Radical Ions. 36. Structural Changes Accompanying the One-Electron Oxidation of Hydrazine and Its Silyl Derivatives[1-3]

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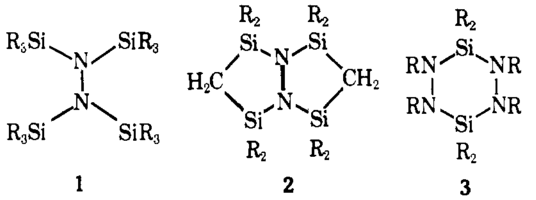
Abstract: Three prototype permethylsilylhydrazines—the tetrasubstituted open-chain $(R_3Si)_2NN(SiR_3)_2$, the bicyclic $\overline{N(SiR_2CH_2R_2Si)_2N}$, and the bifunctional six-membered-ring derivative $R_2Si(RNNR)_2SiR_2$—have been ionized in the gas phase and oxidized in solution. The photoelectron spectroscopically determined vertical ionization energies of the nitrogen lone pairs provide information on the ground-state geometry. Oxidation with $AlCl_3$ in H_2CCl_2 solution produces adiabatically radical cations, for which ESR spectra reveal stabilizing structural changes: the perpendicular $(R_3Si)_2N$ halves of the open-chain molecule twist toward planarity, and the chair conformation of the six-membered ring turns into half-chair by flattening of one SiNNSi link. These observations, as well as literature data on B-, C-, or P-substituted hydrazine radical cations, can be rationalized by a geometry-optimized INDO open-shell hypersurface for the parent ion $N_2H_4^{+\cdot}$, according to which one-electron oxidation should planarize the $>N\underline{\cdots}N<^{+\cdot}$ skeleton and shorten the N-N bond length by ~25 pm! In addition, three-dimensional tables of INDO ^{14}N and ^1H coupling constants allow comparative estimates of the structural changes during the oxidation of hydrazine derivatives in solution.

In general, molecules change their structure on acquisition or on loss of electrons.[4] The latter process, ionization or oxidation, is advantageously investigated by combined photoelectron spectroscopic (PES) and electron spin resonance (ESR) technicques.[1,5] Thus information can be gathered both on the vertical energy differences between molecular and cationic ground states in the gas phase and on the accompanying charge redistribution, i.e., on the "adiabatic" structural changes in solution as deduced from the analysis of the spin population.

Hydrazine derivatives are well suited to search for structural changes during the oxidation process. Although lacking any multiple bond, they usually exhibit low first ionization energies because the nitrogen lone pairs provide a relatively high NN electron density in the molecular ground state, and also permit stabilizing charge delocalization in the resulting radical cation state, especially, if coplanarity of the >N-N< skeleton can be achieved. The two-center/3π-electron system $R_2N\underline{\cdots}NR_2^{+\cdot}$ generated on oxidation would then be comparable to that of isoelectronic ethylene radical anions $R_2C\underline{\cdots}CR_2^{-\cdot}$.[2,5] Therefore, starting from hydrazine or from its sterically unstrained derivatives with dihedral angles close to $\omega \sim 90°$, flattening toward $\omega \rightarrow 0°$ is expected for the radical cations like $H_2N\underline{\cdots}NH_2^{+\cdot}$ in accord with ESR[6] or electrochemical data.[7] In this context, the extensive research of Nelsen and his coworkers[7-10] should be emphasized, who circumvented the easily deprotonating radical cations containing NH bonds[8] and thus could report valuable information on numerous tetraalkylhydrazines and their oxidation to stable radical cations.[9,10] Nelsen and co-workers[9c] also have carried out INDO calculations for $N_2H_4^{+\cdot}$ and suggest a nonplanar ($\beta = 11°$) eclipsed structure as the preferred conformation for unstrained tetraalkylhydrazine radical cations. In contrast, our INDO open-shell hypersurface for $N_2H_4^{+\cdot}$ yields a planar structure at the total energy minimum. A recent crystal-structure investigation on an exceptionally stable tetraalkylhydrazine radical cation and its neutral counterpart[9i] has provided the first detailed experimental access to the structural changes on oxidation.

Our own efforts to generate novel radical cations of organometallic compounds[1-5] involved as one key step the use of $AlCl_3$ in H_2CCl_2 solution as a selective oxidizing agent,[11] which does not break heteroatom bonds to C or N. The oxidation potential of the $AlCl_3/H_2CCl_2$ system corresponds to a vertical ionization energy of ~8 eV,[5] and thus allows oxidation of a great variety of molecules containing donor substituents like trimethylsilyl groups. Therefore, also the prototype open-chain, bicyclic and bifunctional permethylated (R = CH_3) silylhydrazines can be oxidized without decomposition. The radical cations formed proved to be stable even at room temperature, and the discussion of their ESR spectra—based on an INDO open-shell hypersurface for the parent ion $H_2N\underline{\cdots}NH_2^{+\cdot}$—discloses different stabilizing structural changes during the oxidation process.


(1)

	1	2	3
IE_1	7.9 eV	7.15 eV	7.5 eV

Experimental Section

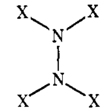
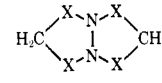
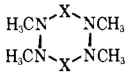
Photoelectron spectra have been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system, and are calibrated using the $Xe(^2P_{3/2})$ = 12.13 eV and the $Ar(^2P_{3/2})$ = 15.76 eV peaks.

Radical cation generation from the parent molecules, tetrakis(trimethylsilyl)hydrazine (**1**),[12a] 2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-2,4,6,8-tetrasilabicyclo[3.3.0]octane (**2**),[12b] and octamethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (**3**)[12c] has been carried out using $AlCl_3$ in H_2CCl_2 as selective oxidizing system.[11]

ESR spectra of the colorless, persistent radical cations $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ have been recorded using Varian 9 equipment. The hyperfine structure of the strong ESR signals becomes apparent upon dilution. The splitting parameters are calibrated using the $(KO_3S)_2NO\cdot$ coupling constant $2a_N$ = 2.618 mT, and are assumed to be correct within ±1% except for ^{29}Si of only 4.7% natural abundance with a limit of about ±5%. Investigation of the temperature dependence revealed that the spectrum of $\mathbf{2}^{+\cdot}$ shows a strong anisotropic broadening of the $M_N \neq 0$ lines even at room temperature;[11a] the unperturbed center line $M_N = 0$ exhibits temperature-dependent ^{29}Si and ^1H (CH_3, CH_2) splittings.[11a]

