Bis(trimethylsilyl)diazene Revisited. Density Functional Theory (DFT) Calculations of Nitrogen NMR Parameters of Some Azo-Compounds

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ABSTRACT: *Calculations of nitrogen NMR parameters [chemical shifts δN and indirect nuclear spin–spin coupling constants J(N,N), J(N,^{13}C), J(^{29}Si,N)] of noncyclic azo-compounds R^1—N=N—R^2 (R^1, R^2 = H, Me, Ph, SiH$_3$, SiMe$_3$) and cyclic azo-compounds [N=NCH$_2$, N=N(CH$_2$)$_3$ N=N(CH$_2$)$_2$SiH$_2$, and N=N(SiH$_2$CH$_2$SiH$_2$)] by density functional theory (DFT) methods [B3LYP/6-311+G(d,p) level of theory] provide data in reasonable agreement with experimental values. The influence of* cis- *and* trans-*geometry is reflected by the calculations, and amino-nitrenes are also included for comparison. The spin–spin coupling constants are analyzed with respect to contact (Fermi contact term, FC) and noncontact contributions (paramagnetic and diamagnetic spin-orbital terms, PSO and DSO, and spin-dipole term, SD). Bis(trimethylsilyl)diazene* **6a** *can be generated by an alternative method, using the reaction of bis(trimethylsilyl)sulfur diimide with bis-(trimethylsilyl)amino-trimethylsilylimino-phosphane.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:84–91, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20075

INTRODUCTION

Reactivity, intriguing structural properties, photochemistry, applications as dyes, and attractive spectroscopic features of azo-compounds [1–3] have stimulated intensive research work for many decades. Our interest has focused on NMR parameters of azo-compounds [4], since these data can be related to molecular and electronic structures. If the n → π* and π → π* electronic transitions are well separated, there is a crudely linear correlation of the chemical shifts δN with the energy of the n → π* transition [4,5]. Coupling constants for azo-compounds are less well understood. Some values $^1J(^{15}N,^{15}N)$ have been measured for azobenzene derivatives [6–8], and for one example with *trans*-geometry a negative sign of $^1J(^{15}N,^{15}N)$ has been determined [8]. However, for many azo-compounds R^1—N=N—R^2 with R^1 = R^2, the determination of $^1J(N,N)$ is difficult, even for doubly ^{15}N labeled species. The discussion of these data is limited, since the sign of $^1J(N,N)$ is unknown in most cases. Moreover, there is no experimental access to the contact (Fermi contact term, FC) and noncontact contributions (spin-orbital terms, SO, and spin-dipole term, SD) [9,10]. The latter may play an important role for $^1J(N,N)$ because of the N=N bond and the mutual influence of the lone pair of electrons at both nitrogen atoms. Similar questions arise with respect to $^1J(N,^{13}C)$ or $^1J(^{29}Si,N)$ in alkyl-, aryl-, or silyl-substituted azo-compounds. Furthermore, there are no experimental data available for

$^3J(^{13}C,^{13}C)$, $^3J(^{29}Si,^{13}C)$, or $^3J(^{29}Si,^{29}Si)$ across the N=N bond. All this indicates that azo-compounds are an attractive challenge for theoretical calculations of NMR parameters. If reliable experimental values can be reproduced, these calculations may be used to predict data that are difficult to obtain otherwise. It has been shown that the calculation of nuclear magnetic shielding provides fairly accurate data or at least predicts most trends correctly [11–13]. In this context, the extreme nuclear magnetic deshielding of nitrogen in $Me_3Si-N=N-SiMe_3$ **6a** ($\delta N = +615$) [4] or in N-(2,2,6,6-tetramethylpiperidyl)nitrene **15** (δN −58.8 and +536.8) [14] are of interest, since they may serve as a test for the performance of theoretical models. More recently, progress has been made in the calculations of indirect nuclear spin–spin coupling constants by coupled perturbed DFT methods [12,15–17], and these have been already applied successfully to numerous classes of compounds [18–22]. The compounds considered in this work are shown in Scheme 1. We also report on a new access to bis(trimethylsilyl)diazene **6a** and on the determination of $^1J(^{29}Si,^{15}N)$ in **6a**.

RESULTS AND DISCUSSION

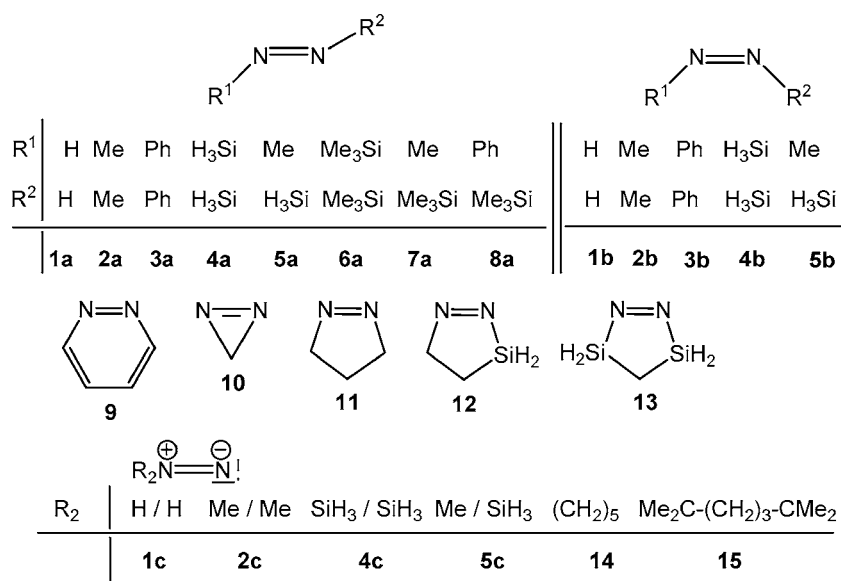### Alternative Synthesis of Bis(trimethylsilyl)diazene **6a**

