

Diazenium Ions

Isolation of a Labile Homoleptic Diazenium Cation**

Wolfgang Baumann, Dirk Michalik, Fabian Reiß, Axel Schulz,* and Alexander Villinger*

Abstract: Following our interest in nitrogen chemistry, we now describe the synthesis, structure, and bonding of labile disilylated diazene, its GaCl_3 adduct, and the intriguing trisilylated diazenium ion $[(\text{Me}_3\text{Si})_2\text{N}=\text{N}-\text{SiMe}_3]^+$, a dark blue and highly labile ($T_{\text{decomp}} > -30^\circ\text{C}$) homoleptic cation of the type $[\text{R}_3\text{N}_2]^+$. Although direct silylation of $\text{Me}_3\text{Si}-\text{N}=\text{N}-\text{SiMe}_3$ failed, the $[(\text{Me}_3\text{Si})_2\text{N}=\text{N}-\text{SiMe}_3]^+$ ion was generated in a straightforward two-electron oxidation reaction from mercury(II) dihydrazide and $\text{Ag}[\text{GaCl}_4]$. Moreover, previous structure data of $\text{Me}_3\text{Si}-\text{N}=\text{N}-\text{SiMe}_3$ were revised on the basis of new data.

The rise of the synthetic dyestuffs industry during the 19th century began with the discovery of diazonium salts, for example, $[\text{R}-\text{N}=\text{N}]^+\text{Cl}^-$, and diazotation reactions by Griess as early as 1858.^[1,2] Azo dyes, compounds that usually contain two aromatic fragments connected by a $\text{N}=\text{N}$ bond, still have a large impact and versatile scientific, medical, ecological, and technical importance.^[3] Although aryl-substituted diazenes have been extensively investigated and represent a class of stable compounds, much less is known about alkyl- and silyl-substituted diazenes $\text{R}-\text{N}=\text{N}-\text{R}$ (also known as diimines). It was not until 1968 that Wiberg et al. succeeded in the isolation of pale blue N,N' -bis(trimethylsilyl)diazene (**2**) from the reaction of *p*-tosylazide with lithium tris(trimethylsilyl)hydrazide (**1**) at low temperatures (Scheme 1).^[4] In 1974 Veith and Bärnighausen published a single-crystal structure determination of **2**, which confirmed the postulated *trans* configuration but revealed an extraordinary short $\text{N}-\text{N}$ distance of 1.171(7) Å.^[5] This value, however, lies outside the reported

range for known *trans* diazenes (1.219–1.254 Å; cf. $\Sigma r_{\text{cov}}(\text{N}=\text{N})=1.20$ Å),^[6] and therefore provoked controversial remarks in the literature. Moreover, computational studies predicted longer $\text{N}-\text{N}$ bonds, which were consistent with experimental and theoretical trends found for other diazenes.^[5,7]

Reports on the chemistry of diazenium cations $[\text{R}_2\text{N}=\text{N}-\text{R}]^+$ (R = alkyl, aryl) are restricted to only a few examples or are even unknown ($\text{R} = \text{SiMe}_3$) in the literature.^[8–10] Herein, we focus on the synthesis of highly labile silylated diazenium species. Interestingly, the formation of mostly transient diazenium ions such as $[\text{Ph}_2\text{N}=\text{N}-\text{H}]^+[\text{Cl}]^-$ was previously discussed in Diels–Alder, thermolysis, and solvolysis reactions, or electrochemically induced redox processes, often without any characterization.^[12–15]

As shown by Wiberg, the reaction of tosylazide with **1** at low temperatures provides ready access to light blue, disilylated *trans* diazene **2** in approximately 65% yield (Scheme 1, Figure 1 left).^[4] The major challenge when dealing with **2** arises from its very low decomposition point T_{decomp}