ESR spectra simulation could be achieved using the program ESPLOT,[11a] which contains some subroutines from the optimization program ESOP kindly provided to us by Professor v. Zelewsky of the University of Fribourg. Because of the unusual requirements for tri-

Table I. Vertical Ionization Energies IE_x (eV) to Radical Cation States of Silyl- and Alkylhydrazines with Predominant Nitrogen Lone Pair n_N Character and n_N/n_N Dihedral Angles ω (deg) Estimated from Their Differences $\Delta IE_{1,x}$ (eV) (cf. Text)

hydrazine derivative	$X = Si(CH_3)_n$				$X = CH_n$			
	IE_1	IE_x	$\Delta IE_{1,x}$	ω	IE_1	IE_x	$\Delta IE_{1,x}$	ω
	{7.95}[a]		≤0.2	~90[d]	8.27 8.38[a]	8.82 8.77[a]	0.55 0.39	~90[9b] 96[15a]
	7.15	9.00	1.85	~0[d]	7.87 7.90	9.44 9.47	1.57 1.57	~30[9b] 38[15b]
	7.5[a] {7.9}[a]	d			7.90[b] 8.45[c]	10.37[b] 9.00[c]	2.47 0.55	180[15b] 71[15b]

[a] Overlapping and undeconvoluted PES bands. [b] Assigned to a RNNR bridge with diaxial nitrogen lone pairs. [c] Assigned to a RNNR bridge with diequatorial nitrogen lone pairs. [d] Not analyzed (cf. text).

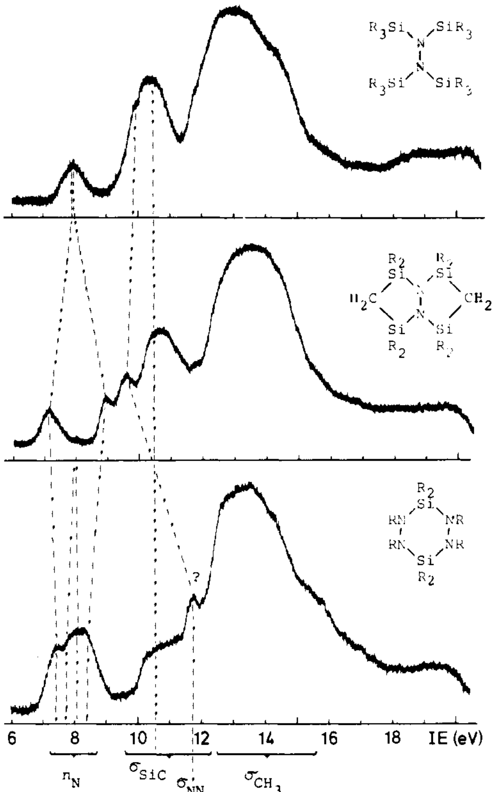


Figure 1. He(I) photoelectron spectra of tetrakis(trimethylsilyl)hydrazine (**1**), of 2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-2,4,6,8-tetrasilabicyclo[3.3.0]octane (**2**), and of octamethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (**3**), together with a tentative assignment.

methylsilyl-containing radical cations, the program capacity has been extended to incorporate up to 10^4 theoretical lines from up to 10^2 equivalent nuclei of eight different sorts. Its value may be exemplified by the analysis of the ESR spectrum of $1^{+\cdot}$ (Figure 2), which exhibits a nitrogen quintet and a partially resolved multiplet of the 36 equivalent trimethylsilyl hydrogens (Figure 2B). Simulation of this multiplet with $a_H = 0.013$ mT and a line width of 0.020 mT resulted in satisfactory overlap except that the line shape remained too narrow unless a ^{29}Si coupling ($I = 1/2$, 4.7% natural abundance) $a_{^{29}Si} = 0.16$ mT had been included.

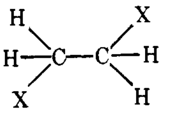
INDO open-shell calculations were performed based on the standard INDO version[13a] coupled to an automatic coordinate change program followed by a Fletcher/Powell geometry optimization subroutine.[13b] Minor modifications concerned input data (distances d_{xy} and angles α and ω and specified variations Δd_{xy} and $\Delta\alpha,\omega$), eligible convergence criteria (used here: $\Delta E_{total} \ll 10^{-8}$ au), and connection to a plot program[13c] for graphical representation of the results. The isotropic proportionality factors, which have been optimized for INDO calculations,[13a] amount to $Q_{^1H} = 53.9864$ mT and $Q_{^{14}N} = 37.9356$ mT. The above program system is available on request.

To compute the hypersurfaces of N_2H_4 and $N_2H_4^{+\cdot}$, the hardly feasible 12 molecular degrees of freedom have been combined into 4 (cf. Figure 4)—the HNH bond angle α, the H_2N group out-of-plane angle β, the dihedral angle ω, and the distance d_{NN}—assuming that both the center of inversion and the mirror plane may be preserved during the distortions. As concerns the assumed constant bond lengths $d_{NH} = 107$ pm, additional calculations including NH bond length optimization demonstrate that small changes exert only negligible effects on the total energy and also on the more sensitive coupling constants. The angles were varied between $\alpha = 95$ and 125° by $\Delta\alpha = 5°$, $\beta = 0–30°$ by $\Delta\beta = 7.5°$, and $\omega = 0–180°$ by $\Delta\omega = 30°$, and the NN bond lengths always optimized using the Fletcher/Powell subroutine. The computations, carried out at the Univac 1108 of the Hochschul-Rechenzentrum of the University of Frankfurt, required 4.6 s CPU time per function value and approximately 30 s for each of the 245 optimized points on the hypersurface. The total energy minimum for $N_2H_4^{+\cdot}$ is found at $\alpha = 120°$, $\beta = 0°$, $\omega = 0°$, $d_{NN} = 128$ pm, and $d_{NH} = 107$ pm. For the neutral molecule N_2H_4, a dihedral angle $\omega = 90°$ is calculated, in close agreement with the experimental value.[14]

Spectroscopic Data and Discussion

Photoelectron spectra of the permethylated silylhydrazines **1**, **2**, and **3** are displayed in Figure 1; their lowest ionization potentials to radical cation states with predominant nitrogen lone pair contribution are compared to those of analogous alkyl derivatives[9b,e,15] in Table I.