Bis(trimethylsilyl)sulfur diimide is known to react with various unsaturated substrates [23]. The reaction of the sulfur diimide in pentane at −78°C with an excess of bis(trimethylsilyl)amino(trimethylsilyl)-iminophosphane led to abstraction of sulfur and

generated bis(trimethylsilyl)diazene **6a** (Scheme 2). Condensation of all readily volatile materials at −30°C afforded a blue solution of **6a** in pentane [24], which was studied by ^{14}N and ^{29}Si NMR at −10°C. The thiophosphorane could not be isolated since it reacts readily with the starting phosphane in a [2+2]cycloaddition as reported by Niecke and Flick [25]. We are currently exploring this route for the synthesis of other less stable diazenes when the corresponding sulfur diimides are readily accessible.
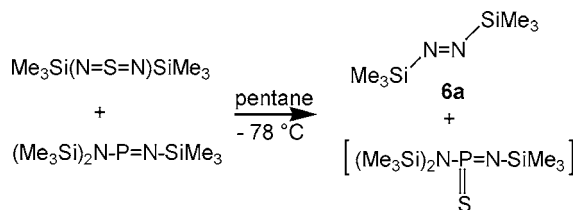
NMR Studies and Calculations

Calculated and experimental NMR parameters of the azo-compounds and nitrenes shown in Scheme 1 are given in Tables 1 and 2, respectively. All geometries were optimized for the gas phase at the B3LYP/6-311+G(d,p) level of theory, and the NMR parameters were calculated at the same level.

The ^{29}Si NMR spectrum of **6a**, recorded by using the HEED (Hahn-echo extended) INEPT pulse sequence [26,27], enabled to detect the ^{15}N satellites according to $^1J(^{29}Si,^{15}N) = 13.7$ Hz. The tilt of the cross peaks [28] in the corresponding 2D HEED $^{29}Si/^1H$ experiment [26,27,29] (Fig. 1) indicated opposite signs of the reduced coupling constants $^3K(^{15}N,Si,C,^1H)$ and $^1K(^{29}Si,^{15}N)$. Since the former usually possesses a positive sign, it is likely that $^1K(^{29}Si,^{15}N)$ is negative [also $^1J(^{29}Si,^{15}N)$], in agreement with the calculations (vide infra). This negative sign of $^1J(^{29}Si,^{15}N)$ in **6a** is remarkable, since for the majority of other Si−N compounds the sign of $^1J(^{29}Si,^{15}N)$ is positive. Qualitatively, this change in sign can be attributed

R^1	H	Me	Ph	H$_3$Si	Me	Me$_3$Si	Me	Ph		H	Me	Ph	H$_3$Si	Me
R^2	H	Me	Ph	H$_3$Si	H$_3$Si	Me$_3$Si	Me$_3$Si	Me$_3$Si		H	Me	Ph	H$_3$Si	H$_3$Si
	1a	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**	**8a**		**1b**	**2b**	**3b**	**4b**	**5b**

R$_2$	H / H	Me / Me	SiH$_3$ / SiH$_3$	Me / SiH$_3$	(CH$_2$)$_5$	Me$_2$C-(CH$_2$)$_3$-CMe$_2$
	1c	**2c**	**4c**	**5c**	**14**	**15**

SCHEME 1   Azo-compounds and amino-nitrenes considered in this work.

Me₃Si(N=S=N)SiMe₃

+

(Me₃Si)₂N-P=N-SiMe₃

$\xrightarrow[- 78\ °C]{\text{pentane}}$

$Me_3Si\underset{\displaystyle \textbf{6a}}{\overset{\displaystyle N=N\diagup SiMe_3}{\diagup}}$

+

$\left[(Me_3Si)_2N\underset{\parallel}{-}P=N-SiMe_3 \right]$
S

SCHEME 2   Reaction of bis(trimethylsilyl)sulfur diimide with bis(trimethylsilyl)amino-trimethylsilylimino-phosphane.

to the influence of the lone pair of electrons [30] at the azo-nitrogen atom. The nature of this lone pair is completely different from that in aminosilanes for which most of the data $^1J(^{29}Si,^{15}N)$ have been determined [31].

Structures

The bond lengths d_{N-N} of the optimized structures of the azo-compounds are calculated to cover a small range between ≈121.5 and 125.5 pm with d_{N-N} = 121.9 pm in diazirine **10** at the short and 125.2 pm for azobenzene at the long end. There is no sys-

FIGURE 1   Contour plot of the 59.6 MHz 2D $^{29}Si/^1H$ HETCOR spectrum of Me₃Si–N=N–SiMe₃ **6a** ($\delta^{29}Si$ −8.0; 10 mm o.d. tube, ca. 5% in pentane with a small amount of C₇D₈ at −10°C), recorded by the HEED method [26] (Hahn-echo delay 0.4 s; acquisition time 1.8 s, repetition delay 2 s; 16 experiments in F₂ (^1H) with 640 transients each; zero filling in both dimensions before Fourier transformation; spectrometer time 12 h). As can be seen, the unwanted magnetization of the ^{29}Si-^{14}N isotopomer is suppressed and the ^{15}N satellites can be observed. The negative tilt of the cross peaks indicates that the signs of $^1K(^{29}Si,^{15}N)$ and $^3K(^{15}N,Si,C,^1H)$ are opposite.

