curtius (as a sulfate salt).[3] Since its discovery, hydrazine has been a basic material for organic synthesis and is used primarily for the production of dyes, pharmaceuticals and crop protection agents.[4,5] But hydrazine also occurs in the nitrogen cycle with its exchange between organic matter and the atmosphere and is essential for all life on Earth. Two of the most important natural processes, nitrogen fixation[6] and the anammox process,[7,8] carried out by specialized bacteria, pass through hydrazine, an extremely reactive substance. As such processes forming hydrazine in situ often involve one-electron steps, corresponding radicals of hydrazine play a crucial role as intermediates, although very little is known experimentally so far.[9] From a broader perspective, the chemistry of persistent and reactive radicals is diverse and is increasingly used in (in)organic synthesis,[10,11] photo redox catalysis,[12] molecular spintronics,[13] optoelectronic and biological fields.[14] In particular, there are a number of theory papers that deal with the bonding situation and thermodynamics of hydrazine-based radicals.[15–24] In most cases, the π-radical type (unpaired spin distribution perpendicular to the plane of the N-radical) proves to be the most stable.[25] Starting from hydrazine, three radicals can be formally formed (Scheme 1): i) Formal oxidation gives the hydrazinium-yl radical cation (A). ii) Bond breaking of the N–H or N–N bond gives rise to the hydrazinyl (B) or two aminyl radicals (C), respectively. Because the hydrogen-substituted radicals A, B and C are extremely reactive, they cannot be easily synthesized and isolated. For example, Adams and Thomas showed that hydrazine can be chemically oxidized in aqueous sulfuric acid solution with ceric ammonium sulfate to the radical cation A, which was identified by in-situ EPR spectroscopy.[20] Furthermore, several studies show that both in solution and in solids, radical species A can be produced and spectroscopically studied by means of hard gamma irradiation.[26–30] In further in-

Scheme 1. Hydrazine-based radicals: A hydrazinium-yl, B hydrazinyl, and C aminyl. Instead of N$_2$H$_4$, N$_2$H$_5^+$ ions were often used as a source for the generation of type-A radicals.
Stable [group 15 element hydrazinium-yl ion of the type (T

in situ investigations, chemical oxidation as well as electrochemical oxidation were transferred to organically (Me, Ph) substituted hydrazine derivatives. In a series of papers since the 1970s, Nelsen et al. reported sterically protected nitrogen-based radical cations in which, for example, an [NN]\(^{+}\) unit is incorporated into a bicyclic system, and later on the very stable [(Pr\(_n\))N\(_2\)]\(^{+}\) with nitrate (T\(_m\) = 140 °C)\(^{44}\) and tosylate anions.

We were intrigued by the idea of preparing a silylated hydrazinium-yl ion of the type [T\(_n\)N–N(H)T]\(^{+}\) (T = Me, Si) with a residual N–H bond, which might be the closest species to the parent [H\(_n\)N–N(H)\(_n\)]\(^{+}\) radical cation, especially as we know that a Me\(_n\)Si moiety can be understood as the “big brother” of the proton, as has been shown in a number of publications. For example, in analogy to the protonated species, such as [H–X–H]\(^{+}\) (X = halogen, pseudohalogen)\(^{51,52}\) [H\(_n\),\([\mathbf{E}^{+}\)]\] (E = group 15 element\(^{53,54}\) for n = 1 and 16\(^{55–59}\) for n = 2) or arsenuim ions\(^{60}\) in aromatic systems, also the silylated species\(^{61–65}\) can be isolated in the presence of a weakly coordinating anion.\(^{66–67}\) Like the protonated analogs, the silylated anions can be used as T–transfer reagents or can migrate along bonds.\(^{68}\) The chemistry of silylated hydrazines has been extensively studied by Wiberg, Wannagat, West and others in the 1960s–1970s.\(^{69–78}\) For example, an organosilylated hydrazinyl radical and phosphinyl-substituted radical\(^{79}\) were even generated in situ and characterized by EPR spectroscopy (both are type B radicals, Scheme 1). Here we report the first isolation of a silylated hydrazinium-yl, [T\(_n\)N–N(H)T]\(^{+}\), radical cation (type A radical in Scheme 1) stabilized by a weakly coordinating anion (wca).