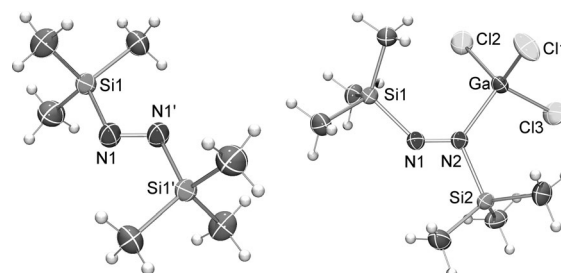
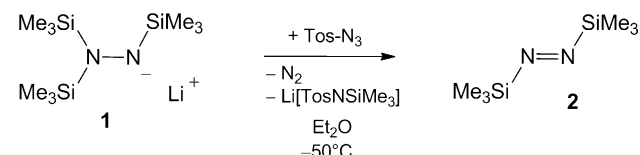


Figure 1. ORTEP representation of the molecular structure of **2** (left) and **3** (right) in the crystal. Thermal ellipsoids correspond to 50% probability at 173 K.



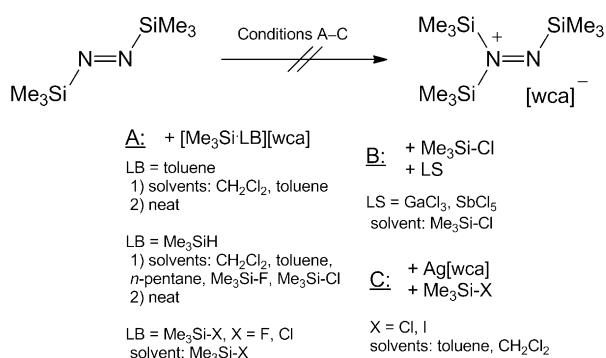
Scheme 1. Synthesis of N,N' -bis(trimethylsilyl) diazene (**2**); Tos = *p*- $\text{MeC}_6\text{H}_4\text{SO}_2$.

[*] Dr. W. Baumann, Dr. D. Michalik, Prof. Dr. A. Schulz, Dr. A. Villinger
Universität Rostock, Institut für Chemie
Albert-Einstein-Strasse 3a, 18059 Rostock (Deutschland)
and
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de
alexander.villinger@uni-rostock.de
Homepage: <http://www.chemie.uni-rostock.de/ac/schulz>

[**] We are indebted to N. Wiberg, G. Fischer, and H. Brand (Ludwig-Maximilians-Universität München).

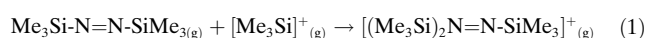
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201310186>.

$< -40^\circ\text{C}$ (cf. $t\text{Bu}-\text{N}=\text{N}-t\text{Bu} > 200^\circ\text{C}$, $\text{Ph}-\text{N}=\text{N}-\text{Ph} > 600^\circ\text{C}$), which even lies below its melting point of about -3°C .^[16,17] Since diazene **2** decomposes at ambient temperatures with a half-time of 7.6 h (zero-order reaction, in a 5:1 mixture of *n*-pentane/toluene) it must be kept at temperatures below -50°C in solution or in the solid state (see Figure S14 in the Supporting Information).^[18] A suitable low-temperature synthesis had to be found to generate the tris(trimethylsilyl)diazenium ion $[(\text{Me}_3\text{Si})_2\text{N}=\text{N}-\text{SiMe}_3]^+$ from diazene **2**.^[19] We thought that the obvious route to the desired $[(\text{Me}_3\text{Si})_2\text{N}=\text{N}-\text{SiMe}_3]^+$ cation was the direct silylation of diazene **2** with salts of the type $[\text{Me}_3\text{Si}-\text{LB}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $[\text{Me}_3\text{Si}]^+[\text{CB}]^-$ at low temperatures (Scheme 2, route A; LB = weak Lewis base = toluene, $\text{Me}_3\text{Si}-\text{H}$, $\text{Me}_3\text{Si}-\text{X}$ with $\text{X} = \text{Cl}$, F; CB = $[\text{CHB}_{11}\text{H}_5\text{X}_6]$, $\text{X} = \text{Br}$, Cl). The calculated gas-phase reaction (1)^[18g] with $\Delta H_{298} = -57.1 \text{ kcal mol}^{-1}$ also supported the idea of direct silylation (cf. -8.9 N_2 , -30.4 toluene ,



Scheme 2. Unsuccessful attempts for the synthesis of salts bearing the diazenium ion 4^+ (A: $[wca] = [B(C_6F_5)_4]$, $[CHB_{11}H_5X_6]$, $X = Br, Cl$; B/C: $[wca] = [B(C_6F_5)_4]$, $[SbCl_6]$, $[AsF_6]$, $[GaCl_4]$).

