formations (A and B) in equilibrium.[6] Form A has an axial–equatorial chemical-shift difference of 0.6 ppm and a free energy of activation for ring inversion of 12.1 kcal/mol at the coalescence temperature of −15° and was assigned a crown conformation. The second form, B, which gives a single line to −170°, was thought to be a boat–chair or distorted boat–chair with ring inversion and pseudorotation barriers inaccessibly low for nmr observation (<6 kcal/mol).[6]

Crystal-structure determinations of a number of eight-membered rings with heteroatoms at the 1,3,5,7 positions, including the cis tetramer of acetaldehyde[7] and *N,N'*-dimethyl-1,5-diaza-3,7-dithiacyclooctane,[8] show that these compounds exist in crown conformations in the crystalline state. Results of an nmr solution study of *N,N'*-dimethyl-1,5-dithia-3,7-diazacyclooctane have been interpreted in terms of a crown conformation with a high ring inversion barrier ($\Delta G^{\ddagger}$ = 14.6 kcal/mol) and a large axial–equatorial chemical-shift difference (0.3 ppm).[9]

Consequently, the sharp singlet in the low-temperature spectrum of $(CH_2S)_4$ is not consistent with the presence of a crown, even as a minor form. The boat–chair, as found in the present X-ray work, provides a satisfactory explanation of the nmr results. The boat–chair of 1,3,5,7-tetrathiocane, by analogy with the boat–chair of 1,3,5,7-tetroxocane, is expected to have low barriers to ring inversion and pseudorotation and thus should give rise to a single line in the nmr spectrum, as observed.

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Silicon-29 Fourier Transform Nuclear Magnetic Resonance Spectroscopy

Sir:

Organosilicon compounds may be studied by direct nmr observation of the 4.70% natural abundance ^{29}Si isotope.[1] As yet, only a few ^{29}Si nmr studies have appeared,[2] and those have been from cw (continuous wave) experiments not utilizing ^1H decoupling. In the most recent study, three ^{29}Si spin–lattice relaxation times (T_1) were determined, along with extensive chemical shift and spin–spin coupling data.[2c] The three reported T_1 values were 16 (tetramethylsilane, TMS), 40 (hexamethyldisiloxane), and 73 sec (tetramethyl orthosilicate). If the reported T_1 values are representative for ^{29}Si nuclei, then standard pulsed Fourier transform operation will not yield sensitivity advantages based solely on the (sweep width/line width)$^{1/2}$ formula.[3] Operational differences between ^{29}Si nmr spectroscopy and the nmr of other nuclei (for example, ^{13}C) also occur as a result of the negative magnetic moment of the ^{29}Si nucleus. The nuclear Overhauser effect (NOE) that can add up to 200% of the integrated signal intensities in proton decoupled ^{13}C experiments (notation: $^{13}C\{^1H\}$) is negative for ^{29}Si nmr. ^{29}Si resonances obtained with wide-band ^1H irradiation can be of greatly reduced intensities, or even *nulled* or *inverted*, depending on the extent that dipole–dipole interactions with protons control spin–lattice relaxation of the ^{29}Si nuclei.[4]

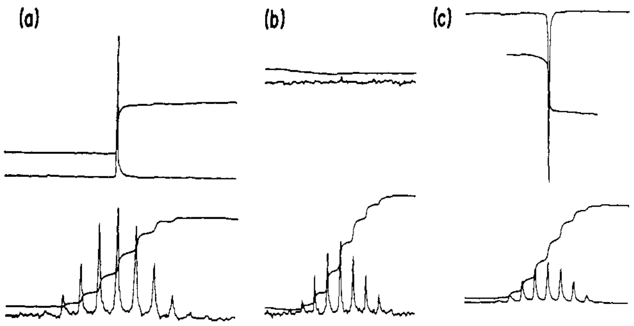

Figure 1. ^{29}Si NOE determinations for TMS at (a) −50°, (b) −62.5°, and (c) −83°. The proton-decoupled spectra are shown above undecoupled spectra. In determining the integral for the undecoupled resonances, the central five peaks were added together and multiplied by 1.17 to account for the other eight lines. In Figure 1a and 1c the decoupled resonance is scaled down. All integrals are shown unscaled. NOE values are listed in Table I.

We now wish to report T_1 and NOE data for TMS, diphenylsilane, and octamethylcyclotetrasiloxane. These data demonstrate the problems associated with ^{29}Si Fourier transform nmr, and suggest experimental methods for overcoming those disadvantages.

^{29}Si spin-lattice relaxation times and NOE measurements for TMS at six temperatures are given in Table I.

Table I. ^{29}Si Spin–Lattice Relaxation Times and Nuclear Overhauser Effects in TMS[a]

Temp, °C[b]	T_1, sec[c]	NOE (η)[d]	T_1^{DD}, sec[e]	T_1^{SR}, sec[e]
+25	19	−0.09		
0	23.3	−0.205	286	25.4
−20	32.5	−0.35		
−50	42.0	−0.495	213.8	52
−62.5[f]	55[g]	−1.0	139[g]	91[g]
−64[f]		−1.03		
−83[f]	37	−1.59	58.6	100

[a] 85% TMS, 15% acetone-d_6. Oxygen removed with N_2. Experiments performed on a Varian XL-100-FT system at 19.9 MHz. [b] ±2–3°. [c] Inversion–recovery pulse sequence. Estimated errors <10%. [d] Theoretical maximum, η −2.52.[4] Determined directly from the decoupled and undecoupled spectra, estimated maximum error <0.1. [e] Estimated error in T_1^{SR} $\lesssim$20%. Chemical-shift anisotropy relaxation assumed insignificant. [f] Sample: 75% TMS, 25% CD_2Cl_2. [g] $^{29}Si\{^1H\}$ signal nulled. T_1 determined from undecoupled pulsed Fourier transform resonance spectra.