For the synthesis of a silylated type A radical cation (Scheme 1), we first had to synthesize an appropriate silylated hydrazine, choosing T\(_n\)N–N(H)T because it promised maximum steric protection while allowing reactivity at the one left N–H bond. Tri-silylated hydrazine T\(_n\)N–N(H)T (1) is best synthesized in a two-step synthesis (Scheme 2): Starting from the hydrazinium hydrochloride, [N\(_n\)H\(_n\)]Cl, this is treated with Me\(_n\)Si–Cl (T–Cl) in the presence of a strong base such as 1,2-diaminoethane to give a mixture of the two di-silylated species, 1,1-T\(_n\)N–N\(_n\)H and 1,2-T\(_n\)N–N(H)T, as well as tri-silylated T\(_n\)N–N(H)T. The mixture of the 1,1- and 1,2-di-silylated species can easily be separated from the tri-silylated species by distillation. The separated mixture of 1,1- and 1,2-T\(_n\)N–H\(_n\) is then treated with nBuLi to give a mixture of lithium hydrazides, Li[T\(_n\)N–NH] and Li[T\(_n\)H–N–NT], which can also be isolated (see the Supporting Information). However, this mixture of lithium hydrazides can also be further converted in situ to T\(_n\)N–N(H)T (1) by adding two equivalents of T–Cl. By this procedure T\(_n\)N–N(H)T can be generated in over 70% yield and obtained in high purity by repeated distillation (b.p.: 138 °C (100 mbar); 71 °C (6 mbar)).

With tri-silylated hydrazine 1 in hand, we treated it with different silver salts of the type Ag[wca] = [GaCl\(_n\)]\(^{+}\), [SbF\(_{6}\)]\(^{−}\), [F\(_2\)CSO\(_4\)]\(^{−}\), [BF\(_4\)]\(^{−}\), [BC(F\(_3\))\(_n\)]\(^{−}\), [CH\(_n\)B\(_n\)F\(_{11}\)]\(^{−}\), and [Al(OCH(CF\(_3\)))\(_n\)]\(^{−}\) in order to oxidize 1 to the radical cation [T\(_n\)N–N(H)T]\(^{+}\) (1\(^{+}\)) as illustrated in Scheme 3. In the case of the anions [GaCl\(_n\)]\(^{−}\) and [BC(F\(_3\))\(_n\)]\(^{−}\), no reaction at all was observed, whereas for [BF\(_4\)]\(^{−}\), [F\(_2\)CSO\(_4\)]\(^{−}\) and [CH\(_n\)B\(_n\)F\(_{11}\)]\(^{−}\), mainly the corresponding hydrazinium salts, for example, [T\(_n\)NN(T)H\(_n\)](CHB\(_n\)F\(_{11}\))(2) or [T\(_n\)NN(H)T]([BC(F\(_3\))\(_n\)]3(3)B(C\(_2\)F\(_3\))) were observed or isolated (Schemes S3 and S4 in the Supporting Information). For both wca\(^{−}\) = [SbF\(_{6}\)]\(^{−}\) and [Al(OCH(CF\(_3\)))\(_n\)]\(^{−}\), the only desired product 1\(^{+}\)wca was observed. However, it should be mentioned that only the combination [T\(_n\)N–N(H)T]\(^{+}\) with the [Al(OCH(CF\(_3\)))\(_n\)]\(^{−}\) anion is suitable for isolation (see the Supporting Information), of which yellow crystals could be obtained from CH\(_3\)Cl at ~80 °C. The problem stems from the fact that the yellow salts with the radical cation 1\(^{+}\) decompose already above ~20 °C in the solid as demonstrates by LT-Raman studies (Figure S13), in solution the decomposition starts even earlier, so that these salts have to be kept at temperatures < ~40 °C. Decomposition probably begins with the deprotonation of 1\(^{+}\), producing the hydrazinyl radical T\(_n\)N–NT\(_n\) radical of type B in Scheme 1, which decomposes further. In addition to deprotonation, 1\(^{+}\) can also act as a T– transfer reagent, which then leads to an in-situ-generated T\(_n\)N–NH\(^{+}\) radical. Therefore, it is not surprising that we were able to isolate simple silylated hydrazinium salts, with the cation [T\(_n\)NN(T)H\(_n\)]\(^{+}\) (2\(^{+}\)) or [T\(_n\)NN(H)T]\(^{+}\) (3\(^{+}\)) very frequently in many reactions (see above). The lability of 1\(^{+}\) contrasts to Nelsen’s fully protected compounds, which are stable at room temperature (see above).

The existence of the radical cation 1\(^{+}\) in solution as well as solid state was unequivocally proven by X-ray, EPR and Raman studies. For EPR analysis (Figure 1), isolated crystals were

Scheme 3. Synthesis of salts containing the radical cation 1\(^{+}\) (observed for wca\(^{−}\) = [SbF\(_{6}\)]\(^{−}\) and [Al(OCH(CF\(_3\)))\(_n\)]\(^{−}\)). Below: resonance scheme of the three-π-electron, two-center bond.