$-31.3 \text{ Me}_3\text{Si-H}$, $-34.8 \text{ Me}_3\text{Si-F}$, $-54.4 \text{ Me}_3\text{Si-CN}$, and $-71.7 \text{ kcal mol}^{-1}$ for $\text{Me}_3\text{Si-N}=\text{C}=\text{N-SiMe}_3$.^[19]

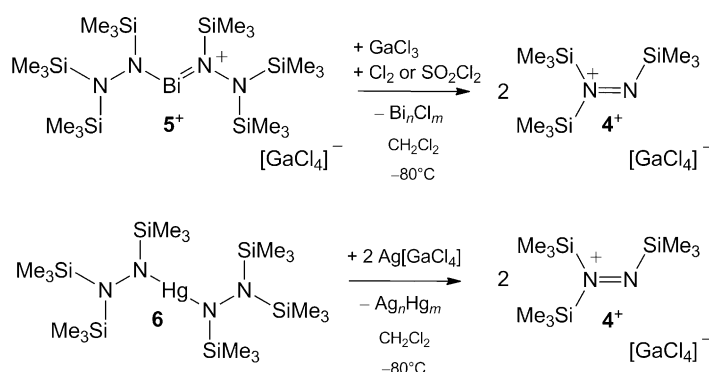


Reactions of all the utilized silylating agents (Scheme 2) with an excess of **2** in the absence of solvent led to violent decomposition even at very low temperatures ($< -150^\circ\text{C}$), but the reactions in all the applied solvents were also not successful due to decomposition of the reactants and the $[B(C_6F_5)_4]^-$ ion. In contrast, $[\text{Me}_3\text{Si}]^+[\text{CHB}_{11}\text{H}_5\text{X}_6]^-$ ($X = \text{Cl}, \text{Br}$) did not decompose under these reaction conditions; however, because of the limited solubility of $[\text{Me}_3\text{Si}]^+[\text{CHB}_{11}\text{H}_5\text{X}_6]^-$ no reaction with **2** below its decomposition temperature was observed. Since all these attempts failed, we then treated **2** with $\text{Me}_3\text{Si-X}$ ($X = \text{Cl}, \text{I}$) in the presence of $\text{Ag}[wca]$ ($wca = \text{weakly coordinating anion}$) or strong Lewis acids (LA) such as GaCl_3 and SbCl_5 (Scheme 2, routes B and C; $[wca] = [\text{AsF}_6]$, $[\text{SbCl}_6]$, $[\text{B(C}_6\text{F}_5)_4]$, $[\text{GaCl}_4]$). Again, only decomposition or undesired side reactions were observed. Although the initially precipitation of AgX ($X = \text{I}, \text{Cl}$) was observed, all the reactions led to the complete decomposition of **2** into N_2 and $\text{Me}_3\text{Si-X}$, along with the formation of $\text{E}^{(III)}\text{X}_3$ ($E = \text{As}, \text{Sb}, \text{Ga}$; $X = \text{F}, \text{Cl}$).^[18] This is in accord with the observation by Wiberg that **2** reduces main group element chlorides such as GeCl_4 with release of N_2 and $\text{Me}_3\text{Si-Cl}$.^[16c] However, the reaction of **2** with GaCl_3 as the Lewis acid or with $\text{Ag}[\text{GaCl}_4]/\text{Me}_3\text{Si-I}$ in dichloromethane at low temperatures resulted in the formation of the diazene adduct $\text{Me}_3\text{Si-N}=\text{N-SiMe}_3 \cdot \text{GaCl}_3$ (**3**, Figure 1, right) in the form of dark blue crystals (yield ca. 95%), which were thermally stable up to -20°C (Scheme 2, routes B and C).