The PE spectra of alkylsilyl-substituted hydrazines (Figure 1) exhibit only a few distinct bands and are dominated by broad ionization humps consisting of numerous overlapping peaks. According to a useful rule of thumb,[16] essentially only p-type valence ionizations show up within the He(I) spectral region below 21.21 eV, so that, e.g., for tetrakis(trimethylsilyl)hydrazine ($C_{12}H_{36}N_2Si_4$) about 37 of the total 55 will be observed. Roughly subdividing along the energy scale, radical cation states of the following predominant contributions are expected: nitrogen lone pairs n_N below 9.5 eV,[1,2,9b,f,15-17] SiC skeleton σ_{SiC} around 10 eV,[18,19] SiN bonds σ_{SiN} above 11 eV,[19] methyl groups σ_{CH_3} from 12 to 15 eV,[16] and σ_{CN} bonds above 15 eV.[17,20] For the NN bond ionization, which has been assigned in 1,1-dimethylhydrazine at 13 eV,[17] a considerable lowering is predicted by comparing substituent effects on the first ionization of ethane (2). Thus the (largely inductive)

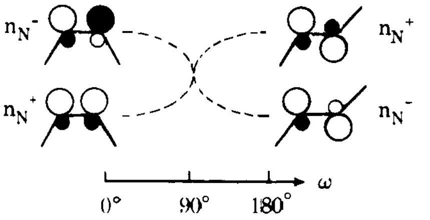

$$H_2XC{-}CXH_2$$

$IE_1(\sigma_{CC})$

X =	H	CH_3	SiR_3	(2)
	12.1 eV[21]	11.2 eV[21]	8.7 eV[22]	

perturbation difference of one trimethylsilyl relative to one methyl group should amount to more than 1 eV, and, therefore, the σ_{NN} ionization should be shifted down to below 10 eV on tetrasilyl substitution and below 12 eV on monosilylation (Figure 1).

The vertical ionization energies of the hydrazine n_N lone pairs $IE_{1,x}$ and their splitting patterns $\Delta IE_{1,x}$ (Table I) supply some clues to the molecular ground-state geometry as elaborated for alkyl derivatives.[9b,f,15] In general, the dihedral angle ω between the nitrogen lone pairs as rationalized by the somewhat oversimplified[9f,23] MO model (3) correlates satisfactorily with the ionization energy difference:[15]



(3)

$$IE_{1,x} = IE(n_N^+) - IE(n_N^-) = A^R \cos\omega + B^R \qquad (4)$$

$$A^R = 2.2 \text{ eV}; B^R = -0.15 \text{ eV}$$

This regression can be adopted for the methylsilyl-substituted hydrazines under the following assumptions: (i) in contrast to alkylhydrazines[14] and alkylamines, nitrogen centers connected to at least two silyl substituents exhibit an essentially planar configuration,[24,25] and therefore in sterically overcrowded permethylated derivatives like **1** and **2** this even should be enforced; (ii) the bicyclic tetrasilylhydrazine supposedly contains a virtually planar ring skeleton ($\omega \sim 0°$) owing to the steric restraint of the ring closing CH_2 bridges; (iii) the alkyl parameters in eq 4 $B^R = B^{SiR_n}$ are transferable. If the above assumptions are valid, then the ionization potentials IE_1 and IE_2 of the bicyclic tetrasilylhydrazine (Table I) yield the parameter $A^{SiR_n} = 2.0$ eV, and dihedral angles may be approximated by insertion of the values $IE_{n,x}$ into the modified regression:

$$\frac{IE(n_N^+) - IE(n_N^-) - B^{SiR_B}}{A^{SiR_3}} = \frac{IE_{n,x} + 0.15}{2} = \cos\omega \qquad (5)$$

For the open-chain tetrasilylhydrazine **1**, which exhibits $\Delta IE_{1,2} \sim 0$ eV (Figure 1 and Table I), a dihedral angle $\omega \sim 86°$ is predicted by (5); i.e., the bulky moieties $-N(Si(CH_3)_3$ expectedly are almost perpendicular to each other, in good agreement with the value $\omega = 82.5°$ determined for $(H_3Si)_2NN(SiH_3)_2$.[24]

For the six-membered derivative, octamethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (**3**), several possible conformations have to be considered.[15b] The rather broad and unstructured ionization band observed in the photoelectron spectrum (Figure 1) and assigned to the four nitrogen lone pair ionizations would be in accord with an assumption of a mixture of conformers in the gaseous phase.

The molecular ground-state geometries of the three prototype silylhydrazines (1), which are partly deduced from their vertical ionization patterns (Table I), are supported by steric considerations. Thus the dihedral angle $\omega \sim 90°$ resulting for the open-chain tetrasilylhydrazine **1** can be traced back to the bulkiness of the $(H_3C)_3Si$ substituents, which in addition to $\pi(N \rightleftarrows Si)$ charge delocalization[25] is responsible for the flattening of the $NNSi_2$ pyramid.[25] On the other hand, the bicyclo[3.3.0]octane derivative **2** with its two bridged five-membered rings must be close to planar. This structure contains two almost collinear nitrogen lone pairs n_N, which are responsible for the substantial lowering of the vertical first ionization potential relative to **1** (Table I): the n'_N/n_N interaction destabilizes the molecular ground state, but facilitates the stabilizing charge delocalization in the radical cation ground state. Contrary to **1** and **2**, the tetraazadisilacyclohexane derivative **3** differs considerably from its CH_2 analogue (Table I): the axial/axial + equatorial/equatorial n_N lone pair arrangement (A) of the latter[26] has been changed presumably to a mixture of conformers. This structural modification accompanying the $CH_2 \rightarrow Si(CH_3)_2$ replacement may not only reduce the enhanced n_N^{Si}/n_N^{Si} interaction but also the steric interference between the eight methyl groups then present.