tematic variation of d_{N-N} with H, Me, or silyl substituents, and there is hardly any change in d_{N-N} for *cis*- and *trans*-geometries. The structural parameters are in good agreement with those from structural analyses [32–34], although the calcd. distances d_{N-N} are slightly shorter when compared with experimental data. The exception is Me₃Si−N=N−SiMe₃ **6a**, for which a rather short bond length d_{N-N} = 117 pm (calcd. 124.7 pm) has been reported [35]. In contrast with d_{N-N}, the bond angles at the nitrogen atoms depend significantly on the nature of the substituents as well as on *cis*- or *trans*-geometry (see Table 3 for some examples). The angles R¹−N−N and R²−N−N are wider in the noncyclic *cis*-isomers, even for R¹ = R² = H. Furthermore, in the noncyclic *cis*-isomers, the silyl group causes a wider bond angle Si−N−N than the methyl group. This effect is less pronounced for the *trans*-isomers. Expectedly [1–3,24,36], the lowest energy is always found for the respective *trans*-isomer, followed by the *cis*-isomer and the amino-nitrene. The structure of the isomer **4b** with silyl groups in *cis*-positions does not present a minimum on the energy potential surface.

In the case of nitrene derivatives, the bond lengths d_{N-N} range from 122.3 pm in Me(SiH₃)NN **5c** to 119.9 pm in **15** (see Table 4). The structure of the bis(silyl)amino-nitrene (H₃Si)₂NN **5c** is not a minimum at the B3LYP/6-311+G(d,p) level of theory.

Chemical Shifts δN

The correlation between calcd. and experimental chemical shifts δN of the azo-compounds is linear, including the extreme values for Me₃Si−N=N−SiMe₃ **6a** and *N*-(2,2,6,6-tetramethylpiperidyl)nitrene **15** [$\delta N_{exp.}$ = 0.91 $\delta N_{calcd.}$ −42; R = 0.99 (12)]. Therefore, the theoretical model appears to be adequate with respect to the molecular and electronic structures. Except of the diimines **1a** and **1b**, the magnetic shielding of the nitrogen nuclei is lower for the *cis*-geometry, in agreement with the experimental data available for some pairs of isomers [5–7]. Similar to the nitrogen shielding in disilyldiazenes **4a, 5a,b, 6a**, and **13** (Table 1), the calcd. chemical shift δN(nitrene) = +1073.6 for **5c** (Table 2) is extreme and reflects the unique influence of silyl substituents on the electronic structures. Apparently, the silyl substituents in the azo-compounds as well as in the amino-nitrenes lower the energy gap for magnetic dipole allowed electronic transitions, in particular of the n → π* type.

Coupling Constants

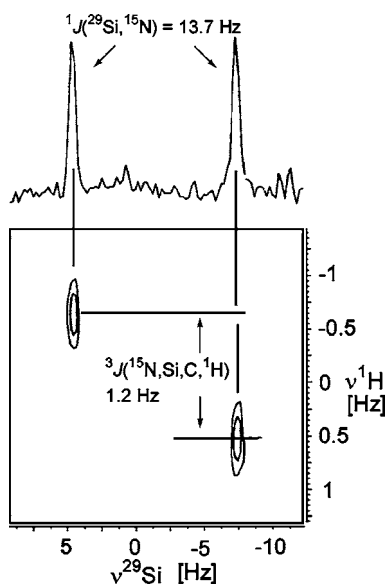All calcd. coupling constants $^1J(N,N)$ in the azo-compounds and in nitrenes possess a negative sign,

TABLE 1 Calculated and Experimental ^{14}N NMR Parameters ^{a,b} of Azo-compounds (see Scheme 1)

