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CARBON-13 AND SILICON-29 NMR SPECTRA OF SOME [TRIS(TRIMETHYLSILYL)METHYL]-SUBSTITUTED SILANES AND RELATED COMPOUNDS

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Summary

Fourier Transform ^{13}C and ^{29}Si NMR spectra are reported for series of [tris(trimethylsilyl)methyl] dimethylsilanes, [tris(trimethylsilyl)methyl] diphenylsilanes, and for related compounds. Analysis of chemical shift values indicates that such information can be useful in determining the structure in these highly hindered, but structurally similar compounds. In particular, the carbon and silicon atoms of the trimethylsilyl groups absorb in a narrow shift range, while other carbon and silicon atoms more characteristically reflect the substitution patterns in these compounds.

Introduction

Although there has been a great deal of recent work by Eaborn and coworkers [1—9] and us [10,11] on the chemistry of trisyl * substituted compounds, only routine spectroscopic properties have so far been reported on these very interesting, highly hindered compounds. Possessing a number of these Tsi compounds from our previous studies, we decided to measure their Fourier Transform ^{13}C and ^{29}Si NMR spectra. We have measured both the ^{13}C and ^{29}Si chemical shifts of $TsiSiPh_2X$ (X = H, Br, Cl, and F) (Series A), $TsiSiMe_2X$ (X = H, Br, Cl, OH, and CH_3) (Series B), and $TsiSiCl_3$. Such data can now be used to help characterize compounds of this and closely similar structural types.

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* $(Me_3Si)_3C$ = trisyl group; also abbreviated Tsi.

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Results and discussion

The spectacular recent advances in NMR spectroscopy have made it routine to carry out multinuclear NMR analyses. Despite these advances it is often problematic when one searches for multinuclear NMR data on compounds of unusual structural types. Thus, when we first obtained $TsiSiMe_2OH$ [10] and $(Me_3Si)_2CHSiPh_2OSiMe_3$ [11] and began their characterization, we found no ^{13}C or ^{29}Si NMR data on similarly structured compounds to help in their structure determination. We decided that there was a need for such information and began the work reported here.

Many collections of ^{13}C and ^{29}Si NMR spectra now exist [12—14]; we have used these to help us in our assignment of the chemical shifts given in Tables 1 and 2. The compounds listed in these tables have similar structural features being either dimethylsilyl-, diphenylsilyl-, or trichlorosilyl-substituted trisyl derivatives ($(Me_3Si)_3CY$ where Y is Me_2SiX, Ph_2SiX, and Cl_3Si, respectively). We have obtained the ^{13}C NMR spectra of these compounds with some trouble (see Experimental); in particular, shifts for the quaternary-substituted carbons were difficult to obtain. Our chemical shifts agree with the unpublished work of Washburne and coworkers [15]. Several comments are appropriate. The Me_3Si carbons of the trisyl group absorb in a very narrow chemical shift range (4.5 to 6.5 ppm), presumably because such carbons are in very similar chemical environments far removed from any perturbing substituents. Further, both the quaternary carbon shifts in series A and B and the Me_2Si carbon shifts in series B vary substantially as the β substituent X varies. Electronegative substituents like X = Br, Cl, and OH cause downfield shifts relative to X = H (Fig. 1). In addition, when X = Me in series B, its quaternary carbon absorbs upfield from the quaternary carbons of the electronegative (X = Br, Cl, and OH) members of the

TABLE 1

^{13}C NMR CHEMICAL SHIFT [a] VALUES FOR $(Me_3Si)_3CSiPh_2X$ (A), $(Me_3Si)_3CSiMe_2A$ (B), AND $(Me_3Si)_3CSiCl_3$ (C)

Compound	Me_3Si	Quaternary [c]	C-1	Ph_2Si			Me_2Si
				ortho	*meta*	*para*	
A—H	5.1	−0.3 (5.7) [b]	137.5	136.0	127.1	128.6	—
A—Br	6.6	6.3 (5.7) [b]	135.9	136.5	126.9	129.5	—
A—Cl	6.3	5.2	136.2	135.9	126.9	129.4	—
A—F	5.7	5.9 [c]	137.8 (137.2) [d]	134.6	127.2	129.2	
B—H	4.2	−4.3	—	—	—	—	1.4
B—Br	4.9	2.8 (−0.1) [c]	—	—	—	—	9.8
B—Cl	4.8	3.1 (−0.4) [c]	—	—	—	—	8.7
B—OH	4.5	2.9 (−0.5) [c]	—	—	—	—	6.1
B—CH_3	5.4	−1.8	—	—	—	—	—
C	4.5	12.4	—	—	—	—	—

[a] Ppm from tetramethylsilane determined using internal reference chloroform-*d*. [b] This is an impurity of $(Me_3Si)_3CSiPh_2F$. [c] We experienced great difficulty obtaining the quaternary carbon's chemical shift; oftentimes small impurities gave peaks as large as those of the quaternary carbon making assignment difficult; in such cases we have listed both absorptions; in other cases footnoted here we have listed a single absorption, but it is a very small peak and is difficult to assign with assurance. [d] Probably an impurity.

