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PROTON NUCLEAR MAGNETIC RESONANCE OF SOME BIS(ORGANOSILYL)METHYLHYDRAZINES*

BLAKE BICHLMEIR AND ROBERT WEST
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

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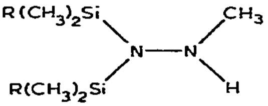
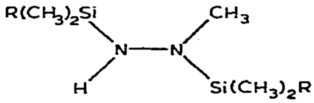
SUMMARY

A reinvestigation of the proton magnetic resonance spectra of some *N,N*-bis(organosilyl)methylhydrazines resolves previous conflicting interpretations. Variable temperature NMR data permits unequivocal assignment of the NCH_3 and NH proton absorptions and coupling constants of both *N,N*- and *N,N'*-bis(organosilyl)methylhydrazines.

Two differing interpretations of the proton NMR spectra of *N,N*-bis(organosilyl)methylhydrazines have appeared in the literature[1,2], leading to some confusion. Neither of the assignments was fully correct. Recently we have reexamined the NMR spectra of carefully purified samples of these compounds, using improved NMR equipment. The compounds in question, *N,N*-bis(trimethylsilyl)methylhydrazine (I) and *N,N*-bis(ethyldimethylsilyl)methylhydrazine (II) show unexpected NH to NCH_3 coupling which complicates the spectra and the interpretation.



(I) R = CH_3
(II) R = C_2H_5



(III) R = CH_3
(IV) R = C_2H_5

The NMR spectrum of (I) was first reported by Wannagat and Höfler[1], who found a single trimethylsilyl proton resonance as expected, and two peaks in about a 2/1 ratio at 7.49 and 7.58 τ respectively, assigned to the NCH_3 protons. The two absorptions were attributed to diminished independent rotation about the N–C bond. Presumably with rotation about this bond being slow relative to the NMR time scale, one of the three hydrogen atoms would be in a different environment from the other two. The other interpretation is due to West, Ishikawa, and Bailey, who published the NMR spectrum of (I) and (III) incidental to a study of anionic rearrangements[2,3].

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They attributed the larger peak at 7.49 τ in the spectrum of (I) to the NCH_3 protons and the smaller at 7.58 τ to the NH proton.

Reexamination of the NMR of (I) shows that, at room temperature, there are actually *three* peaks in the 7–8 τ region (Fig. 1). The previously undetected broad resonance at 7.19 τ is due to the NH proton, broadened by the ^{14}N nuclear quadrupole relaxation interaction. The other two peaks, in approximately a 2/1 ratio, must be due to the NCH_3 protons; but hindered rotation seemed most unlikely as an explanation for the splitting*.

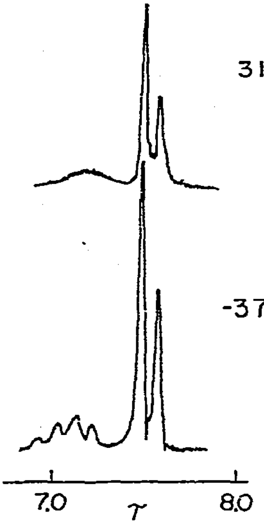

Fig. 1. Variable temperature proton NMR spectra of the NH and NCH_3 region of *N,N*-bis(trimethylsilyl)-methylhydrazine(I) in chlorobenzene.

Compound (I) was then studied by variable temperature NMR in chlorobenzene. The results are shown in Fig. 1. At −37° the ^{14}N nuclear quadrupole relaxation time is shortened sufficiently so that the NH and NCH_3 proton coupling may be observed as a quartet and a doublet respectively with a coupling constant of 5.6 Hz. The spectral changes are reversible and spectra taken from room temperature to 70° show no further change.

The coupling constant of 5.6 Hz is not unexpected and it is within the range of 5–7 Hz observed for spin–spin coupling in other secondary amines[4]. The NH quartet and the NCH_3 doublet have also been observed in the room temperature NMR of *N*-methyl-*O*-(trimethylsilyl)hydroxylamine[5].

The width of the NH signal of (I) at room temperature can be attributed to coupling with the NCH_3 group and the quadrupolar effect of the ^{14}N nucleus. The temperature dependence of spin–spin splitting between a nucleus with spin 1, possessing a quadrupole moment, and a nucleus with spin $\frac{1}{2}$ has been adequately demonstrated

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* Although conformational changes in certain tetraalkylhydrazines have been observed at low temperatures[10,11], we find no change in our NMR spectra even at −80°. It is possible that silylhydrazines containing the SiH or SiH_2 moiety may yield interesting information on barriers to rotation and inversion.

for $^{14}N-^{1}H$ (ref. 6), $^{14}N-^{19}F$ (ref. 7), and $^{2}H-^{1}H$ (ref.8). This characteristic dependence is attributed to a more effective quadrupole relaxation of the spin 1 nucleus at lower temperatures with a consequent narrowing of the ^{1}H or ^{19}F NMR absorption signals[9].

The approximate 2/1 ratio of the NCH_3 peaks arises from the usual second-order effect on transition probabilities; the intensities of the four components of the NH quartet show similar inequalities, since the $H-N-CH_3$ coupling constant is of the same order of magnitude as the chemical shift separation of 27 Hz. Thus the doubling of the NCH_3 resonance is fully accounted for without assuming any hindrance to rotation.

Close examination of the NMR spectra of the N,N' isomers (III) and (IV) show that long range interactions between NCH_3 and NH protons exist in these compounds also, so that the NCH_3 absorption appears as a doublet with *J* 0.4 Hz. However, the broad NH absorption could not be resolved even at low temperatures. Chemical shifts and coupling constants for all four compounds appear in Table 1.

TABLE 1

PROTON NMR SPECTRAL DATA OF BIS(ORGANOSILYL)METHYLHYDRAZINES, τ

No.	Compound	$SiCH_3$	SiEt	NH	NCH_3	$J(H-N, N-CH_3)$(Hz)
(I)	$(Me_3Si)_2NNHMe$	9.92		7.19	7.56 7.48	5.6
(III)	$Me_3SiNHN(Me)SiMe_3$	10.00 9.97		8.00	7.45	0.4
(II)	$(EtMe_2Si)_2NNHMe$	9.95	9.80– 8.87	7.18	7.56 7.48	5.6
(IV)	$EtMe_2SiNHN(Me)SiMe_2Et$	10.03 10.00	9.80– 8.87	7.95	7.45	0.4

EXPERIMENTAL

The preparation and manipulation of the bis(organosilyl)methylhydrazines were carried out under an atmosphere of dry nitrogen according to published procedures[3]. The hydrazine isomers were separated by gas chromatography on a 3/8″ × 15′ column of 20% SE-30 on 20–40 mesh Chromosorb W. Prepared isomers were used immediately since addition of small amounts of water or dilute acid causes rapid proton exchange in the molecule which destroys the coupling. Carbon tetrachloride and chlorobenzene were refluxed over barium oxide, distilled, and stored under nitrogen and over molecular sieves. NMR samples were prepared under nitrogen atmosphere. Solutions were 10% by volume although neat samples showed no qualitative change in the spectra.

Proton NMR spectra were obtained with a Varian A-60A spectrometer equipped with a Varian variable temperature probe and programmer. Temperatures were checked by measurement of the chemical shift difference in methanol or ethylene glycol.

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