Although gas-phase computations predict an almost barrier-free approach of the $[\text{Me}_3\text{Si}]^+$ ion to diazene **2** (see Figure S16 in the Supporting Information), all the synthetic routes used did not succeed in preparing the diazenium ion.^[18] We therefore decided to attempt the preparation of the diazenium salt $[(\text{Me}_3\text{Si})_2\text{N}=\text{N-SiMe}_3]^+[\text{GaCl}_4]^-$ (**4** $[\text{GaCl}_4]$) by redox reactions starting from heavy metal hydrazide derivatives already bearing a $[(\text{Me}_3\text{Si})_2\text{N-N-SiMe}_3]^-$ unit. For example, the dihydrazinobismuth cation in $[\text{Bi}\{\text{N}(\text{SiMe}_3)_2\}_2]^+[\text{GaCl}_4]^-$ (**5** $[\text{GaCl}_4]$)^[20] and the neutral mercury(II) dihydrazide $\text{Hg}\{\text{N}(\text{SiMe}_3)_2\}_2$ (**6**)^[21] seemed to

be promising candidates, since the 100% signal in the Cl^+ mass spectra of **5** $[\text{GaCl}_4]$ and **6** could be assigned to diazenium cation 4^+ , thus indicating their potential as diazenium sources. Indeed, the reaction of **5** $[\text{GaCl}_4]$ with GaCl_3 and elemental chlorine or sulfonyl chloride as the oxidizer in dichloromethane at temperatures below -50°C gave, after filtration to remove precipitates, concentration in vacuum, and storage at -80°C , low yields of blue, highly temperature-sensitive crystals, which were identified as **4** $[\text{GaCl}_4]$ by X-ray studies (Scheme 3, top).^[18] However, the decomposition of the bismuth salt **5** $[\text{GaCl}_4]$ to **4** $[\text{GaCl}_4]$ and bismuth chlorides was difficult to carry out because of the high reactivity of Cl_2 and SO_2Cl_2 leading to many side reactions and low yields.

Finally, we found that treatment of mercury salt **6** with two equivalents of $\text{Ag}[\text{GaCl}_4]$ at -80°C led in a clean, almost quantitative reaction to pure, crystalline **4** $[\text{GaCl}_4]$ as well as elemental mercury and silver. The latter form an amalgam which can be easily removed by low-temperature filtration (Scheme 3, bottom).^[18h] It is interesting to note, that the



Scheme 3. Synthesis of **4** $[\text{GaCl}_4]$.

analogous reaction of **6** with other silver salts such as $\text{Ag}(\text{toluene})_3[\text{B(C}_6\text{F}_5)_4]$, $\text{Ag}[\text{CF}_3\text{SO}_3]$, $\text{Ag}[\text{CHB}_{11}\text{H}_5\text{X}_6]$, or $\text{Ag}[\text{AsF}_6]$ was not successful.^[18] The overall process represents a remarkable two-electron oxidation of the $[(\text{Me}_3\text{Si})_2\text{N-N-SiMe}_3]^-$ ion according to the following formal Equations (2) and (3).^[18h]



Blue **4** $[\text{GaCl}_4]$ is extremely air and moisture sensitive, and decomposes at temperatures above -30°C . In solution it also decomposes rapidly at temperatures above -30°C . Nonetheless, **4** $[\text{GaCl}_4]$ could be fully characterized by low-temperature ^1H , ^{13}C , $^{14/15}\text{N}$, ^{29}Si NMR, and Raman spectroscopy as well as by single-crystal X-ray diffraction (Table 1). ^{15}N NMR spectroscopy (-60°C , CD_2Cl_2) is particularly well suited to distinguish between two-coordinate and the three-coordinate nitrogen atoms found in diazene species (**2**: $\delta = 605$ (N1/N2) versus **4** $^+$: 612 (N1) and 214 ppm (N2)). Silylation at N2 results in the resonance for N2 being dramatically upfield shifted by more than $\Delta\delta = 404$ ppm, while the resonance for

Table 1: Spectroscopic data of diazene species **2**, **3**, **4**[GaCl₄] and for comparison mercury(II) dihydrazide **6**.