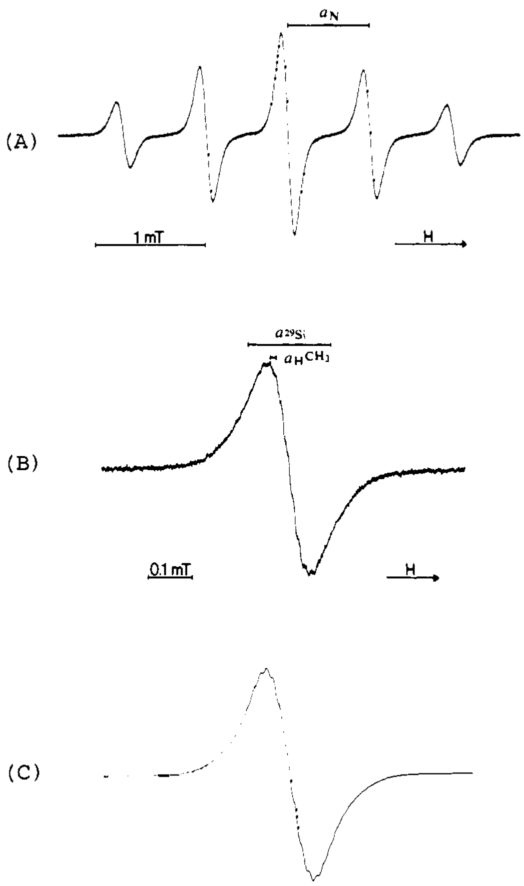


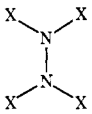
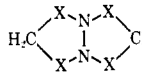
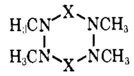
Figure 2. ESR spectrum of the radical cation generated by $AlCl_3/H_2CCl_2$ oxidation from tetrakis(trimethylsilyl)hydrazine (**1**) at 300 K (A), the high-resolution center line (B), and its computer simulation (C).

Electron spin resonance spectra of the silylhydrazine radical cations $1^{+\cdot}$ and $2^{+\cdot}$ together with their improved[2] computer simulation are shown in Figures 2 and 3; the spectrum of $3^{+\cdot}$ has been published previously.[1] The coupling constants obtained are summarized in Table II together with those of the corresponding CH_n analogues.[9c,e] All three prototype silylhydrazines (1) are easily oxidized by $AlCl_3$ in H_2CCl_2 solution[11] (cf. Experimental Section) as well as by $SbCl_5$ or $AgBF_4$ or electrochemically in a mixture of butyronitrile/propionitrile containing $Bu_4N^+BF_4^-$. The radical cations generated are unexpectedly stable: if sealed in ampules, their ESR signals remain for months, and in 1,2-dichlorobenzene solution they even can be observed at 120 °C.

The ESR spectrum of tetrakis(trimethylsilyl)hydrazine radical cation $1^{+\cdot}$ (Figure 2A) displays the expected nitrogen quintet. Upon dilution the multiplet of the 36 $Si(CH_3)_3$ protons appears (Figure 2B). To simulate the ESR spectrum, an additional ^{29}Si coupling (natural abundance 4.5%, $I = \frac{1}{2}$) has to be included (Figure 2C).

The ESR spectrum of the bicyclic silylhydrazine radical cation $2^{+\cdot}$ (Figure 3A) is also dominated by the nitrogen quintet. On high resolution (Figure 3A), the additional coupling due to 24 and to 4 equivalent protons, respectively, as well as due to a ^{29}Si isotope-labeled species, becomes visible (Figures 3B,C). In addition, a strong temperature dependence is observed (Table II, footnote *b*), showing up especially in a

Table II. ESR Coupling Constants a (mT) of Silylhydrazine Radical Cations ($X = Si(CH_3)_n$) and of the Alkyl Analogues ($X = CH_n$)[9c,e]

hydrazine derivative	$X = Si(CH_3)_n$					$X = CH_n$				
	$a_{^{14}N}$	$a_H^{NCH_3}$	$a_{H(\gamma)}^{CH_2}$	$a_H^{SiCH_3}$	$a_{^{29}Si}$	$a_{^{14}N}$	a_H^{NCH}	$a_{H(\beta)}^{CH_2}$	$a_{H(\gamma)}^{CH_2}$	ref
	0.752			0.013	0.16	1.34	1.27			9c
	0.868		0.04[a]	0.030	0.5[b]	1.76		1.56	0.08	9c
	1.050[c]	1.375[d]		(0.03)[e]	0.5	1.456[c]	1.343[d]	1.567		9e

[a] Temperature dependent (300 K, 0.038 mT; 170 K, 0.043 mT). [b] Temperature dependent (300 K; 0.485 mT; 180 K, 0.515 mT). [c] Observed quintet (2 N). [d] Observed septet (6 H). [e] Assumed $SiCH_3$ proton coupling.

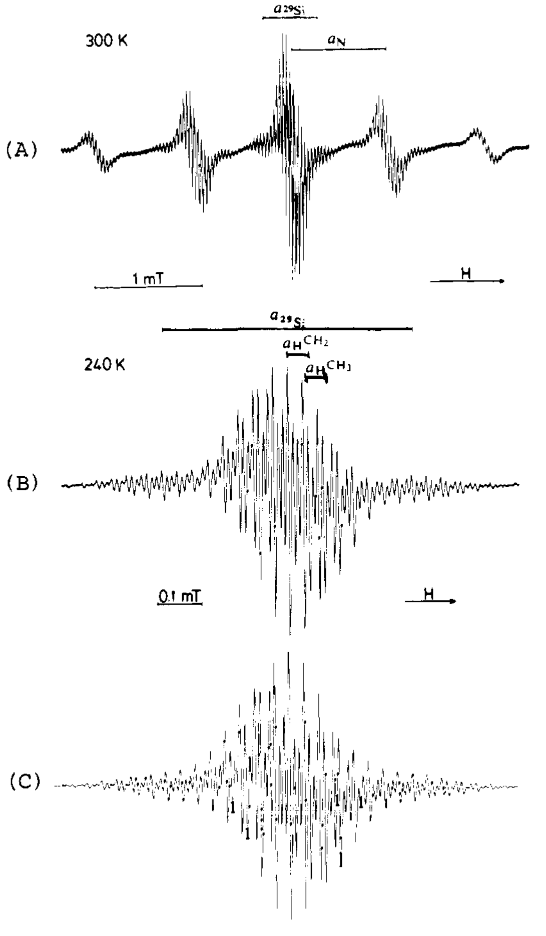
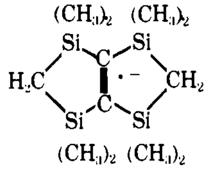


Figure 3. ESR spectrum of the radical cation generated by $AlCl_3/H_2CCl_2$ oxidation from 2,2,4,4,6,6,8,8-octamethyl-1,5-diaza-2,4,6,8-tetrasilabicyclo[3.3.0]octane (**2**) at 300 K (A), the high-resolution center line at 240 K (B), and its computer simulation (C).

strong anisotropic broadening of the outer lines of the N quintet.[11a]

The radical cation of the octamethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane $\mathbf{3}^{+\cdot}$ gives rise to an ESR spectrum (cf. ref 1) with surprisingly few lines: only six equivalent protons and two equivalent nitrogens couple. On high resolution, the ^{29}Si satellites and additional hyperfine structure due to the $Si(CH_3)_2$ hydrogens and at least one other coupling, presumably from the -RNNR- bridge opposite, can be detected. To explain this result, one has to assume that the spin population is confined to only one $-R_2SiRNNRSiR_2-$ linkage of the six-membered ring.

