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### $^{37}\text{Cl}/^{35}\text{Cl}$ Isotope Effects on the $^1\text{H}$ NMR Spectra of Some Chloromethane Derivatives. Practical Consequences

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In Gombler's notation, $^1\Delta\text{A}(m'/m\text{X})$  is the shift in the nuclear magnetic resonance frequency of A arising from substitution of  $m\text{X}$  by  $m'\text{X}$  ( $m' > m$ )  $n$  bonds from A. In general,  $m'\text{X}$  causes increased screening of A (lower frequency, negative shifts); isotope shifts are largest when  $n = 1$ , are proportional to the chemical shift range of A, are related to the fractional change in mass upon isotope replacement, and are roughly additive. $^{2,3}$  In view of these characteristics, it is perhaps expected that relatively few  $^n\Delta\text{A}$  values are available for  $^{37}/^{35}\text{Cl}$ .  $^1\Delta\text{A}$  has been reported for  $^{31}\text{P}$  in  $\text{PCl}_3$ ,  $^{195}\text{Pt}$  in  $[\text{PtCl}_6]^{2-}$ , and  $^{19}\text{F}$  in  $\text{CCl}_3\text{F}$ .  $^{13}\text{C}$  in some chlorine derivatives of hydrocarbons is  $-0.1$  Hz at 25 MHz, or  $-4$  ppb (parts per billion). $^7$  To our knowledge, no  $\Delta^1\text{H}(^{37}/^{35}\text{Cl})$  measurements have been reported.

Figure 1 displays  $^1\text{H}$  NMR spectra at 300 MHz for  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ . The  $^2\Delta^1\text{H}$  values are small but significant. From the figure and its caption it is clear that  $^2\Delta^1\text{H}$  ranges from  $-0.04$  to  $-0.08$  Hz, that is, from  $-0.13$  to  $-0.26$  ppb. To within experimental error the isotope shifts are additive within a molecule ( $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ ) and appear to be very slightly larger in acetone- $d_6$  than in  $\text{CS}_2$  solution.

The observed isotope shifts have some practical consequences. The  $^1\text{H}$  NMR spectrum of, for example, 1,1-dichloroethane at 300 MHz displays no evidence for  $^3\Delta^1\text{H}$  but, in the methine region, the outer peaks of the quartet demonstrate a  $^2\Delta^1\text{H}$  of  $-0.066$  (1) Hz, the same as seen for  $\text{CH}_2\text{Cl}_2$  in the same solvent,  $\text{CS}_2$ . In a 2.5 mol % acetone- $d_6$  solution,  $^2\Delta^1\text{H}$  is  $-0.065$  (4) Hz for the ethane derivative. The inner peaks of the quartet are a jumble because isotope shifts are superimposed on second-order splittings of similar magnitude. Consequently, precise spectral parameters are only attainable if the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope effects are built into an analysis.

Figure 2 shows the  $^1\text{H}$  NMR spectrum of the methine proton of benzyl chloride together with computed spectra that do and do not take the isotope shifts into account.

Because chloroform is often used as a line shape standard, $^8$  it may be noted that its  $^1\text{H}$  NMR spectrum consists of a number of peaks (Figure 1). At 500 MHz, now a common frequency in NMR, and at 600 MHz, not yet common, the  $^1\text{H}$  NMR spectrum will display a characteristic