	δN calcd. [found]	$^1J(^{14}N,^{14}N)$ calcd. [found]	FC SD PSO	$^1J(^{14}N,X)$ calcd.^{c} [found]	FC SD PSO	$^2J(^{14}N,N,X)$ calcd.^{c}	FC SD PSO	$^3J(X,NN,X)$ calcd.^{c}	FC SD PSO
1a	273.4	−10.1	−1.5 −1.1 −7.5	+23.6 (^{1}H)	+24.7 −0.2 −1.0	+2.2 (^{1}H)	+5.7 −0.2 −3.2	+40.8 (^{1}H,^{1}H)	+42.9 +0.6 +2.9^d
1b	227.3	−9.3	−3.3 −1.4 −5.8	+16.3 (^{1}H)	+16.9 0.0 −0.7	+0.3 (^{1}H)	+2.2 0.0 −1.9	+41.0 (^{1}H,^{1}H)	+41.6 0.0 −0.7^d
2a	190.5 [145.0]^e	−8.6	−2.4 −0.3 −5.9	−5.3 (^{13}C)	−4.8 +0.4 −1.0	+6.4 (^{13}C)	+6.9 0.0 −0.5	+18.2 (^{13}C,^{13}C)	+18.3 +0.1 0.0
2b	201.2	−10.5	−5.4 −0.0 −5.1	−12.4 (^{13}C)	−12.3 +0.5 −0.7	−2.3 (^{13}C)	−1.2 −0.1 −1.0	+24.3 (^{13}C,^{13}C)	+24.5 0.0 −0.2
3a	160.1 [129.0]^f	−8.6 [−7.9]^g	−2.2 −0.4 −6.0	−2.3 (^{13}C) [−1.1]^g	−1,2 +0.4 −1.8	+4.4 (^{13}C) [+3.6]^g	+4.9 −0.3 −0.3	+15.3 (^{13}C,^{13}C)	+14.7 +0.3 +0.3
3b	214.0 [146.5]^f	−13.7	−8.0 −0.3 −5.4	−10.1 (^{13}C) [−6.6]^h	−8.9 +0.3 −1.6	+2.9 (^{13}C)	−2.5 +0.1 −0.6	+11.9 (^{13}C,^{13}C)	+12.0 −0.1 −0.1
4a	785.0	−30.5	−3.0 −14.7 −12.8	+13.8 (^{29}Si)	+16.7 −3.0 +0.1	−9.8 (^{29}Si)	−9.3 −0.6 −0.0	+44.3 (^{29}Si,^{29}Si)	+44.1 +0.1 −0.2
5a	358.3 (Me) 339.1 (Si)	−11.8	−2.7 −1.6 −7.6	−7.5 (^{13}C) +11.6 (^{29}Si)	−6.5 +0.3 −1.3 +10.9 −0.7 +1.4	+5.2 (^{13}C) −9.1 (^{29}Si)	+6.2 −0.1 −0.9 −9.2 −0.1 +0.1	−28.3 (^{29}Si,^{13}C)	−27.9 −0.2 −0.2
5b	380.0 (Me) 354.3 (Si)	−13.6	−5.5 −1.3 −6.8	−11.8 (^{13}C) +24.9 (^{29}Si)	−10.6 +0.2 −1.4 +25.2 −0.9 +0.7	−2.9 (^{13}C) +0.3 (^{29}Si)	−1.3 −0.2 −1.3 +1.9 −0.9 −0.8	−35.0 (^{29}Si,^{13}C)	−34.9 +0.1 +0.2
6a	729.7 [630.0]^i	−29.7	−3.2 −10.4 −12.2	+12.0 (^{29}Si) [9.8]	+11.9 −1.0 +1.0	−5.6 (^{29}Si)	−5.1 −0.5 −0.1	+26.5 (^{29}Si,^{13}C)	+26.1 +0.4 +0.1
7a	328.9 (Me) [275.0]^j 358.7 (Si) [206.0]^i	−11.8	−2.8 +0.3 −1.2	−7.4 (^{13}C) +9.3 (^{29}Si)	−6.6 +0.3 −1.2 +8.7 −0.6 +1.2	+4.8 (^{13}C) −6.2 (^{29}Si)	+5.8 −0.1 −0.9 −6.2 −0.1 +0.1	−21.8 (^{29}Si,^{13}C)	−21.4 −0.3 −0.2
8a	323.6 (Ph) 378.9 (Si)	−12.8	−2.8 −2.0 −8.0	−6.5 (^{13}C) +7.9 (^{29}Si)	−5.7 +0.6 −1.5 +7.2 −0.6 +1.3	+3.1 (^{13}C) −7.0 (^{29}Si)	+3.3 −0.1 +0.2 −7.1 −0.1 +0.1	−19.4 (^{29}Si,^{13}C)	−19.0 −0.2 −0.2
9	74.7 [20.2]^k	−13.2 [−11.2]^l	−10.1 −0.1 −3.0	−7.5 (^{13}C) [+4.5]^l	−3.0 +0.4 −5.0	−3.8 (^{13}C) [−3.4]^l	−3.2 −0.4 −0.1	+20.8 (^{13}C,^{13}C)	+17.9 +1.8 +1.0
10	75.8 [−46.5]^m	−8.3	−3.5 +0.3 −5.1	−7.1 (^{13}C)	−7.1 −0.3 +0.2	–	–	–	–

Continued

TABLE 1   Continued

	δN calcd. [found]	$^1J(^{14}N,^{14}N)$ calcd. [found]	FC SD PSO	$^1J(^{14}N,X)$ calcd.[c] [found]	FC SD PSO	$^2J(^{14}N,N,X)$ calcd.[c]	FC SD PSO	$^3J(X,NN,X)$ calcd.[c]	FC SD PSO
11	248.0	−8.2	−4.2 +0.4 −4.4	−9.5 (^{13}C)	−8.9 +0.5 −1.1	−3.0 (^{13}C)	−2.0 −0.1 −0.9	+9.9 (^{13}C,^{13}C)	+10.3 0.0 −0.4
12	308.1 (CH$_2$) 267.7 (Si)	−11.2	−0.9 −4.8 −5.7	−11.7 (^{13}C) +20.4 (^{29}Si)	−10.7 +0.3 −1.3 +19.9 −1.1 +1.5	−3.5 (^{13}C) +3.9 (^{29}Si)	−2.0 −0.2 −1.3 +4.2 0.1 −0.3	−18.5 (^{29}Si,^{13}C)	−18.3 −0.2 +0.4
13	637.0	−20.2	−5.5 −5.2 −9.4	+22.6 (^{29}Si)	+22.9 −1.5 +1.2	+2.9 (^{29}Si)	+4.2 −1.1 −0.3	+30.3 (^{29}Si,^{29}Si)	+30.3 −0.4 +0.4