Comparison of the ESR coupling constants with those for the analogous alkyl derivatives reported by Nelsen and coworkers[9c,e] reveals considerable differences (Table II). In general, the nitrogen coupling is much smaller in the iso(valence)electronic silylhydrazine radical cations, which can be rationalized by the ($N \overset{\curvearrowleft}{\leftarrow} Si$) bonding components already introduced to discuss the photoelectron spectra. This R_nSi substituent effect, which also has been observed for radicals[27a] and radical anions,[27b] is of about the same order of magnitude as the spin delocalization into adjacent phenyl rings.[28] The bicyclic derivatives with $X = Si(CH_3)_2$ and with $X = CH_2$[9e] exhibit especially large differences despite their formal relationship, as is further illustrated best by the doubled value of the N coupling constant a_N of the latter (Table II). Even the isoelectronic ethylene radical anion with $X = Si(CH_3)_3$[29] is


(A)

$$a_{H(\gamma)}^{CH_2} = 0.048 \text{ mT}$$
$$a_{^{29}Si} = 0.672 \text{ mT}$$
$$a_H^{SiCH_3} = 0.048 \text{ mT}$$

more closely related in its spin distribution. For the two 1,2,4,5-tetraazacyclohexanes with $X = Si(CH_3)_3$ and $X = CH_2$,[9e] coupling of only two equivalent nitrogens and of six equivalent hydrogens can be detected. Accordingly, the spin density must be localized in one of the two dimethylhydrazine bridges—an assumption supported by comparable coupling constants, $a_N = 1.47$ mT and $a_H^{NCH_3} = 1.26$ mT, observed for (*Z*)-1,2-dimethylhydrazine radical cation.[30a] Therefore, intramolecular electron transfer between the two dimethylhydrazine subunits must be slow within the ESR time scale of $\sim 10^{-6}$ s.[9e]

Summarizing, the ESR spectra of the exemplary silyl radical cations $\mathbf{1}^{+\cdot}$, $\mathbf{2}^{+\cdot}$, and $\mathbf{3}^{+\cdot}$ are completely analyzed (Figures 2 and 3, Table II) and can be assigned with the help of computer simulation (Table II). Nevertheless, comparison of the coupling constants raises several questions, e.g., why the ^{29}Si coupling constant triples from the open-chain derivative $\mathbf{1}^{+\cdot}$ to the bicyclic system $\mathbf{2}^{+\cdot}$ although the ^{14}N splitting changes only little, or why the ^{14}N coupling increases in the silylhydrazine radical cations in the sequence $\mathbf{1}^{+\cdot} < \mathbf{2}^{+\cdot} < \mathbf{3}^{+\cdot}$, contrary to the one for the corresponding alkyl analogues (Table II). To obtain an answer, one obviously has to investigate the geometry dependence of the $R_2N\text{-}NR_2^{+\cdot}$ coupling constants.

$H_2N\text{-}NH_2^{+\cdot}$ INDO open shell hypersurface calculations (cf. Experimental Section) have been performed to elucidate how structural changes in hydrazine radical cations will affect both the ^{14}N coupling constants as well as those of the adjacent atoms like ^{1}H (Figure 4). Our calculations, in which the 12 degrees of freedom for a hexaatomic molecule have been either assumed to be constant (d_{NH}) or symmetry contracted down to 4 (cf. Experimental Section) reproduced the ground-state geometry of H_2NNH_2 ($\omega \sim 90°$) and of $H_2NNH_2^{+\cdot}$ ($\omega \sim 0°$). The flattening of the nitrogen pyramid upon removal of an electron is a well-known phenomenon also for other chemically related compounds like ammonia radical cation $H_3N^{+\cdot}$.[4]

In this context with INDO results by Nelsen and co-workers[9c] deserve some comment. Although obviously similar to ours, they were interpreted on the assumption that INDO might "not give the proper conformation as having the lowest total energy". Accordingly, from a comparison of experimental coupling constants[6] and the INDO results, the authors suggested a nonplanar, eclipsed structure with a bending angle $\beta = 11°$. In our opinion, INDO values in general, but especially the calculated coupling constants, are much too far from being accurate to base on them such detailed statements. Instead we rather like to point out the general trend as illustrated by the three-dimensional plots (Figure 4). Returning to the bending angle $\beta = 11°$, it has been suggested also from the INDO total energy minimum assuming a N-N distance of 140 pm.[9c] In our calculations, which include geometry optimization for every single point, the total energy minimum unambiguously correlates to a fully planar configuration with an N-N distance of 128 pm[11a]—just as verified later on by the structure determination of the tetraalkylhydrazine radical cation quoted,[9i] which yielded the experimental bond length $d_{NN} = 126.9\ (7)$ pm. The effect of the $H_2N\overset{\cdots}{-}NH_2^{+\cdot}$ structural changes on the INDO open shell coupling constants (Figure 4) may be summarized as follows: (i) with increasing dihedral angle ω, the coupling constant $a_{^{14}N}$ decreases less steeply (Figure 4A: minimum $\omega \sim 90°$) than $a_{^{1}H}$ (Figure 4B: minimum $\omega \sim 53°$); (ii) at $\omega = 90°$, $a_{^{14}N}$ exhibits a minimum (Figure 4A) and $a_{^{1}H}$ a maximum (Figure 4B); (iii) both $a_{^{14}N}$ and $a_{^{1}H}$ are rather insensitive to changes of the HNH angle α (Figures 4A,B); (iv) with increasing angle β, the coupling $a_{^{14}N}$ increases continuously (Figure 4C), but $a_{^{1}H}$ only around $\omega \sim 90°$ (Figure 4D).

Interestingly, the peculiar dependence of a_H on the dihedral angle ω most likely reflects a changeover in the mechanism of the spin distribution to the hydrogens: at $\omega = 0°$, spin polarization induces a negative spin density, whereas at $\omega = 90°$ hyperconjugation gives a positive spin density.