![Scheme 2. Synthesis of tri-silylated hydrazine 1 (EN = 1,2-diaminoethane).](image-url)
dissolved at a temperature of −40 °C and then cooled down to −73 °C. The EPR spectra of 1+ in CH2Cl2 solution confirm their radical nature. The hyperfine structure is consistent with a hyperfine coupling to the two N atoms and the one H atom. The coupling constant of A_u = 11.7 G and A_H = 9.1 G are in the same range as for the transient [N3H]+ radical cation (A_u = 11.0 G and A_H = 11.5 G) [25,30]. Also in the low-temperature 1H solution NMR experiment at −50 °C in CD2Cl2 the radical is also recognized because, signals due to 2+ are absent (1): δ[H] = 2.111 N–H, 0.08 C–H and a very broad peak, shifted to higher frequency (1+ : δ[H] = 11.8 with ν1/2 = 5300 Hz) shows up. No discrimination of individual atom sites is possible. In line with this observation, only signals of the anion show up in the 13C NMR spectrum.

The Raman spectrum of 1+ also shows large differences compared to the neutral starting material 1. For example, the N–H stretching vibration shifts to a smaller wavenumber (1: 3348 vs. 1+ : 3303 cm⁻¹), while the N–N vibration is shifted by about 250 cm⁻¹ to a higher wavenumber (1: 1072 vs. 1+ : 1321 cm⁻¹). The latter implies a significant enhancement of the N–N bond strength and indicates a significant N–N double bond character in 1+ (cf. 1555 in diazene T=N=N=T, 1570 in [T=N=N-T]+, 1062 cm⁻¹ in Hg[T=N=N-T]+) [28].

To experimentally investigate the structural changes upon oxidation of 1 to the radical cation 1+, some structural formulas along the reaction pathway were determined by single-crystal X-ray structural analysis (Figure 2), including the decomposition products [T=N=N(T)H][CHB1HBr1] or [T=N=N(H)T][B(CF3)2] and the lithium hydrazide salt [Li(TN–NT)]4 [Li4N, see the Supporting Information]. Selected structural parameter are summarized in Table 1. The radical cation salt 1+[Al(OCH2CF3)4] crystallizes like the neutral parent compound 1 in the monoclinic space group P2/c with Z = 4, but the volume of the unit cell has more than doubled (1646 vs. 3917 Å³), which is due to the larger space requirement of the anion in 1+[Al(OCH2CF3)4] but there are only very weak interactions between the radical cation and the alkoxyl-aluminate counterion (cf. smallest F_monomic−H1_cation = 2.68 Å), but these do not affect significantly the molecular parameters of the radical cation.

Table 1. Selected experimental structural parameters (Figure 2) of 1, 1+, 2+, 3+ and for comparison [T=N=N-T]+ (5+). In addition, calculated values are given in italics (M06/def2tztpp).

| Bond length [Å] | Bond angle [°] |
|-----------------|----------------|
| N1–N2           | N1–Si1         | N1SiN12Si3 | Si3N2Si2 |
| [T,N=N(T)H][CHB1HBr1] | 1.458(3) | 1.718(6) | 96.9(5) | 135.7(3) |
| [T,N=N(H)T][B(CF3)2] | 1.437 | 1.737 | 89.59 | 133.8 |
| [T,N=N(T)H][B(CF3)2] | 1.343(2) | 1.822(2) | −179.0(1) | 122.7(4) |
| [T,N=N(H)T][B(CF3)2] | 1.332 | 1.839 | −173.09 | 121.7 |
| [T,N=N(T)H][B(CF3)2] | 1.467(3) | 1.891(2) | 85.6(2) | 127.8(1) |
| [T,N=N(H)T][B(CF3)2] | 1.444 | 1.915 | 85.15 | 126.9 |
| [T,N=N(T)H][B(CF3)2] | 1.499(5) | 1.875(5) | 104.8(3) | 123.6(2) |
| [T,N=N(T)H][B(CF3)2] | 1.465 | 1.892 | 107.21 | 122.3 |
| [T,N=N(T)H][B(CF3)2] | 1.517(2) | 1.697(2) | −68.12 | 126.2(1) |
| [T,N=N(T)H][B(CF3)2] | 1.480 | 1.706 | −70.13 | 124.0 |
| [T,N=N(T)H][B(CF3)2] | 1.254(2) | 1.829(1) | −175.3(1) | 124.1(4) |