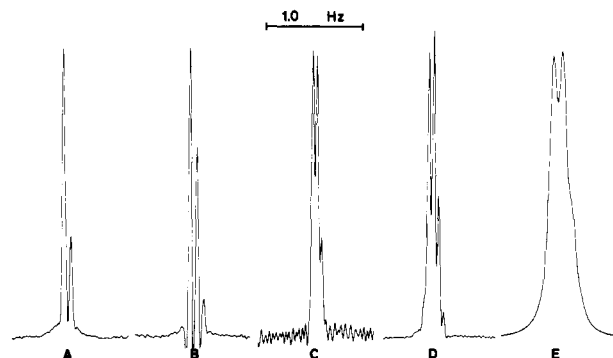


Figure 1. In A, the  $^1\text{H}$  NMR spectrum of a ca. 2 mol % solution of  $\text{CH}_3\text{Cl}$  in  $\text{CS}_2$ , containing also 10 mol % of  $\text{C}_6\text{D}_{12}$  and 0.5 mol % TMS, is shown at a spectrometer frequency of 300.135 MHz (Bruker AM300) and a probe temperature of 297 K. The digital resolution was 0.006 Hz/point and a line broadening of 0.60 was used. The peak widths at half-height are less than 0.04 Hz. The natural abundance of  $^{35}\text{Cl}$  is 75.5% and that of  $^{37}\text{Cl}$  is 24.5%, implying relative areas of 1.00:0.32 for the isotopically shifted peaks. Apparently the resolution enhancement procedures have not markedly distorted the relative heights of the peaks, which have the same width to within experimental error. The shift to low frequency (increased screening) for the  $\text{CH}_3^{37}\text{Cl}$  molecules is 0.07 $_0$  Hz or 0.23 ppb. An almost identical spectrum appears for a ca. 2 mol % solution in acetone- $d_6$ , with a shift of 0.07 $_8$  Hz. In B, the  $^1\text{H}$  NMR spectrum of  $\text{CH}_2\text{Cl}_2$  as a 1 mol % solution in acetone- $d_6$  is shown, some distortion of peak intensities arising from the resolution enhancement procedures. The three peaks have theoretical intensities of 1.00:0.65:1.1, quite close to the observed heights of 1.00:0.65:0.12. The isotope shifts appear to be additive, the two values both being 0.07 $_0$  Hz in magnitude. In C, the  $^1\text{H}$  NMR spectrum of a 1 mol % solution of  $\text{CHCl}_3$  in the  $\text{CS}_2/\text{C}_6\text{D}_{12}/\text{TMS}$  mixture is shown. Only three of four peaks are apparent, the intensity ratios being predicted as 1.00:0.97:0.32:0.03. The isotope shifts are again additive, amounting to 0.04 $_4$  Hz. In D the test sample for the spectrometer (10%  $\text{CHCl}_3$  in acetone- $d_6$ ) has its  $^1\text{H}$  NMR spectrum shown. All four peaks are visible at the cost of peak distortions. The three shifts are 0.05 $_1$  Hz each. Another sample, 1 mol % in acetone- $d_6$ , gave 0.04 $_8$  Hz for the isotope shifts. The  $^1\text{H}$  NMR spectrum of the  $\text{H}^{13}\text{CCl}_3$  molecules in the test sample was noisy and, to within experimental error, no evidence was found for a  $^{13}\text{C}$  isotope effect on the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope effect on the proton screening constant or of a  $^{37}\text{Cl}/^{35}\text{Cl}$  isotope effect on  $^1J(\text{C,H})$ .  $^1J(\text{C,H})$  is 214.92 $_8$  Hz for the  $\text{H}^{13}\text{C}^{35}\text{Cl}_3$  molecule and 214.93 $_0$  Hz for the  $\text{H}^{13}\text{C}^{35}\text{Cl}_2^{37}\text{Cl}$  molecule. $^{11}$   $\Delta^1\text{H}(^{13}/^{12}\text{C})$  is  $-0.80_3$  Hz or  $-2.6_8$  ppb in both molecules. In E the  $^1\text{H}$  NMR spectrum of the test sample is simulated at 600 MHz with a line width of 0.1 Hz for each of the four peaks.