Species ^[a]	2	3	4 [GaCl ₄]	6
Mp/T _{decomp} /°C	−3/−30 ^[d]	36/−20	−/−30	−/156
NMR ^[a]				
¹⁵ N, N1	605	596	612	−269
¹⁵ N, N2	605	248	214	−309
²⁹ Si, N1	5.2	23.8	24.26	9.77
²⁹ Si, N2	5.2	45.6	44.99	5.18
¹³ C, N1	−4.0	−1.6	−0.9	3.09
¹³ C, N2	−4.0	−1.8	−0.4	2.63
¹ H, N1	0.17	0.64	0.70	0.277
¹ H, N2	0.17	0.46	0.55	0.284
ν _{NN,Raman} /cm ^{−1}	1555 ^[b]	1568 ^[b]	1570 ^[b]	1062
N1–N2/Å	1.227(2) ^[e]	1.243(2)	1.254(2)	1.462(4)
N1–Si1/Å	1.807(3) ^[e]	1.826(2)	1.829(1)	1.725(3)
N2–Si2/Å	1.807(3) ^[e]	1.884(2)	1.894(1)	1.735(3)
N2–Si3/Å	–	–	1.899(1)	1.737(3)
Si1–N1–N2/°	117.3(2) ^[e]	134.6(1)	140.5(1)	123.8(2)
Si1–N1–N2–Si2/°	180	175.5(1)	175.3(1)	−98.0(3) ^[g]
q(N1)/e	−0.55	−0.43	−0.40	−1.15
q(N2)/e	−0.55	−0.59	−0.59	−1.21
Q _{CT} /e ^[f]	–	0.24	0.33	0.48

[a] δ [ppm], −75 °C, CD₂Cl₂. [b] The sample decomposes in the laser beam. [c] No signals were detected. [d] Slow decomposition starts earlier. [e] Only structural parameters of part A with the larger occupancy of the disordered molecule are listed. [f] Q_{CT} = total charge transfer from the diazene to the Lewis acid. [g] The hydrazide group adopts an almost perpendicular arrangement as a result of Pauli repulsion between the lone pairs of electrons localized on the two N atoms (see Figure S1).

dicoordinated N1 is only shifted by about δ = 8 ppm to a higher field (cf. δ = 357/−11 ppm by the addition of GaCl₃ to **3**). These values display an extreme nuclear magnetic deshielding of both nitrogen atoms in **2** and N1 in **3** and **4**⁺, a fact which was already observed and studied by Wrackmeyer and co-workers in a series of diazenes (cf. **2**: δ = 618–630, Ph–N=N–SiMe₃: 251,^[18] Ph–N=N–Ph: 131, Et–N=N–Et: 151 ppm).^[17a,22] Wrackmeyer and co-workers found that the remarkable downfield shift of δ [¹⁴N] upon substituting one or both alkyl or phenyl groups in R–N=N–R by Me₃Si can be attributed to a decrease in the energy gap for magnetic dipole allowed electronic transitions, in particular of the *n* → π* type, and thus reflects the unique influence of silyl substituents on the electronic structures, and is also responsible for the blue color.^[22,23] Thus, the ¹⁵N resonance of azo compounds of the type R–N=N–SiMe₃ was observed approximately in the middle of the ¹⁵N resonances of the symmetrically substituted compounds. A similar effect can be discussed when **2** is silylated to yield **4**⁺. The ²⁹Si NMR data illustrate that when silylation occurs both ²⁹Si resonances are shifted downfield with respect to those of diazene **2** by Δδ = 19 (N1) and 39 ppm (N2) (**2**: δ = 5.2 (N1/N2) versus **4**⁺: 24.3 (N1) and 45.0 ppm (N2)). The Raman data of all the considered diazene species (Table 1) show sharp bands in the expected region between 1560 and 1600 cm^{−1}, which can be assigned to the ν_{NN} stretching frequency (cf. 1589 cm^{−1} in Ph–N=N–Ph). The coordination of [Me₃Si]⁺ and GaCl₃ to diazene **2** causes no significant shift in the band to lower wave numbers, thus indicating an almost pure nonbonding character of the lone pair of electrons at the nitrogen donor center. It should be