(a) Only values of the main part A are listed. [b] Si3N2Si4 is listed. [c] Data were taken from ref. [49].
with respect to each other. Upon the oxidation of 1, an electron is removed from one electron pair and a partial N–N π bond is formed, which in turn leads to a favorable planar N₂Si₃ framework. This can also be seen from the significantly shorter N–N distance of 1.343(2) Å in 1⁺⁺ that is about 0.115 Å shorter than in 1 (1.458(3) Å, cf. \( \Sigma_{\text{cpl}}(N-N) = 1.42 \) and \( \Sigma_{\text{cpl}}(N-N) = 1.20 \) Å)[28] and is well in line with the N–N distance of 1.333(4) Å in \(((\text{Pr})_3\text{N})_2\text{N}^+\).[44] This mediate value indicates a partial double bond character which is in 1⁺⁺ somewhat smaller as in 5⁺ (1.254(2) Å).[49] Finally, it should be noted that all tri-coordinated silylated nitrogen atoms in all considered species are almost trigonal planar due to hyperconjugative effects between the lone pairs located at the N atoms (in p-type atomic orbitals) and antibonding \( \sigma^*(\text{Si}–\text{C}) \) bond orbitals (see the Supporting Information). In contrast to 1⁺⁺, \(((\text{Pr})_3\text{N})_2\text{N}^+\).[44] as well as \([\text{H}_2\text{N}–\text{NH}_3]^+\)[88] feature a larger deviation from planarity due to the absence of significant hyperconjugation in both species in accordance with computations that predict a \( C_{\text{sh}} \) symmetric gas-phase structure of the parent system \([\text{H}_2\text{N}–\text{NH}_3]^+\).[86]

To better understand the structure, bonding situation and charge distribution, DFT calculation was performed using the M06 functional in combination with the def2tzvpp basis set. As shown in Table S13, the quantum mechanical calculations also reveal a nearly planar \( N_5\text{Si}_3\text{H} \) framework for 1⁺⁺ as well as a significantly shortened N–N bond, in agreement with the experimental SC-XRD data. The agreement for all other species 1, 2⁺, 3⁻ and 4⁻ is also very good (Table 1). The calculated Mulliken spin density is mainly localized at both N atoms, with a slightly smaller value for N1 (0.43) than for N2 (0.45).[87] The spin densities at the three Si atoms are much smaller, about 0.02, while they are negligible for the C and H atoms. That is, the radical cation 1⁺⁺ can be described in good approximation as a nitrogen-centered radical. The N–N bonds are nearly covalent according to the NBO analysis (NBO = natural bond analysis), with a N–N \( \sigma \) bond and a one-electron \( \pi \) bond localized besides a one electron lone pair at each N atom; this agrees with the EPR measurements, showing a distinct coupling to both nitrogen atoms. This description corresponds to a three-\( \pi \) electron, two-center bond in the MO picture, where the bonding \( \pi \)-MO is doubly and the antibonding \( \pi^* \) MO is singly occupied (Figure 3).[86] This gives a formal \( \pi \) bond order of 0.5 (calcld: 0.46), which is also consistent with the calculated total NLMO bond order for the N–N bond of 1.44 (cf. 0.99 for 1, see the Supporting Information, NLMO = natural localized molecular orbital), in accord with the rather short N–N bond. This also makes it clear that the spin density has local \( \pi \) symmetry along the N–N axis (Figure 3).

In summary, upon oxidation of tris(trimethylsilyl)hydrazine 1 with silver salts, the highly labile trisilylated radical cation \([\text{T}_3\text{N}–\text{NH}_2\text{HT}]^+\) (1⁺⁺) was observed in solution. The high lability of 1⁺⁺ is largely determined by the remaining N–H bond. The radical character was studied by EPR experiments, which clearly indicated the presence of a nitrogen–nitrogen-centered radical cation. Calculations confirmed that the spin density is mainly localized at both nitrogen atoms. In the presence of the alkoxyaluminate anion, \( [\text{T}_3\text{N}–\text{NH}_2\text{HT}]^+ \) could be crystallized and structurally characterized. \([\text{T}_3\text{N}–\text{NH}_2\text{HT}]^+ \) represents a silylated hydrazinium-y1 ion that could be structurally characterized, thus closing a gap in hydrazine/nitrogen chemistry.

Experimental Section

A full set of analytical and theoretical data along with the detailed description of the synthesis are given in the Supporting Information.

X-ray crystallography: Deposition Numbers 2154462 (for 1), 2154465 (for \([\text{Al}([\text{OCH}([\text{CF}_3])_2])_2\]), 2154463 (for \([\text{C}_2\text{FB}([\text{CF}_3])_2])_2\]), 2154466 (for \([3\text{C}_2\text{FB}([\text{CF}_3])_2])_2\]), 2154464 (for \([\text{Li}[\text{Al}([\text{OCH}([\text{CF}_3])_2])_2])_2\]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

The University of Rostock and especially M. Willert are acknowledged for access to the cluster computer and support with software installations. We thank Prof. N. Wiberg for providing original samples of \([\text{Li}[\text{TN}–\text{NT}]_2])_2\], Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: hydrazide · nitrogen · radicals · silyllium · synthesis

Figure 3. Left: Plot of the SOMO of 1⁺⁺ (isosurfaces set at 0.068 a.u.). Right: Plot of the spin density of 1⁺⁺ (isosurfaces set at 0.006 a.u.). Optimization of structures/calculations at the M06/def2tzvpp level of theory in the gas phase.