[a]Calculated σ(N) data are converted to δN by $\delta N = \sigma(N)[NH_3] - \sigma(N) -399.3$, with σ(N) [NH$_3$] = 259.4, δN [NH$_3$] = −399.3 and δN [neat MeNO$_2$] = 0 [44]; coupling constants and contributions FC, SD, and PSO are given in Hz.
[b]The calculations yield coupling constants for the ^{14}N isotopomers; data $J(^{14}N,^{14}N)$ can be converted to $J(^{15}N,^{15}N)$ by multiplication with the factor 1.968, and $J(^{14}N,X)$ can be converted to $J(^{15}N,X)$ by multiplication with the factor 1.403.
[c]Nucleus X is given in parentheses.
[d]The diamagnetic spin-orbital term (DSO) contributes −5.5 Hz for **1a** and −0.4 Hz for **1b**.
[e]Wrackmeyer, B.. Unpublished ^{14}N NMR measurements; at 23°C in hexane.
[f]Ref. [3a].
[g]Ref. [8]; data determined for 4-acetylamino-azobenzene.
[h]Ref. [38]; the same sign has been assumed.
[i]Reported in [4] +618 (measured in hexane at 25°C relative to an external sample of NaNO$_3$, saturated aqueous solution, with δN = 0; repeated here in pentane at −10°C with modern instrumentation.
[j]Ref. [4].
[k]Ref. [45].
[l]Ref. [37]; determined for 3-methyl-pyridazine.
[m]Ref. [5].

in agreement with the experimental finding for **3a** [8]. The calcd. value ^1J(N,N) for **15** is very close to the experimental one [14], and this suggests that the calcd. negative sign is correct. The dominating term for ^1J(N,N) arises from the negative contribution by the paramagnetic spin-orbital term (PSO) for all azo-compounds. The contact term FC is also negative in all cases but remains fairly small. The spin-dipole term (SD) becomes significant, in particular in the case of **6a**, for which the extreme magnetic deshielding of the nitrogen atoms and the low-energy UV transition (12,750 cm^{-1}) indicate an unusual electronic structure. Although the pyridazine **9** is not an azo-compound, the calcd. value ^1J(N,N) is noteworthy, since it agrees both in magnitude and sign with the experimental value determined for 3-methyl pyridazine [37]. In contrast with the azo-compounds, the negative contribution from the contact term FC dominates for **9**. For ^1J(N,N) of the amino-nitrenes, both the FC and the PSO terms are negative and of similar magnitude.

The one-bond coupling constants $^1J(^{15}N,X)$ (X = ^{1}H, ^{13}C) for the diazenes are remarkably small and positive (X = ^{1}H) or negative (X = ^{13}C). In the latter case, there is agreement with experimental data [8,37]. Except of **9**, this coupling is transmitted through single bonds and therefore, the noncontact contributions are small when compared with FC. The negative sign of $^1J(^{15}N,^{13}C)$ is then mainly the result of the influence of the lone pair of electrons at the azo-nitrogen atom [30]. The effect of the *cis*- or *trans*-configuration on the magnitude of $^1J(^{15}N,^{13}C)$ in azo-compounds has been noted [38], and is correctly reproduced by the calculations. For X = ^{29}Si, the situation is comparable with that for ^{13}C. The calcd. reduced coupling constants $^1K(^{29}Si,^{14}N)$ are negative (in the tables: $^1J(^{29}Si,^{14}N)$ > 0, since $\gamma(^{29}Si) < 0$) owing to the large negative FC-contribution. The calcd. negative sign of $^1K(^{29}Si,^{14}N)$ is in agreement with the experimental evidence obtained here for **6a** (vide supra). In the nitrenes, the lone pair of electrons at the amino-nitrogen atom is engaged in bonding, and it is therefore expected that the contact contribution is less affected than in the azo-compounds. The calculations show that the coupling constants $^1J(^{14}N,X)$ are large and positive (X = ^{1}H) and small and of either sign (X = ^{13}C). The calcd. sign of the reduced coupling constant $^1K(^{29}Si,^{15}N)$ is positive, following the trend for X = ^{13}C.

TABLE 2 Calculated and Experimental ^{14}N NMR Parameters ^{a,b} of Amino-nitrenes $R_2N=N$ (see Scheme 1)

	δN calcd. [found]	$^1J(^{14}N,^{14}N)$ calcd. [found]	FC SD PSO	$^1J(^{14}N,X)$ calcd.^{c}	FC SD PSO	$^2J(^{14}N,N,X)$ calcd.^{c}	FC SD PSO	$^3J(X,NN,X)$ calcd.^{c}	FC SD PSO
1c	−109.7 (NH$_2$) 983.3 (N)	−8.2	−4.2 −0.1 −3.9	+59.6 (^{1}H)	+58.6 −0.2 ü0.7	+0.4 (^{1}H)	+1.0 +2.5 −2.8	+47.9 (^{1}H,^{1}H)	+48.1 +0.3 +0.3^d
2c	−113.5 (NMe$_2$) 738.7 (N)	−7.4	−4.7 +0.5 −3.2	+3.0 (^{13}C)	+3.4 +0.5 −0.3	+0.4 (^{13}C)	+1.2 +0.1 −0.9	+28.7 (^{13}C,^{13}C)	+28.6 −0.1 −0.2
14	−87.1 (C$_2$) 724.7	−8.0	−4.9 +0.4 −3.5	+2.8 (^{13}C)	+2.4 +0.5 +0.3	+0.1 (^{13}C)	+1.0 +0.1 −0.9	+18.9 (^{13}C,^{13}C)	+19.6 −0.1 −0.2
15	−59.7 (NC$_2$) [−58.8]^e 619.3 (N) [536.8]^e	−7.8 [7.9]^e	−5.1 +0.6 −3.3	−0.3 (^{13}C)	−0.7 +0.6 +0.2	−0.3 (^{13}C)	+0.4 +0.1 −0.8	+16.5 (^{13}C,^{13}C)	+16.5 0.0 −0.1
5c	−20.0 (NC,Si) 1073.6 (N)	−11.0	−4.5 −1.3 −5.2	−0.3 (^{13}C) −9.8 (^{29}Si)	−0.6 +0.5 −0.2 −9.1 −0.9 +0.2	−0.4 (^{13}C) −5.8 (^{29}Si)	+1.5 −0.3 −1.5 −1.2 −2.7 −1.9	−39.1 (^{29}Si,^{13}C)	−39.1 0.0 0.0