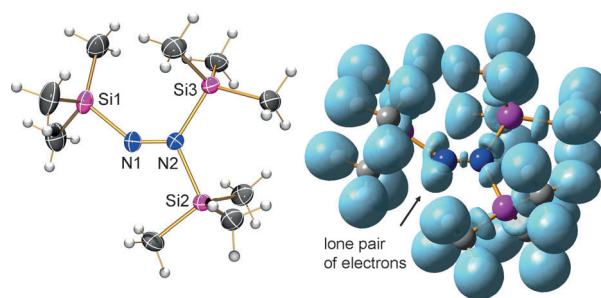


Figure 2. Left: ORTEP representation of the molecular structure of **4**⁺ in the crystal. Thermal ellipsoids correspond to 50% probability at 173 K. Right: Three-dimensional representation of the ELF at 0.82.

mentioned that **2**, **3**, and **4**[GaCl₄] quickly decompose in the laser beam to form molecular nitrogen and the hydrazine derivative (Me₃Si)₄N₂, which is in accord with observations by Wiberg et al.^[4]

X-ray diffraction analysis (Figure 2) revealed unequivocally the existence of diazenium cation **4**⁺ with an almost planar N₂Si₃ skeleton (deviation from planarity less than 5°). There are neither significant cation–anion nor anion–anion contacts. Both N atoms are in a planar environment with two slightly different sets of N–Si bond lengths (N1–Si1 1.829(1), N2–Si2 1.894(1), and N2–Si3 1.899(1); cf. Σ_{r_{cov}}(Si–N) = 1.87 Å,^[6] which can be attributed to hyperconjugation of the lone pair of electrons localized at N1 into the N2–Si and Si1–C σ* orbitals, respectively. The most striking feature is the N–N bond length of 1.254(2) Å, which lies in the typical range of a N=N bond (cf. Σ_{r_{cov}}(N–N) = 1.42, N=N 1.20, N≡N 1.08 Å; 1.243(3) Å in azobenzene)^[6,24] and in accord with those found in tetracyclic and hexacyclic formal bis(trialkyldiazenium) bis(tetrafluoroborate) salts reported by Nelsen et al. (1.244(5)–1.261(5) Å), where the N₂ units are, however, part of a six-membered ring.^[10b] Comparison of the structural data of **4**⁺ with those of **2** and **3** reveal only small differences (Table 1). For all species, the N–Si skeleton is planar and two slightly different Si–N bond lengths are observed, except for the C₂-symmetric diazene (*trans* configuration). The shortest Si–N bonds are found in **2** because of stronger hyperconjugative effects. The two Me₃Si groups in **2** and **3** adopt a *trans* arrangement. The Ga–N donor–acceptor bonds in **3** at 2.036(2) Å^[25] are in the expected range (cf. 2.011(4) in NH(SiMe₃)₂·GaCl₃, 1.965(2) Å in Me₃Si–N=S=N–SiMe₃·GaCl₃).^[26,27]

Finally, it is interesting to note that the previous structure determination of diazene **2** needs to be revised on the basis of our data.^[5] Although the cell data are in agreement (space group *P2₁/c*, *Z* = 2), the previously reported structure of **2** was refined without taking into account that the whole molecule is disordered, which results for example in an unrealistically short N–N bond length of 1.171(7) Å and a large N–N–Si angle of 120.0(4)°. However, if the molecule is refined as disordered over two positions then a significantly longer N–N distance of 1.227(2) Å (cf. Σ_{r_{cov}}(N=N) = 1.20 Å) and a smaller N–N–Si angle of 117.3(2)° in accordance with the computations are obtained (e.g. 1.247 from B3LYP/6-311 + G(d,p),^[22] 1.242 Å from M06-2X/aug-cc-pvTZ), which now lie in the expected range for diazenes.^[18]

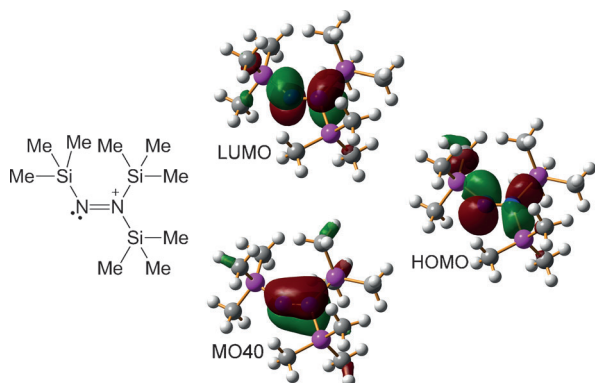


Figure 3. Left: Lewis representations of 4^+ according to NBO/NRT analysis. Right: MO40 (π), HOMO (n/σ), and LUMO (π^*).