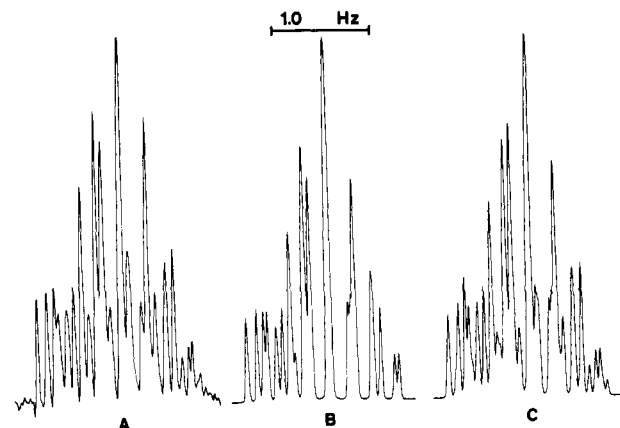


Figure 2. The  $^1\text{H}$  NMR spectrum at 300 MHz of the methine proton in benzyl chloride is shown, together with theoretical spectra computed without (B) and with (C) the presence of a  $^2\Delta^1\text{H}(^{37}/^{35}\text{Cl})$  of  $-0.07_6$  Hz. The spectral parameters were obtained from a complete analysis of the seven-spin  $^1\text{H}$  NMR spectrum for a 2.5 mol % solution in acetone- $d_6$ . In  $\text{CS}_2$  solution a  $^2\Delta^1\text{H}$  of  $-0.05_1$  Hz appears to be present. The line widths of the computed spectra are 0.03 Hz.

asymmetry if the isotope shifts are not resolved, but reasonably good resolution (0.1 Hz) is nevertheless attained (see the theoretical spectrum in Figure 1). It is also apparent that  $^1\Delta^{13}\text{C}$ -

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( $^{37}\text{Cl}/^{35}\text{Cl}$ ) numbers will be ubiquitous at these spectrometer frequencies.

Finally, it is clear that longitudinal and, particularly, transverse relaxation times of the protons in these molecules are long enough to attain the small line widths displayed in the spectra. Scalar relaxation of the second kind<sup>9</sup> by the rapidly flipping  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclei causes only a small broadening. At 300 MHz the line widths of the shifted peaks appear to be equal, perhaps a consequence of the very similar magnetic properties<sup>9</sup> of the two chlorine isotopes. However, from the reported  $T_2$  of 1.5 s for the proton<sup>10</sup> in  $\text{SiHCl}_3$ , it follows that isotope shifts in chlorosilanes will be observed only at the highest available frequencies.

**Acknowledgment.** We thank Craig Takeuchi for help with a measurement and the Natural Sciences and Engineering Research Council of Canada for financial support.

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### A Silicon-Nitrogen Analogue of the [PPN]<sup>+</sup> Cation: Synthesis and Structural Characterization of the [Ph<sub>3</sub>SiNSiPh<sub>3</sub>]<sup>-</sup> Ion

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Alkali metal derivatives of silylamides have attracted considerable attention due to interest in their unusual structures, their utility as amide transfer agents, their strong nucleophilic character, and also the apparent multiple nature of their Si-N bonds.<sup>2</sup> Usually silicon-nitrogen bonds are about 1.73 Å in length, but this value is thought to be short because it is significantly less than the predicted sum of the radii of Si and N, which is approximately 1.84 Å.<sup>2</sup> The shortening may be accounted for in terms of delocalization of the nitrogen lone pair into silicon d-orbitals although other explanations are possible.<sup>2</sup> A number of structures of alkali metal silylamides have been reported.<sup>3-8</sup> However, these invariably involve a metal-nitrogen interaction and, unless a chelating ligand is used, the compounds are generally associated. Noting the isoelectronic nature of the [PNP]<sup>+</sup> and [SiNSi]<sup>-</sup> arrays we hoped to synthesize a compound involving an unassociated ion of the type [R<sub>3</sub>SiNSiR<sub>3</sub>]<sup>-</sup> which should also have, by comparison with the [PPN]<sup>+</sup> (i.e., bistrisphenylphosphiniminium) cation,<sup>9</sup> a significant degree of multiple bonding between Si and N. We now report that sequential treatment of the crowded hexaphenyldisilylamine  $\text{HN}(\text{SiPh}_3)_2$  (**1**) with *n*-BuLi and 12-crown-4