Three NOE determinations are shown in Figure 1. The short T_1 values at higher temperatures (Table I)

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[1] Sensitivity in natural abundance ^{29}Si nmr, based on the ^{29}Si magnetogyric ratio and isotopic abundance, is *ca.* twice that in natural abundance ^{13}C nmr, not 20 times as great, as given by Wells (P. R. Wells, *Determination Org. Struct. Phys. Methods*, **4**, 237 (1971)).

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indicate that spin–rotation (SR) relaxation dominates for TMS near its boiling point (possibly vapor phase relaxation), and that spin–rotation relaxation contributes significantly even at fairly low temperatures. The experimental NOE values confirm that $^{29}Si-^{1}H$ dipole–dipole (DD) relaxation is not significant near room temperature. However, below −70°, dipole–dipole relaxation dominates for TMS. At −62.5°, the signal *null* temperature (see Figure 1b), the $^{29}Si-^{1}H$ dipole–dipole mechanism contributes 40% (calculated from $-1.0/-2.52$) to relaxation of the TMS silicon nucleus.

In larger molecules with nonprotonated silicon nuclei (silicons with no directly attached protons) Hunter and Reeves observed very long T_1 values.[2c] To determine the contribution of the dipole–dipole mechanism to nonprotonated silicon relaxation in larger molecules, we examined octamethylcyclotetrasiloxane. The ^{29}Si T_1 and NOE, 100 sec and −1.83, respectively (38°), indicate that dipole–dipole relaxation is more able to compete with spin–rotation relaxation in molecules significantly larger than TMS.

Protonated ^{29}Si nuclei are relaxed predominantly by $^{29}Si-^{1}H$ dipole–dipole interactions.[5] In diphenylsilane, T_1 for the silicon is 16.5 sec and the observed NOE is -2.51 ± 0.10 (sample: 25% acetone-d_6, at 38°). The ^{29}Si T_1 in diphenylsilane can be compared with the protonated carbon T_1 values observed in the same sample. The ^{13}C T_1 values, measured at 25.2 MHz, were C_o, 5.5 sec, C_m, 5.5 sec, and C_p, 3 sec.[6] ^{29}Si relaxation times (dipole–dipole) are expected to be *ca.* nine times longer than analogous ^{13}C T_1 values because of (a) longer bond lengths and (b) the smaller magnetic moment for ^{29}Si. The ring carbon T_1 values are for CH carbons; CH_2 carbons would relax approximately twice as fast. Taking the multiplicity of attached protons into account, the differential between the ^{29}Si and ^{13}C T_1 values is in close agreement with theoretical expectations.

Conclusions and Comments. (1) As a result of longer spin–lattice relaxation times and a smaller chemical-shift range, pulsed Fourier transform operation is not expected to give as much sensitivity advantage as for ^{13}C nmr. Refocusing pulse schemes such as DEFT[7] may help to overcome the longer T_1 values for ^{29}Si nuclei if the spin–spin relaxation times (T_2) are sufficiently long (and if ^1H coupling is restricted to a single frequency or a narrow bandwidth).

(2) Pulse-modulated ^1H decoupling methods such as the one proposed by Freeman[8] to suppress the NOE for decoupled ^{13}C spectra may be particularly suited for $^{29}Si\{^1H\}$ studies because of the long ^{29}Si relaxation times. Also, suppression of the NOE in $^{29}Si\{^1H\}$ spectra would eliminate the problem of *nulled* or *inverted* signals. In any case total signal strength will not be less than $1.0/1.52 = 67\%$ of the signal obtained with the NOE.

(3) TMS, with a relatively short T_1 and very low NOE at room temperature, should make a good ^{29}Si nmr standard for use above 0°.

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[5] In very small molecules with protonated silicon nuclei, spin–rotation relaxation should be competitive.

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The Exo–Endo Steric Impediment in Norbornene. Electrocyclic Closure in Bicyclo[4.2.1]nona-2,4-dienes

Sir:

One of the most remarkable features of the chemistry of norbornene and its derivatives is the fact that electrophilic reagents nearly always attack from the exo side of the molecule.[1] The origin of this peculiarity has been vigorously debated for a number of years and the matter still remains unresolved.[2] A variety of reasons have been advanced: steric hindrance,[3] torsional interactions,[4] polar effects,[5] and stereoelectronic factors.[6] However, an adequate explanation is still lacking. One of the difficulties inherent in the problem is that all the examples cited concern additions in which the attacking reagent is forming a bond to the C-2 atom of the norbornene skeleton and that necessarily both electronic and steric effects are simultaneously and inextricably at play. Thus, an evaluation of just the steric factor by itself is hard, if not impossible, to get. We now report on an experiment in which steric factors alone are expected to determine the formation of exo and endo derivatives of norbornane.

The substrate we have selected is bicyclo[4.2.1]nona-2,4-diene (**1**). Photochemically the diene system may be expected to undergo two disrotatory closures either to give the exo cyclobutene derivative **2** or its endo isomer **3**.[7] Inspection of a suitable model of **1** indicates that the atoms of the diene moiety and the bridgehead atoms C-1 and C-6 all lie in the same plane. Consequently, electrocyclic closure between C-2 and C-5 will entail the formation of a σ bond in the plane defined by the C-1, C-2, C-5, and C-6 atoms and parallel to the axis which cuts through the C-1 and C-6 atoms. Accordingly, the creation of the norbornane skeleton by this internal bond should be electronically indifferent to the presence of the methylene or ethylene bridges. At the moment of junction, the configurational fate of the cyclobutene fragment should be de-

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