DFT calculations of the electronic structure as well as ELF, MO, and NBO/NRT analyses (ELF = electron localization function,^[28] NBO = natural bond orbital, NRT natural resonance theory)^[29] were carried out to gain insight into the structure and bonding of diazenium ion 4^+ . MO and NBO calculations show a localized N=N bond and a lone pair of electrons that according to NRT analysis is mainly localized at N1 (Figure 3). This is in accordance with the ELF of 0.82 that exhibits a small dumbbell-shaped region of localized electrons between the two N atoms, which is a good indicator of a classical double bond, along with a monosynaptic valence basin for the lone pair of electrons localized at N1 (Figure 2, right). The calculated natural atomic orbital population (NAO) net charges are $q(\text{N1}) = -0.40$ and $-0.59 e$ (N2), which means that N1 becomes slightly less negative and N2 even more negative upon formal $[\text{Me}_3\text{Si}]^+$ addition, that is, the overall charge along the N1-N2 unit remains almost constant (cf. **2**: $q(\text{N1}) + q(\text{N2}) = -1.10$, **3**: -1.02 , 4^+ : $-0.99 e$, Table 1), in accordance with the charge distribution in the adduct **3**. According to TD-DFT calculations,^[18] the blue color arises from the weak $n/\sigma \rightarrow \pi^*$ HOMO–LUMO electronic transition at $\lambda_{\text{max,calc}} = 731 \text{ nm}$ in cation 4^+ (Figure 3, right).^[17b]

In summary, a highly labile salt bearing the trisilylated homoleptic diazenium ion 4^+ is presented for the first time. Although the direct silylation of **2** failed because of side reactions or low solubility, diazenium ion 4^+ was formed in a straightforward two-electron oxidation process starting from mercury(II) dihydrazide and $\text{Ag}[\text{GaCl}_4]$. Structural and spectroscopic data are in accordance with those of diazene **2** and the hitherto unknown diazene- GaCl_3 adduct **3**. Furthermore, we found that the previous structural data of diazene **2** needed to be revised on the basis of a new single-crystal structure determination, thus solving an old problem in diazene chemistry.

Received: November 23, 2013

Published online: February 14, 2014

Keywords: diazenes · diazenium ions · oxidation · silylium ions · structure elucidation

[1] P. Griess, *Liebigs Ann. Chem.* **1858**, 106, 123.

