In any circumstance, the yields are surely quite large and they seem to be independent of 10-PP concentration; thus the present results support the dimer cation equilibrium as an effective means for lowering the triplet generation efficiencies in susceptible systems. Moreover, they reinforce most directly the hypothesis, advanced earlier, that initial excitation frequently is very efficient in these systems and that low luminescence yields often result from inefficiencies subsequent to electron transfer.

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X-Ray Crystallographic and Solution Nuclear Magnetic Resonance Studies of 1,3,5,7-Tetrathiocane

Sir:

Nmr results on 1,3,5,7-tetrathiocane $(CH_2S)_4$, described below, suggest that this cyclic tetramer of thioformaldehyde does not exhibit the crown conformation commonly found in analogous heterocyclic eight-membered ring compounds. Unit cell parameters have been reported for crystalline $(CH_2S)_4$,[1] and the space group was reported to be $P2_1/c$, with three crystallographically nonequivalent molecules in the asymmetric unit. We have determined the crystal structure of this compound with X-ray diffractometer data. The unit cell parameters, a = 20.27, b = 8.73, and c = 13.44 Å, β = 99.72°, are essentially the same as those previously reported.[1]

X-Ray crystallographic data were collected with a Syntex P$\bar{1}$ automated diffractometer, with graphite monochromatized Mo Kα radiation. The reflection intensities were measured from a crystal of cuboidal shape having average linear dimensions of 0.2 mm. All independent reflections were measured out to a value of $(\sin\theta)/\lambda = 0.6$ Å^{-1}. Standard reflections were observed to decrease in intensity in an approximately linear fashion during data collection, and this was ascribed to crystal decomposition and sublimation. The intensities were corrected for this fall-off, which amounted at most to 25%. In all, 1783 reflections were taken to be observable.

Values of $|E|_{hkl}$ as customarily defined were calculated for all reflections by the application of Wilson[2] statistics. Signs for all E values of magnitude greater than 1.7, about 400 in all, were determined by application of Sayre's relation[3] in the computer program of Long.[4] A three-dimensional E map then revealed 12 peaks of about the same height, at least twice as high as any other peaks observed. These were taken to be the 12 independent sulfur atoms, and the positions were used to calculate a set of signs. All carbon atom positions were then determined by two iterations of difference electron density maps. Refinement of the atomic positions by full-matrix least-squares methods[5] with anisotropic temperature parameters converged with an R value of 0.092.

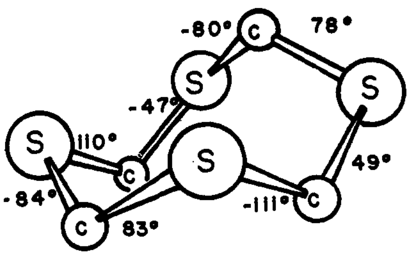

Figure 1. 1,3,5,7-Tetrathiocane molecule in the boat–chair conformation. Torsion angles are indicated about each bond.

At the present stage of refinement, the esd's for sulfur and carbon atom positions are 0.006 and 0.02 Å, respectively. Within limits of error, the three crystallographically nonequivalent molecules exhibit the identical boat–chair conformation, illustrated in Figure 1. The molecular geometry averaged overall gives the following values: S–C bond length = 1.82 Å, S–C–S bond angle = 116°, and C–S–C bond angle = 103°, with no significant deviations from these values. The torsion angles shown in Figure 1 for successive bonds are averaged over the three molecules, whose respective values do not in any case differ significantly. Atomic positions are given in Table I.

Table I. Fractional Coordinates and Isotropic Thermal Parameters for the Atoms in the Three Crystallography Independent Molecules in the Structure of 1,3,5,7-Tetrathiocane[a]

Atom	x	y	z	B
S(1a)	0.016	0.204	0.439	3.1
S(2a)	−0.015	0.152	0.206	3.1
S(3a)	0.135	0.176	0.199	3.2
S(4a)	0.166	0.215	0.432	3.2
C(1a)	−0.031	0.095	0.331	2.7
C(2a)	0.063	0.055	0.197	2.1
C(3a)	0.135	0.294	0.309	2.5
C(4a)	0.095	0.105	0.460	1.9
S(1b)	0.306	0.243	0.251	2.8
S(2b)	0.342	0.177	0.040	2.9
S(3b)	0.492	0.150	0.139	3.4
S(4b)	0.455	0.220	0.346	3.8
C(1b)	0.307	0.106	0.147	2.3
C(2b)	0.419	0.069	0.056	2.2
C(3b)	0.478	0.074	0.260	3.0
C(4b)	0.389	0.328	0.270	2.0
S(1c)	0.662	0.283	0.141	3.2
S(2c)	0.653	0.320	−0.092	3.0
S(3c)	0.805	0.265	−0.068	3.4
S(4c)	0.814	0.235	0.163	3.6
C(1c)	0.630	0.387	0.025	3.8
C(2c)	0.740	0.403	−0.090	2.6
C(3c)	0.792	0.147	0.041	2.4
C(4c)	0.745	0.366	0.173	2.3

[a] a, b, and c in parentheses refer to the different rings.

The 251-MHz proton spectrum of 1,3,5,7-tetrathiocane in $CHCl_2F$ is a sharp singlet at room temperature (τ 5.95) and remains unchanged down to −170°. In contrast, the proton spectrum of the related 1,3,5,7-tetroxocane, $(CH_2O)_4$, shows the presence of two con-

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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.

Acknowledgments. The authors wish to thank Professor K. N. Trueblood for his helpful criticisms, and acknowledge support by National Science Foundation Grants GP 10949 and GP 27241.

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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 ^{1}H 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 ^{1}H 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]

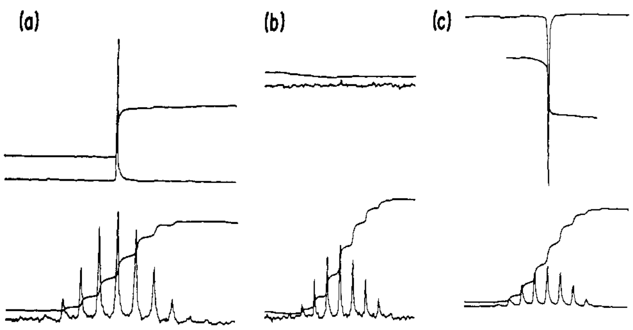

Figure 1. ^{29}Si NOE determinations for TMS at (a) −50°, (b) −62.5°, and (c) −83°. The proton-decoupled spectra are shown above undecoupled spectra. In determining the integral for the undecoupled resonances, the central five peaks were added together and multiplied by 1.17 to account for the other 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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