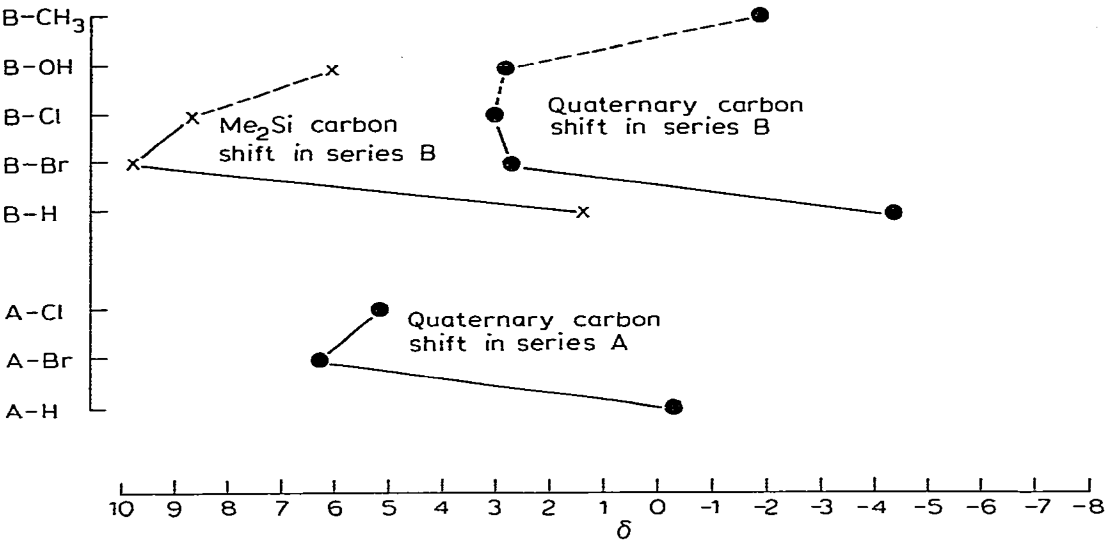


Fig. 1. ^{13}C NMR shifts in series A and B.

series. Finally, the aromatic carbons in series A absorb over narrow ranges with the meta carbon being almost invariant (126.9 to 127.2 ppm) as X varies. Interestingly, the aromatic carbon shifts may be particularly characteristic probes for this series; for example, while the series A aromatic carbon shifts vary little, the chemical shifts of the C-1 and *ortho* aromatic carbons of I [12] and II [11] are quite different (Fig. 2).

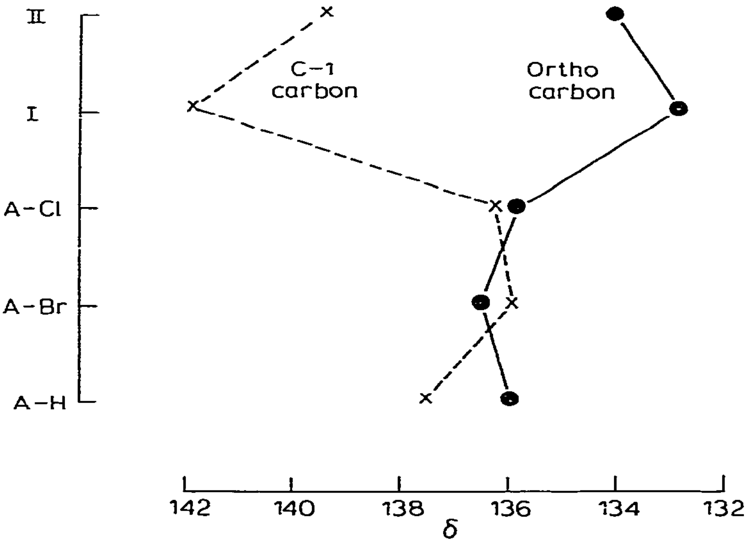


Fig. 2. ^{13}C NMR shifts of C-1 and *ortho*-carbons.