- [2] R. Wizinger-Aust, *Angew. Chem.* **1958**, 70, 199.
- [3] A. Bafana, S. Devi, T. Chakrabarti, *Environ. Rev.* **2011**, 19, 350.
- [4] N. Wiberg, W.-C. Joo, W. Uhlenbrock, *Angew. Chem.* **1968**, 80, 661.
- [5] M. Veith, H. Bärnighausen, *Acta Crystallogr.* **1974**, B30, 1806.
- [6] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, 15, 12770.
- [7] A. Modelli, F. Scagnolari, D. Jones, G. Distefano, *J. Phys. Chem. A* **1998**, 102, 9675.
- [8] H. Wieland, E. Wecker, *Chem. Ber.* **1910**, 43, 3260.
- [9] U. Kuhlmann, DE1419789B1, **1969**.
- [10] a) S. F. Nelsen, R. T. Landis II, *J. Am. Chem. Soc.* **1974**, 96, 1788; b) S. F. Nelsen, H. Chang, J. J. Wolff, D. R. Powell, *J. Org. Chem.* **1994**, 59, 6558.
- [11] S. Hünig, H. Balli, E. Breither, F. Brühne, H. Geiger, E. Grigat, F. Müller, H. Quast, *Angew. Chem.* **1962**, 74, 818; *Angew. Chem. Int. Ed. Engl.* **1962**, 1, 640.
- [12] See, for example: a) G. Cauquis, M. Genies, *Tetrahedron Lett.* **1968**, 32, 3537; b) G. Cauquis, M. Genies, *Tetrahedron Lett.* **1971**, 48, 4677.
- [13] A. Ferguson, *Tetrahedron Lett.* **1973**, 30, 2889.
- [14] a) W. R. McBride, H. W. Kruse, *J. Am. Chem. Soc.* **1957**, 79, 572; b) W. R. McBride, E. M. Bens, *J. Am. Chem. Soc.* **1959**, 81, 5546.
- [15] E. Allred, *J. Am. Chem. Soc.* **1982**, 104, 5422.
- [16] a) N. Wiberg, W. Uhlenbrock, W. Baumeister, *J. Organomet. Chem.* **1974**, 70, 259; b) N. Wiberg, W. Uhlenbrock, *J. Organomet. Chem.* **1974**, 70, 239; c) N. Wiberg, W.-C. Joo, G. Schwenk, W. Uhlenbrock, M. Veith, *Angew. Chem.* **1971**, 83, 379; *Angew. Chem. Int. Ed. Engl.* **1971**, 10, 374.
- [17] a) J. Kroner, W. Schneid, N. Wiberg, B. Wrackmeyer, G. Ziegler, *J. Chem. Soc. Faraday Trans. 2* **1978**, 74, 1909; b) H. Bock, K. Wittel, M. Veith, N. Wiberg, *J. Am. Chem. Soc.* **1976**, 98, 109.
- [18] Supporting information: a) Synthesis details, b) details of X-ray structure elucidation, c) kinetics of the decomposition of diazene, d) IR, Raman, NMR spectra, e) ^1H , ^{15}N HMBC spectra, and f) computational details, g) applied level theory: pbe1pbe/aug-cc-pwCVDZ, h) the precipitate could be identified as a mixture of amalgam $\text{Ag}_{11}\text{Hg}_9$ along with traces of AgCl by a Rietveld refinement of the powder diffraction data, i) diazene **2**: The asymmetric unit was split in two parts and the occupancy of each part was refined freely (0.652(12)/0.348(12)); j) we observed two resonances at $\delta = 310$ (N_{Si}) and 255 ppm (N_{Ph}).
- [19] a) M. Lehmann, A. Schulz, A. Villinger, *Angew. Chem.* **2009**, 121, 7580; *Angew. Chem. Int. Ed.* **2009**, 48, 7444; b) A. Schulz, A. Villinger, *Chem. Eur. J.* **2010**, 16, 7276; c) M. F. Ibad, P. Langer, F. Reiß, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2012**, 134, 17757.
- [20] W. Baumann, A. Schulz, A. Villinger, *Angew. Chem.* **2008**, 120, 9672; *Angew. Chem. Int. Ed.* **2008**, 47, 9530.
- [21] K. Seppelt, W. Sundermeyer, *Chem. Ber.* **1970**, 103, 3939.
- [22] B. Wrackmeyer, C. Köhler, *Heteroat. Chem.* **2005**, 16, 84.
- [23] H. Seidl, H. Bock, N. Wiberg, M. Veith, *Angew. Chem.* **1970**, 82, 42; *Angew. Chem. Int. Ed. Engl.* **1970**, 9, 69.
- [24] C. J. Brown, *Acta Crystallogr.* **1966**, 21, 146.
- [25] E. I. Davydova, T. N. Sevastianova, A. V. Suvorov, A. Y. Timoshkin, *Coord. Chem. Rev.* **2010**, 254, 2031.
- [26] C. J. Carmalt, J. D. Mileham, A. J. P. White, D. J. Williams, *Dalton Trans.* **2003**, 4255.
- [27] C. Hubrich, A. Schulz, A. Villinger, *Z. Anorg. Allg. Chem.* **2007**, 633, 2362.
- [28] a) B. Silvi, A. Savin, *Nature* **1994**, 371, 683; b) H. Grützmacher, T. F. Fässler, *Chem. Eur. J.* **2000**, 6, 2317.
- [29] F. Weinhold, C. Landis, *Valency and Bonding, A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, **2005** and references therein.