^{a}Calculated $\sigma(N)$ data are converted to δN by $\delta N = \sigma(N)[NH_3] - \sigma(N) -399.3$, with $\sigma(N)$ [NH$_3$] = 259.4, δN [NH$_3$] = −399.3, and δN [neat MeNO$_2$] = 0 [44]; coupling constants and contributions FC, SD, and PSO are given in Hz.
^{b}The calculations yield coupling constants for the ^{14}N isotopomers; data $J(^{14}N,^{14}N)$ can be converted to $J(^{15}N,^{15}N)$ by multiplication with the factor 1.968, and $J(^{14}N,X)$ can be converted to $J(^{15}N,X)$ by multiplication with the factor 1.403.
^{c}Nucleus X is given in parentheses.
^{d}The diamagnetic spin-orbital term (DSO) contributes −4.8 Hz for **1c**.
^{e}Ref. [14].

The geminal coupling constants $^2J(N,N,X)$ in the azo-compounds and nitrenes are small and may be of either sign. In the cases, for which comparable experimental data are available [8,37], sign and magnitude are in agreement with calcd. data. The vicinal coupling constants $^3J(X,NN,X)$ are all positive (reduced coupling constants in the case of X = ^{29}Si/^{13}C). However, there is no systematic in-

fluence of cis- and trans-configuration at the N=N bond on the magnitude of $^3J(X,NN,X)$, in contrast with the well-known situation for the C=C bond. In the case of the cyclic azo-compounds **11–13**, the calcd. values for $^3J(X,NN,X)$ represent the effect of coupling pathways across two and three bonds, and these contributions may be of opposite sign.

TABLE 3 Selected Calculated^a Structural Parameters of Some Azo-compounds R^1–N=N–R^2 with trans- (**1a–7a**) and cis-Configuration (**1b–3b, 5b**)

	R^1	R^2	d_{N-N} (pm)	Angle (°) R^1–N–N	Angle (°) R^2–N–N		d_{N-N} (pm)	Angle (°) R^1–N–N	Angle (°) R^2–N–N
1a	H	H	124.1	106.5	106.5	**1b**	123.7	113.0	113.0
2a	Me	Me	123.5	113.5	113.5	**2b**	123.5	122.4	122.4
3a	Ph	Ph	125.2	115.4	115.4	**3b**	124.3	124.0	124.0
4a	SiH$_3$	SiH$_4$	124.8	112.9	112.9	**4b**^{b}	–	–	–
5a	Me	SiH$_3$	123.1	113.9	116.5	**5b**	123.4	120.8	128.9
6a	SiMe$_3$	SiMe$_3$	124.7	118.2	118.2	**6b**^{c}	–	–	–
7a	Me	SiMe$_3$	123.9	114.2	117.9	**7b**^{c}	–	–	–

^{a}Optimized by B3LYP/6-311+G(d,p) calculations.
^{b}Optimization of this structure did not give a minimum.
^{c}Structure was not calculated.

TABLE 4 Selected Calculated[a] Structural Parameters of Some Amino-nitrenes $R_2N=N$ (**1c, 2c, 4c, 5c, 14, 15**)

	R_2	d_{N-N} (pm)	Angle (°) R–N–N	Angle (°) R–N–R
1c	H/H	121.4	123.9	112.25
2c	Me/Me	120.8	123.9	112.2
4c[b]	SiH$_3$/SiH$_3$	–	–	–
5c	Me/SiH$_3$	122.3	123.1 (Me) 115.3 (SiH$_3$)	121.5
14	(CH$_2$)$_5$	120.9	124.2	111.6
15	Me$_2$C-(CH$_2$)$_3$CMe$_2$	119.9	120.5	118.7

[a]Geometries were optimised by B3LYP/6-311+G(d,p) calculations.
[b]Optimization of this structure did not give a minimum.

CONCLUSIONS

Trends in nitrogen nuclear magnetic shielding in azo-compounds and nitrenes are correctly predicted by simple DFT hybrid methods. The sign and magnitude of coupling constants involving nitrogen nuclei is reproduced by calculations and thus, reasonable predictions can be made, when it is difficult to obtain the experimental NMR data. The importance of noncontact contributions to the indirect nuclear spin–spin coupling must be emphasized, in particular for $^1J(N,N)$ of the N=N bonds. The exceptional effects of silyl substituents on the electronic structure of azo-compounds, mirrored already by various experimental spectroscopic data, are also revealed by calculations of the NMR parameters.

EXPERIMENTAL

Preparative work was carried out using standard procedures to exclude oxygen and moisture. Starting materials for the alternative synthesis of **6a**, such as bis(trimethylsilyl)sulfur diimide [39] and bis(trimethylsilyl)amino-trimethylsilyliminophosphane [40] were prepared following the literature methods.