These trends calculated by open-shell INDO allow us to rationalize most known ESR data of hydrazine radical cations $R_2N\text{-}NR_2^{+\cdot}$. Thus, the experimental coupling constants for $H_2N\text{-}NH_2^{+\cdot}$, $a_{^{14}N} = 1.15$ and $a_{^{1}H} = 1.47$ mT,[6] compare reasonably with the INDO values at minimum total energy (cf. Experimental Section), $a_{^{14}N} = 1.06$ and $a_{^{1}H} = 1.10$ mT, respectively. Relative to $(H_3C)_2N\text{-}N(CH_3)_2^{+\cdot}$ as well as to other sterically unhindered alkylhydrazine radical cations,[9c,e,h] the overcrowded, and, therefore, presumably strongly twisted 1,2-di(*tert*-butyl)-1,2-dimethyl derivative shows the smallest nitrogen coupling of only $a_{^{14}N} = 1.19$ mT[9c] observed so far for alkylated species (cf. Table II, X = CH_n), in good agreement with the trend illustrated in Figure 4A. On the other hand, radical cations of five-membered-ring alkylhydrazines, and especially those of bicyclic compounds, cannot achieve planarity around the nitrogens for conformational reasons,[9c] and therefore possess, as $a_{^{14}N}$ increases with the bending angle β (Figure 4C), relatively large nitrogen coupling constants (cf. Table II, X = CH_n). The correlation between nitrogen coupling constants and bending angle has been investigated in detail both for amine radical cations[32] and hydrazine radical cations.[9c]

The ESR coupling constants of our prototype silylhydrazine radical cations also fit well into the overall model deduced from the three-dimensional INDO coupling constant tables (Figure 4). This includes again the assumption that the configuration around $NNSi_2$ is (and remains) essentially planar, not only because of the reasons outlined earlier, but also because electron removal should flatten the N pyramid. Furthermore, a bending would cause increased steric interference between the bulky permethylsilyl groups, which is known to result in an unusually high ratio $a_{^{29}Si}/a_H$ both in radical anions[33] and radical cations;[34] no such effect is observed here. The difference of coupling constants between the virtually planar $\mathbf{2}^{+\cdot}$ and the open-chain derivatives $\mathbf{1}^{+\cdot}$ should therefore be caused primarily by the change in the dihedral angle ω. The decrease of a_N in going from $\mathbf{2}^{+\cdot}$ to $\mathbf{1}^{+\cdot}$ and in particular the considerable decrease of a_{Si} from about 0.50 to 0.16 mT suggest that ω deviates considerably from 0° in the tetrakis(trimethylsilyl)hydrazine radical cation. If a proportionality between a_H from the INDO calculations on $N_2H_4^{+\cdot}$ and $a_{^{29}Si}$ *were* present, a dihedral angle of $\omega \sim 45$ would result[1] (Figure 4). In any case, however, an energetically preferred planar conformation for tetrakis(trimethylsilyl)hydrazine radical cation is prevented by a considerable steric interference of the bulky $(H_3C)_3Si$ groups, and a structure with an intermediate dihedral angle results in solution.

In contrast to the joint discussion of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ or of their alkyl analogues, the tetraazadisilacyclohexane radical cation $\mathbf{3}^{+\cdot}$ and the corresponding hexahydrotetrazine species[9c] (Table II, X = $Si(CH_3)_2$, CH_2) offer hardly any common features, especially because no ^{13}C coupling constants could be detected so far for alkylhydrazines. The nitrogen coupling constant of $\mathbf{3}^{+\cdot}$, $a_N = 1.050$ mT (Table II), is halfway between tetrasilyl and tetraalkyl derivatives, and the identical ^{29}Si coupling of $\mathbf{2}^{+\cdot}$ and $\mathbf{3}^{+\cdot}$, therefore, may be considered as being rather accidental.

Altogether, the INDO open-shell calculations for $H_2N\text{—}NH_2^{+\cdot}$, in which all angles have been varied and the N-N distance was always optimized, helped to interpret the ESR data: they reproduce the planarization of the >N-N< skeleton during the oxidation of hydrazine derivatives, eluci-

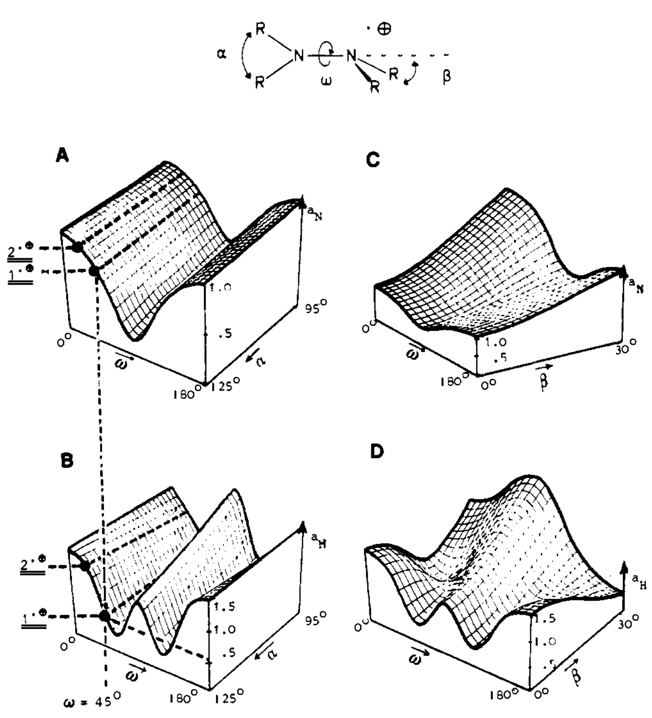
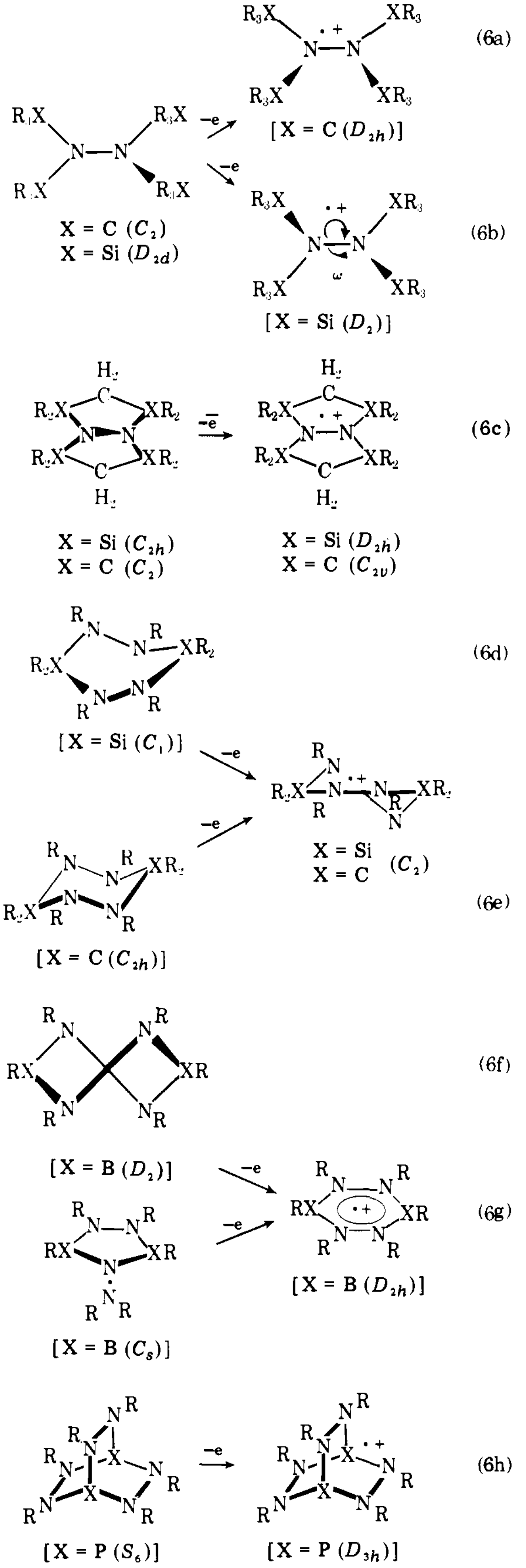