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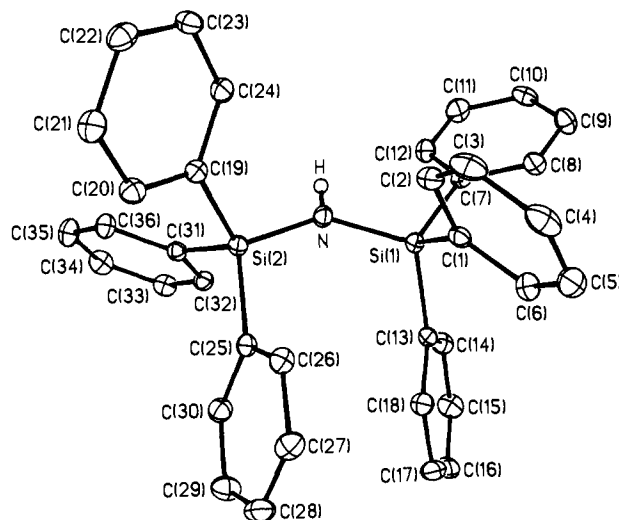
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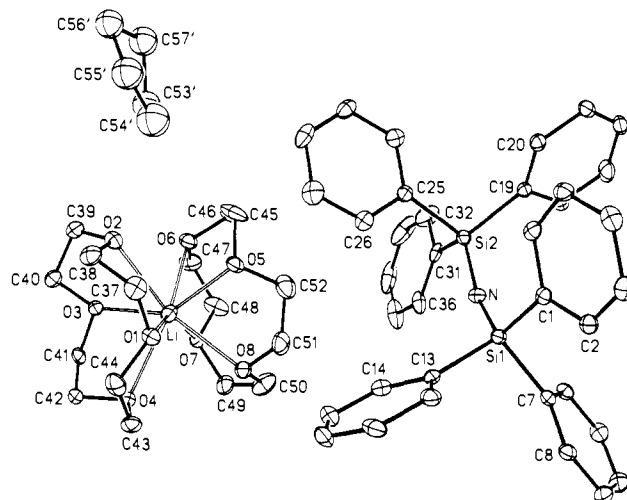
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**Figure 1.** Computer-generated plot of **1** (thermal ellipsoids at 30% probably level, arbitrary fixed radius circle used for H). Important bond distances (Å) and angles (deg) are the following: NSi(1) = 1.718 (3), NSi(2) = 1.726 (3), NH = 0.69 (4), Si(1)C(1) = 1.871 (4), Si(1)C(7) = 1.880 (3), Si(1)C(13) = 1.877 (3), Si(2)C(19) = 1.871 (4), Si(2)C(25) = 1.872 (4), Si(2)C(31) = 1.874 (4), Si(1)NiSi(2) = 136.1 (2), Si(1)NH = 109 (4), Si(2)NH = 115 (4).



**Figure 2.** Computer-generated plot of **2** (30% probability level). THF molecule was symmetry generated from the refined THF position to show closest approach of C(54) (refined as an oxygen) to anion and cation (3.4 Å). Important bond distances (Å) and angles (deg) are the following: Si(1)N = 1.633 (4), Si(2)N = 1.634 (4), Si(1)C(1) = 1.909 (5), Si(1)C(7) = 1.900 (5), Si(1)C(13) = 1.920 (5), similar SiC distances for Si(2), SiNSi = 154.9 (3).

in THF results in the isolation of crystals of the complex  $[\text{Li}(12\text{-crown-4})_2][\text{N}(\text{SiPh}_3)_2]\cdot\text{THF}$ , (**2**), which has the novel ion  $[\text{Ph}_3\text{SiNSiPh}_3]^-$  as part of its crystal lattice.

The precursor disilylamine  $\text{HN}(\text{SiPh}_3)_2$ <sup>10</sup> (**1**) was synthesized by the treatment of  $\text{H}_2\text{NSiPh}_3$ <sup>11</sup> with *n*-BuLi and then  $\text{Ph}_3\text{SiCl}$  in THF. Its structure<sup>12</sup> (Figure 1) has a number of interesting features. The most notable is the wide Si-N-Si bond angle of 136.1 (2)° which suggested that a significantly wider angle might be obtained on deprotonation. The Si-N distances in **1** are normal, having an average value 1.722 (3) Å, and the HNSi(1)Si(2) array is planar. The structure may be contrasted to that of HN-

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