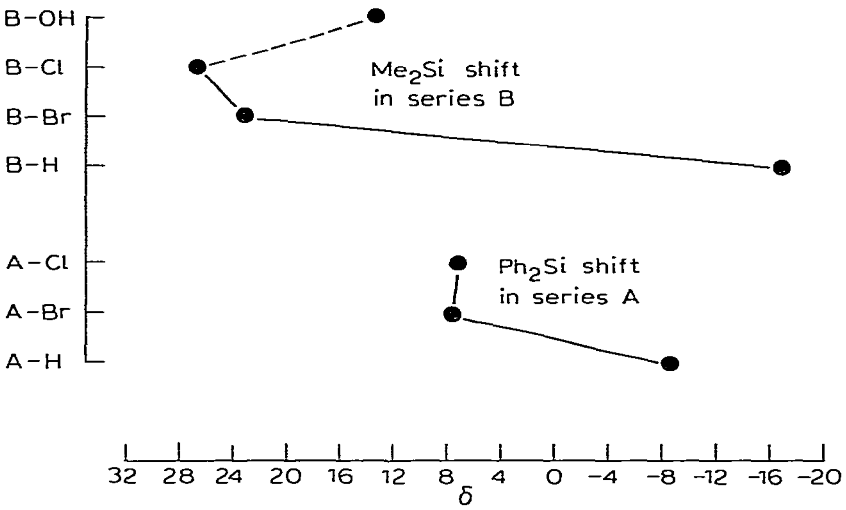
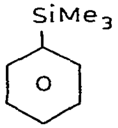
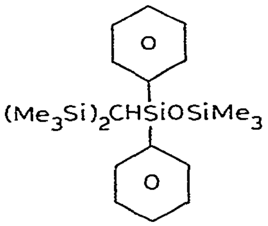


Fig. 3. ^{29}Si NMR shifts in series A and B.



(I)



(II)

The ^{29}Si chemical shifts given in Table 2 again demonstrate that the Me$_3$Si groups in both series A and B are very similar; the ^{29}Si shifts of these groups vary from −0.1 to −2.2 ppm, a remarkably narrow range. Even compound C, TsiSiCl$_3$, has its corresponding shift at only −6.7 ppm. The trends in the chemical shifts of the silicon bearing substituent X look strikingly like the ^{13}C effects

TABLE 2

^{29}Si NMR CHEMICAL SHIFT [a] VALUES FOR $(Me_3Si)_3CSiPh_2X$ (A), $(Me_3Si)_3SiMe_2X$ (B), AND $(Me_3Si)_3CSiCl_3$ (C)

Compound	Me$_3$Si	Ph$_2$Si	Me$_2$Si	SiCl$_3$
A—H	−0.2	−8.6	—	—
A—Br	−0.1	7.7	—	—
A—Cl	−0.5	7.4	—	—
B—H	−1.0	—	−16.8	—
B—Br	−1.0	—	23.3	—
B—Cl	−1.3	—	26.7	—
B—OH	−2.2	—	13.4	—
B—CH$_3$	−1.5	—	—	—
C	−6.7	—	—	−3.3

[a] Ppm from tetramethylsilane.

just mentioned for carbons β to the X substituent (Fig. 3). The phenyl groups of series A greatly attenuate this effect, a fact not clearly discernible from the ^{13}C data. Both the attenuation by the phenyl groups and the variation of ^{29}Si chemical shifts with X are consistent with previously published reports [13,14].

Conclusions

We have for the first time reported the ^{13}C and ^{29}Si chemical shifts of a variety of trisyl compounds. These highly hindered, novel compounds promise to continue to provide a rich chemistry [1—11]. The importance of the NMR study reported here rests on its use in characterizing other compounds in the trisyl series and in closely related structural series. That the ^{13}C and ^{29}Si chemical shifts of the Me_3Si portion of the trisyl group absorb in a narrow range indicates that these will be used as characterizing parameters for trisyl compounds. In addition, the variation of ^{13}C and ^{29}Si chemical shifts of carbons β and silicon bonded to substituent X should prove useful in the characterization of compounds similar to those reported here. Finally, we suggest that aromatic trisyl compounds of the series A type may be uniquely characterized by their C-1 and *ortho* ^{13}C chemical shifts.

Experimental

^{13}C and ^{29}Si NMR spectra we obtained using a JEOL FX90Q nuclear magnetic resonance spectrometer using a 5 mm probe insert. All spectra were measured at ambient temperature in a chloroform-*d* solution. An 8 K data capacity was used. All chemical shifts are accurate to 0.1 ppm. Because of the long relaxation times of these molecules, $Cr(acac)_3$ in concentrations of 0.1—0.2 *M* was required for all spectra measurements.

^{13}C spectra were obtained at 22.50 MHz using an inverse gated spin decoupling mode. Chemical shifts were determined from internal standard chloroform-*d* and reported relative to tetramethylsilane. General conditions used for a 6002 Hz spectral window were an irradiation pulse at ~30° flip angle, a relaxation delay time of 15 seconds, and an acquisition time of 0.6820 seconds. The number of scans ranged from 284 to 1083.

^{29}Si spectra were obtained at 17.76 MHz using an inverse gated spin decoupling mode. Chemical shifts were determined and reported relative to internal tetramethylsilane. General conditions used for a 6002 Hz spectral window were an irradiation pulse at ~30° flip angle, a relaxation delay time of 4 seconds, and an acquisition time of 0.6820 seconds. The number of scans ranged from 729 to 2839.

Acknowledgements

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