NMR spectra of **6a** ($\approx$5% in pentane/C$_7$D$_8$; 10 mm o.d. tube) were measured at $-10°$C using a Bruker AC 300 NMR spectrometer, equipped with a multinuclear unit. The 1D and 2D ^{29}Si HEED-INEPT NMR experiments [26] were done by using $^2J(^{29}$Si,^{1}H$_{Me}$) = 7.2 Hz for polarization transfer and a Hahn-echo delay of 0.4 s in order to suppress most of the unwanted magnetization of the ^{29}Si-^{14}N isotopomer. Chemical shifts are given relative to neat MeNO$_2$ (δ^{14}N = 0; $\Xi(^{14}$N) = 7.226324 MHz) and SiMe$_4$ (1% in CDCl$_3$; δ^{29}Si = 0; $\Xi(^{29}$Si) = 19.867187 MHz).

Synthesis of Bis(trimethylsilyl)diazene **6a**

A solution of bis(trimethylsilyl)sulfur diimide (3 g, 14.5 mmol) in pentane (40 mL) was cooled to $-78°$C, and a solution of bis(trimethylsilyl)amino-trimethylsilylimino-phosphane (8.4 g, 30 mmol) in pentane (20 mL) was added under vigorous stirring within 10 min. The color of the reaction solution turned blue. The mixture was warmed to $-30°$C, kept stirring for 30 min, and then all volatile materials were removed in vacuum (10^{-3} Torr) and collected in a cold trap. The NMR spectra of these materials showed the presence of pure **6a** in pentane (5% w/w; yield 82%).

All calculations were performed using the Gaussian 03 package [41]. The gas phase geometries were optimized with DFT methods (B3LYP) [42] and the 6-311 + G(d,p) basis set [43]. The structures of the molecules shown in Scheme 1, except of **4b** and **4c**, were found to be minima on the respective potential energy surface, based on the criteria of stabilities of the wave functions and harmonic frequencies. Calculations of NMR parameters using pure HF-methods gave poor results for coupling constants. If not noted otherwise in the Tables 1 and 2, the diamagnetic spin-orbital (DSO) contribution was much less than 1 Hz.

REFERENCES

[1] (a) Zollinger, H. Azo and Diazo Chemistry—Aliphatic and Aromatic Compounds; Interscience: New York, 1961, 444 pp; (b) Schantl, J. G. J Heterocycl Chem 2000, 37, 541.

[2] (a) Kisch, H.; Holzmeier, P. Adv Organomet Chem 1992, 34, 67; (b) Wiberg, N. Adv Organomet Chem 1984, 23, 131; (c) Sheppard, C. S. In: Encyclopaedia of Polymer Science Engineering; Kroschwitz J. I. (Ed.); Wiley, New York, 1985, Vol. 2, pp. 143–57; (d) Nuyken, O. In: Encyclopaedia of Polymer Science Engineering; Kroschwitz J. I. (Ed.); Wiley: New York, 1985, Vol. 2, pp. 158–175.

[3] (a) Lycka, A. Annu Rep NMR Spectrosc 2000, 42, 1; (b) Curtis, R. D.; Hilborn, J. W.; Wu, H.; Lumsden, M. D.; Wasylishen, R. E.; Pincock, J. A. J Phys Chem 1993, 97, 1856; (c) Griffiths, J. Chem Soc Rev 1972, 1, 481; (d) Rau, H. Angew Chem 1973, 85, 248; Angew Chem Int Ed 1973, 12, 224.

[4] Kroner, J.; Schneid, W.; Wiberg, N.; Wrackmeyer, B.; Ziegleder, G. J. Chem Soc, Faraday Trans 2 1978, 74, 1909.

[5] Mason, J.; Vinter, J. G. J Chem Soc, Dalton Trans 1975, 2522.

[6] Porter, N. A.; Dubay, G. R.; Green, J. G. J Am Chem Soc 1978, 100, 920.

[7] Bubnov, N. N.; Bilevich, K. A.; Polyakava, L. A.; Okhlobystin, O. Yu. J Chem Soc, Chem Commun 1972, 1058.

[8] Kuroda, Y.; Fujiwara, Y.; Kuwae, A.; Matsushita, K. J Chem Soc Perkin Trans 2 1986, 675.

[9] Ramsey, N. F. Phys Rev 1953, 91, 303.

[10] (a) Gräfenstein, J.; Cremer, D. Chem Phys Lett 2004, 383, 332; (b) Gräfenstein, J.; Cremer, D. Chem Phys Lett 2004, 387, 415; (c) Gräfenstein, J.; Cremer, D. Magn Reson Chem 2004, 42, S. 138; (d) Cremer, D.; Krarak, E.; Wu, A.; Lüttke, W. Chem Phys Chem 2004, 5, 349.

[11] Bühl, M. In: Encyclopedia of Computational Chemistry; Schleyer, P. v. R. (Ed.); Wiley: Chichester, 1999; Vol. 3, pp. 1835–1845.

[12] Keal, T. W.; Tozer, D. J.; Helgakar, T. Chem Phys Lett 2004, 391, 374.

[13] Fadda, E.; Casida, M. E.; Salahub, D. R. J Chem Phys 2003, 118, 6758.

[14] Dervan, P. B.; Squillacote, M. E.; Lahti, P. M.; Sylwester, A. P.; Roberts, J. D. J Am Chem Soc 1981, 103, 1120.

[15] (a) Helgaker, T.; Watson, M.; Handy, N. C. J Chem Phys 2000, 113, 9402; (b) Helgaker, T.; Jaszunski, M.; Ruud, K. Chem Rev 1999, 99, 293.

[16] Peralta, J. E.; Scuseria, G. E.; Cheeseman, J. R.; Frisch, M. J Chem Phys Lett 2003, 375, 452.

