^{29}Si–{^{1}H} Nuclear Overhauser Effects for Phenylsilanes

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Summary The ^{29}Si–{^{1}H} nuclear Overhauser effect is found to be substantial for Ph_3SiH but small for $PhSiH_3$; the difference in behaviour is attributed to the low barrier to internal rotation about the Si–C bond in phenylsilane itself.

MUCH information has been obtained recently regarding ^{13}C–{^{1}H} nuclear Overhauser effects.[1–3] This information, together with values of ^{13}C spin-lattice relaxation times, allows some of the contributions to relaxation rates to be evaluated separately. Specifically, the nuclear Overhauser effect (NOE) is determined by the competition between certain dipolar relaxation mechanisms and other contributions. The results give information about molecular dynamics. Similar data can be obtained from other appropriate nuclei. In particular the ^{29}Si nucleus is of interest. Its natural abundance (4·67%) is higher than that of ^{13}C, and silicon has a rich chemistry. However, there are few studies of ^{29}Si n.m.r. in the literature, and only two, so far as we are aware, relating to quantitative NOE measurements.[4,5] Since ^{29}Si has a negative magnetogyric ratio ($-5{\cdot}314 \times 10^7$ rad T^{-1} s^{-1}), the NOE is expected to be generally negative. We report results for two compounds, phenylsilane and triphenylsilane, which show opposite extremes of behaviour.

We define the nuclear Overhauser enhancement,[1] as follows:

$$\eta = (I_{\mathrm{DR}}/I_{\mathrm{SR}}) - 1$$

where I_{DR} and I_{SR} are the total integrated intensities of the ^{29}Si signal under double resonance, ^{29}Si–{^{1}H}, and single resonance conditions respectively. If the interrupted scalar coupling relaxation mechanism is not present and if extreme narrowing conditions apply (both these restrictions are likely to be valid in the present cases) η for ^{29}Si–{^{1}H} experiments is expected[2] to lie between $-2{\cdot}52$ [when the intramolecular dipolar (Si,H) relaxation mechanism predominates] and zero (when other mechanisms predominate). Our results show that at ambient temperature (38 °C)η values for triphenylsilane and phenylsilane are $-2{\cdot}41 \pm 0{\cdot}1$ and $-0{\cdot}07 \pm 0{\cdot}1$ respectively. The former value is in close agreement with that reported[4] ($-2{\cdot}51$) for diphenylsilane.

The probable reason for this marked divergence in behaviour lies in the differences in internal motion for the molecules. In the cases of diphenyl- and triphenyl-silane, barriers to internal motion about the Si–C bonds are twofold in character and are likely to be appreciable. On the other hand phenylsilane is a toluene-like molecule and the barrier is likely to be very low (it has been estimated[6] to be 35 ± 10 cal mol^{-1}). It is probable that in these circumstances the spin–internal rotation relaxation mechanism predominates for phenylsilane, whereas the (Si,H) intramolecular dipolar relaxation mechanism predominates for

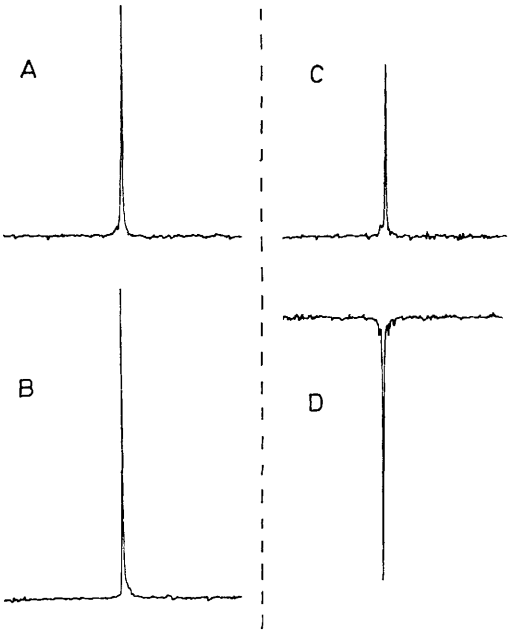

FIGURE. ^{29}Si-{^{1}H} *spectra of* (A) $PhSiH_3$ *without the NOE;* (B) $PhSiH_3$ *with the NOE;* (C) Ph_3SiH *without the NOE;* (D) Ph_3SiH *with the NOE. Spectra* A *and* C *were obtained using the gated decoupling technique. The changes due to the NOE were evaluated using computer-integrated intensities since peak heights are unreliable measures of intensities.*

Ph_2SiH_2 and Ph_3SiH. Since all three molecules contain direct Si–H bonds the dipolar mechanism is expected *a priori* to be important; however, as internal motion about the Si–C bond becomes relatively free (in $PhSiH_3$) the dipolar relaxation rate will be substantially reduced. The spin–internal rotation mechanism is known to be operative for ^{13}C relaxation of the methyl group in toluene.[7] An anti-correlation of spin rotation and dipolar relaxation rates has also been shown to occur for ^{13}C nuclei in a range of molecules.[3,8]

Our NOE measurements were made on degassed samples in solution in 75% C_6H_6/25% C_6D_6 v/v using 12 mm n.m.r. tubes and a Varian XL100 spectrometer in the Fourier Transform mode at 19·87 MHz. The values of η were obtained from integration of decoupled spectra using the gated decoupling technique.[9] Multipulse averaging was used, with 50 pulses for Ph_3SiH and 25 pulses for $PhSiH_3$; there was a pulse interval of 180 s in each case. Since η (^{29}Si) for triphenylsilane is substantially negative the ^{29}Si signal including the NOE is itself negative. The Figure shows the spectra obtained, illustrating the marked difference between Ph_3SiH and $PhSiH_3$.

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