Figure 4. Three-dimensional tables of INDO open-shell coupling constants $a_{^{14}N}$ and $a_{^{1}H}$ as a function of the dihedral angle ω and of the HNH angle α (A and B), or of the twist angle β (C and D). For the structure approximation of $\mathbf{1}^{+\cdot}$ in solution (---) see text.



(Symmetry groups given in brackets characterize only the (R)NN(X) subunits and are deduced mostly from spectroscopic data; cf. text. All R = CH_3 except for (6a) where R = H.)

date the rather complex angular dependence of the individual coupling constants, and even allow, e.g., for tetrasilylhydrazine radical cation $\mathbf{1}^{+\cdot}$, an approximation of its structure in solution.

Structural Changes and Spin Distribution

The structural changes observed during the adiabatic oxidation of our prototype silylhydrazines (6b–d) as well as those deduced from recently published ESR data for derivatives with substituents X = BR,[1,3] CHR,[9c,e] or P[1,35] (6a,c,e–h), can be rationalized on the basis of the INDO closed- and open-shell calculations (cf. Experimental Section). Accordingly, the ground state of unstrained hydrazine derivatives is energetically favored in a conformation ($\omega \sim 90°$) with the two nitrogen lone pairs perpendicular to each other,[14,36] and that of the corresponding radical cations in a planar one ($\omega \sim 0°$). Steric factors, however, can play a dominating role[1,9,10,15,37] as demonstrated by the differing examples (6).

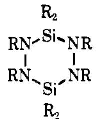
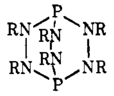
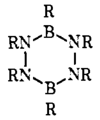
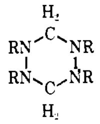
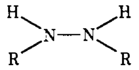
(a,b) Open-chain hydrazines supposedly possess structures with a $>$N-N$<$ skeleton of approximately C_2 symmetry,[9b,14] and, if the nitrogen pyramids are flattened ($\beta \rightarrow 0°$) as in polysilyl derivatives[24]—cf. the assignment of the PE spectra—approximately D_{2d} ($\omega \sim 90°$, $\beta \sim 0°$). Removal of an electron yields a radical cation, the $>$N-N$<^{+\cdot}$ skeleton of which, in general, will be close to planar (D_{2h}: $\omega \sim 0°, \beta \sim 0°$), unless bulky substituents sterically interfere, and—as has been discussed in detail for $\mathbf{1}^{+\cdot}$ (Figure 4)—then permit only intermediate dihedral angles $90° > \omega > 0°$ (6b).

(c) Bicyclic hydrazine derivatives display conformations which strongly depend on ring size and on substituents.[37] For the alkyl derivative (6c, X = C) a dihedral angle $\omega \sim 30°$ [9b] has been estimated, and the X_2NNX_2 bridge exhibits C_2 symmetry. On the other hand, the bicyclic tetrasilylhydrazine **2**, with two connected five-membered rings, should be—as suggested by stereomodels—close to planar. Oxidized $\mathbf{2}^{+\cdot}$ most probably achieves full planarity (D_{2h}: $\omega = 0°$, $\beta = 0°$), whereas the corresponding carbon analogue (6c) is still puckered with a C_{2v} arrangement of the $C_2N\text{-}NC_2{}^{+\cdot}$ bridge.[9c]

(f,g) Discussion of the six-membered-ring hydrazine derivatives starts advantageously with the boron compounds (6f and 6g). For the 3,6-bis(dimethylamino) derivative of 1,2,4,5-tetraaza-3,6-diboracyclohexane (6f), the structure of D_2 symmetry has been proven by X-ray.[38] Oxidation should level out the -(R)NN(R)- bridges, which connect the planar BN_2 subunits, yielding either rapidly inverting boat or twist conformations, or, as suggested by the dark-blue color developing on oxidation, more probably a completely planar six-center/seven-electron π system. This radical cation would be isoelectronic to benzene radical anion, with the degeneracy removed due to its D_{2h} symmetry. Energetically, this species must be quite favorable because it is also produced by oxidative isomerization from the corresponding five-membered ring analogue (6g).