[17] (a) Sychrovsky, V.; Gräfenstein, J.; Cremer, D. J Chem Phys 2000, 113, 3530; (b) Wu, A.; Gräfenstein, J.; Cremer, D. J Phys Chem A 2003, 107, 7043; (c) Gauss, J.; Stanton, J. F. Adv Chem Phys 2002, 123, 344; (d) Vaara, J.; Jokisaari, J.; Wasylishen, R. E.; Bryce, D. I. Progr NMR Spectrosc 2002, 41, 233.

[18] Boranes: (a) Onak, T.; Jaballas, J.; Barfield, M. J Am Chem Soc 1999, 121, 2850; (b) Wrackmeyer, B.; Berndt, A. Magn Reson Chem 2004, 42, 490; (c) Wrackmeyer, B. Z Naturforsch in press.

[19] Hydrocarbons: (a) Krivdin, L. B.; Sauer, S. P. A.; Peralta, J. E.; Contreras, R. H. Magn Reson Chem 2002, 40, 187; (b) Krivdin, L. B. Magn Reson Chem 2003, 41, 157; (c) Krivdin, L. B. Magn Reson Chem 2003, 41, 885; (d) Krivdin, L. B. Magn Reson Chem 2004, 42, 500; (e) Ruden, T. A.; Helgaker, T.; Jaszunski, M. Chem Phys 2004, 296, 53; (f) Jaszunski, M.; Ruud, K.; Helgaker, T. Mol Phys 2003, 101, 1997.

[20] Carbon-oxygen compounds: Wrackmeyer, B. Z Naturforsch Teil B 2004, 59, 286.

[21] Phosphanes: (a) Del Bene, J. E.; Elguero, J.; Alkorta, I. J Phys Chem A 2004, 108, 3662; (b) Wrackmeyer, B. Z Naturforsch Teil B 2003, 58, 1041.

[22] Se-Se bonds: Wrackmeyer, B. Struct Chem in press.

[23] Bussas, R.; Kresze, G.; Münsterer, H.; Schwöbel, A. Sulfur Rep 1983, 2, 215.

[24] (a) Wiberg, N.; Joo, W. Ch.; Uhlenbrock, W. Angew Chem Int Ed 1968, 7, 640; (b) Wiberg, N.; Joo, W. Ch.; Schwenk, G.; Uhlenbrock, W.; Veith, M. Angew Chem Int Ed 1971, 10, 374.

[25] Niecke, E.; Flick, W. J Organomet Chem 1976, 104, C23.

[26] Kupce, E.; Wrackmeyer, B. J Magn Reson 1992, 97, 568.

[27] Wrackmeyer, B.; Kupce, E.; Köster, R.; Seidel, G. Magn Reson Chem 1995, 33, 812.

[28] Bax, A.; Freeman, R. J Magn Reson 1981, 45, 177.

[29] Kupce, E.; Wrackmeyer, B Magn Reson Chem 1991, 29, 351.

[30] Gil, V. M. S.; von Philipsborn, W. Magn Reson Chem 1989, 27, 409.

[31] Wrackmeyer, B.; Kupce, E. In: Topics of Physical Organometallic Chemistry; Gielen, M. (Ed.); Freund Publishing: Tel Aviv, 1992; Vol. 4, pp. 289–352.

[32] (a) Bouwstra, J. A.; Schouten, A.; Kroon, J Acta Crystallogr C 1983, 30, 1121; (b) Mostad, A.; Rømming, C. Acta Chem Scand 1971, 25, 3561; (c) Schmittel, M.; Schulz, A.; Rüchardt, C.; Hädicke, E. Chem Ber 1981, 114, 3533.

[33] (a) Conner, J. A.; Kennedy, R. J.; Dawes, H. M.; Hursthouse, M. B.; Walker, N. P. C. J Chem Soc Perkin Trans 2 1990, 203; (b) Maciejewska, D.; Wolska, I.; Kowalska, V. J Mol Struct 2004, 693, 27.

[34] Norikane, Y.; Kitamoto, K.; Tamaoki, N. J Org Chem 2003, 68, 8291.

[35] Veith, M.; Bärnighausen, H. Acta Crystallogr B 1974, 30, 1806.

[36] Wiberg, N.; Bachhuber, H.; Fischer, G. Angew Chem Int Ed 1972, 11, 829.

[37] Kuroda, Y.; Fujiwara, Y.; Matsuhito, K. J Chem Soc, Perkin Trans 2 1985, 1533.

[38] Simova, S.; Fanghänel, E.; Radeglia, R. Org Magn Reson 1983, 21, 163.

[39] Scherer, O. J.; Wies, R. Z. Naturforsch Teil B 1970, 25, 1486.

[40] Scherer, O. J.; Kuhn, N. Chem Ber 1974, 104, 2123.

[41] Gaussian 03, Revision B.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, O. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachar, K. I.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh PA, 2003.

[42] (a) Becke, A. D. J Chem Phys 1993, 98, 5648; (b) Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 41, 785; (c) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. J Phys Chem 1994, 98, 11623.

[43] (a) McLean, D.; Chandler, G. S. J Chem Phys 1980, 72, 5639; (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. J Chem Phys 1980, 72, 650.

[44] Mason, J. In: Multinuclear NMR; Mason, J. (Ed.); Plenum: New York, 1977; p. 336.

[45] Städeli, W.; von Philipsborn, W.; Wick, A.; Kompis, J. Helv Chim Acta 1980, 63, 504.