(h) The structure of the bicyclic phosphine, 2,3,5,6,7,8-hexamethyl-2,3,5,6,7,8-hexaaza-1,4-diphosphabicyclo[2.2.2]-octane (6h), belongs to the S_6 symmetry group with the methyl groups staggered.[39] Upon adiabatic electron removal the PN skeleton is expected to maintain D_{3h} symmetry; the arrangement with each of the six-membered rings in boat conformation is obviously well suited for rapid electron transfer within the ESR time scale, leading to the six equivalent nitrogens observed[1,30] (Table III). The possibility that (6h) might be a Dabco-like species, with an electron removed from an orbital made up of the symmetric combination of the P lone pairs and the NN σ bonds,[40] can be disproved both by PES analysis[41] and with ESR arguments:[35] Phosphorus lone pairs display too little conjugation to yield an effective lowering of the first ionization potential[42] and the Dabco-like orbital is assigned to an ionization at ~9.5 eV.[41] In addition, much larger ^{31}P coupling constants and completely different ^{14}N and ^{1}H couplings should result for such a radical cation; the n_N lone pair combination a_2'' is in very good agreement with the observed ESR results.[1,35]

Table III. ESR Coupling Constants a (mT) of RNNR Bridged Heterocycles and of (Z)-1,2-Dimethylhydrazine, Their Sums, and the Effective (s) Spin Density at the Heteroatom Centers $\rho(O)_X$

radical cation	ref	$a_{^{14}N}$	$a_H^{NCH_3}$	a_X	$\sum_N a_{^{14}N}$	$\sum_H a_H^{NCH_3}$	$\rho(O)_X = \sum_X a_X/A_X^{iso}$ [a]
	1	1.050 (2 N)	1.375 (6 H)	0.5 (^{29}Si)	2.100	8.250	0.0083
	1, 35	0.402 (6 N)	0.505 (18 H)	1.9 (^{31}P)[b]	2.412	9.090	0.0105
	1, 3	0.690 (4 N)	0.793 (12 H)	0.32 (^{11}B)	2.760	9.516	0.0089
	9e	1.456 (2 N)	1.343 (6 H)	[c]	2.912	8,058	
	43	1.47 (2 N)	1.26 (6 H)	[c]	2.94	7.56	

[a] The isotropic hyperfine coupling constants employed are $A_{^{11}B}^{iso}$ = 72.0, $A_{^{29}Si}^{iso}$ = 120.8, and $A_{^{31}P}^{iso}$ = 363.6 mT.[44] [b] Temperature dependent.[35] [c] Not determined.

(d,e) Most intricate among the six-membered hydrazine derivatives are the silicon and carbon derivatives (6d and 6e). Their molecular ground-state structures have been estimated from their PES ionization patterns for X = Si to contain a mixture of conformers and for X = C to prefer an axial/axial-equatorial/equatorial conformation.[9b,15b,26] Adiabatic oxidation produces their radical cations with the spin distributed each over only one -RN-NR-$^{+\cdot}$ bridge (Figure 4, Tables II and III), suggesting a half-chair conformation (6d,e). The preference of a C_2 structure is further supported by the fact that the ESR spectrum remains unchanged between 180 and 310 K; this temperature independence is due to a considerably increased lifetime to the C_2 conformers and therefore can be traced back to the extensive conformational changes necessary for rapid electron transfer.[9b] Recently, it has been demonstrated that electron transfer from hydrazines with parallel lone pairs to a solid electrode is orders of magnitude faster than from those with gauche lone pairs.[9j]

How will these pronounced structural differences (6a-6h) affect the spin distribution in the individual hydrazine radical cations? Comparison of the experimental data (Table II) offers hardly any straightforward generalization: as pointed out already in the discussion of the ESR coupling constants of the prototype silylhydrazine radical cations and their alkyl analogues (Table II and Figure 5), the geometry around the nitrogen centers (ω, β, α) in general differs in differently substituted subunits like -NSi$_2$ and -NC$_2$. This, in return, leads to structural differences in the otherwise chemically related compounds, showing up, e.g., in the values a_X (Table II) for the bicyclic five-membered-ring species with X = CH$_2$ and X = Si(CH$_3$)$_2$. On the other hand, the spin population in the isoelectronic ethylene radical anion[5a,29] (A) closely resembles that in the hydrazine radical cation **2**$^{+\cdot}$ (Table II): the slight reduction in the peripheral coupling constants indicates only a small increase in the spin density of the central bond $>C{-}C<^{-\cdot} \rightarrow >N{-}N<^{+\cdot}$ due to the increase in the effective nuclear charge C → N.

Among all the hydrazine derivatives discussed, the six-membered-ring radical cations containing two or three bridges -(H$_3$C)NN(CH$_3$)- and that of 1,2-dimethylhydrazine[43] are best suited for a comparison of their spin distributions. Their total coupling constants $\Sigma_N a_{^{14}N}$ and $\Sigma_H a_H^{NCH_3}$ are given in Table III. Furthermore, the heteroatom total coupling $\Sigma_X a_X$ has been divided by the isotropic hyperfine coupling constants A_X^{iso} (Table III, footnote a)[44] to obtain the effective (s) spin densities $\rho(O)_X$ (Table III).

From these data (Table III) one notes that most of the spin density is centered at the nitrogens as revealed both by the total nitrogen coupling[45] and the total N(CH$_3$) hydrogen[46] coupling, that the small, presumably negative, X spin populations may contribute to increased $a_H^{NCH_3}$ values relative to (H$_3$C)HN-NH(CH$_3$)$^{+\cdot}$, and that the heteroatoms X are located more or less in nodal planes. Therefore, the spin distribution in the six-membered-ring hydrazine radical cations may be represented—in a qualitative and rather generalizing approach, which neglects, e.g., the conformational differences discussed—by a completely antibonding nitrogen lone pair combination as the highest occupied molecular orbital, in accordance with the assignment of the corresponding radical cation ground state to the first ionization in the photoelectron spectra.

Concluding remarks

The structural changes of the three prototype silylhydrazines (1) during oxidation—supplemented by recently published ESR data for chemically related compounds[1-3,9c,e,30b]—constitute an exemplary story of how molecules may reorganize on ion formation, i.e., by varying the number of their valence electrons (6), and consequently their energy.

As exemplified again and again, the energetically favored ground-state conformations of unstrained hydrazines like **1** ($\omega \sim 90°$) and of their radical cations like **2**$^{+\cdot}$ ($\omega \sim 0°$) are modified by dominating steric factors; thus, the bicyclic tetrasilylhydrazine **2** containing two connected five-membered rings possesses a structure close to planar, whereas six-membered rings with RNNR bridges like **3** may exhibit a variety of dihedral angles ranging from $\omega \sim 60°$ to $\omega \sim 180°$. The reverse argument holds for the oxidized species: bulky substituents like (H$_3$C)$_3$Si groups in **1**$^{+\cdot}$ or sterically induced rigidity as in $3^{+\cdot}$ may prevent the otherwise favorable formation of a flat >N–N<$^{+\cdot}$ skeleton.

Displaying several novel facets, the story of the structural changes of hydrazine derivatives during their oxidation adds to the already accumulated experience that acquisition or loss of electrons produces new species with different charge distribution in their states of various energy.[4] And again, limitations of oversimplified MO models—as useful as they are for a general overview and especially for planar π systems or vertical excitations—are exposed for adiabatic processes accompanied by nonnegligible relaxation phenomena.

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