

**Table I.** Cyclic Voltammetry Data<sup>a</sup>

donor <sup>b</sup>	$E_{1/2}(1)$ , V	$E_{1/2}(2)$ , V	$\Delta E_{1/2}$ , V
TMTTF	0.36	0.84	0.48
TMTSF	0.55	0.94	0.39
HMTSF	0.56	0.93	0.37
TTF	0.47	0.81	0.34
TSF <sup>c</sup>	0.62	0.90	0.28
TTeF	0.59	0.84	0.25

<sup>a</sup>Volts vs. SCE at Pt button electrode; 0.2 M tetrabutylammonium tetrafluoroborate in  $\text{CH}_2\text{Cl}_2$ ; 200 mV/s sweep rate. <sup>b</sup>TMTTF = tetramethyltetrathiafulvalene; TMTSF = tetramethyltetraselenafulvalene; HMTSF = hexamethylenetetraselenafulvalene; TTF = tetrathiafulvalene; TSF = tetraselenafulvalene. <sup>c</sup>Calculated from data reported by: Engler, E. M.; Kaufman, F. B.; Green, D. C.; Klots, C. E.; Compton, R. N. *J. Am. Chem. Soc.* 1975, 97, 2921.

TTeF was prepared in 36% yield utilizing a synthetic methodology that should be useful in producing a variety of new tetratellurafulvalenes (Scheme I). Acetylene was bubbled through a THF solution of hexamethylditin containing a catalytic amount of tetrakis(triphenylphosphine)palladium to give (Z)-1,2-bis-(trimethylstannyl)ethylene, according to a literature procedure by Mitchell et al.<sup>10</sup> (unfortunately, this reaction is applicable only to terminal alkynes or tetramethyltetratellurafulvalene (TMTTeF) could have been easily made as well).<sup>11</sup> The purified distannylalkene (**1**) was then treated with 1.1 equiv of *n*-BuLi at  $-78^\circ\text{C}$  (1 h); then 0.90 equiv of elemental tellurium was added and the reaction mixture was warmed to  $-20^\circ\text{C}$ . After all of the tellurium had completed reacting, the first two steps were repeated. The reaction mixture was then cooled to  $-78^\circ\text{C}$ , whereupon 0.5 equiv of tetrachloroethylene was added. An immediate reaction took place as evidenced by a temperature increase and a rapid color change. The reaction mixture was then allowed to slowly warm up to  $25^\circ\text{C}$  over an 18-h period. After filtration of the reaction mixture, the  $\text{CS}_2$  extractable solids were isolated to give a 36% (unoptimized) yield. This yield is somewhat lower than that of some other previously synthesized tetratellurafulvalenes (e.g., BDMT-TTeF, 75%<sup>9f</sup>). This can be accounted for due to the equilibrium that exists in the first transmetalation reaction. The extent of this equilibrium was determined by treating compound **1** with 1 equiv of alkyllithium and trapping **2** with  $\text{D}_2\text{O}$ . The ratio of the expected product to the starting material, **1** was determined to be 1:1-2:1 by NMR spectroscopy.

Chromatography (silica,  $\text{CS}_2$ ) followed by spectroscopic study proved the compound to be the heterofulvalene TTeF.<sup>12</sup> The mass spectrum of TTeF exhibits a molecular ion  $\text{M}^+$  ( $m/z$  588, relative intensity 70%) with an isotope pattern closely resembling a computer simulation. Other major cluster fragments (>25% relative intensity) are  $562 \text{ M} - \text{C}_2\text{H}_2$  (28%),  $306 \text{ C}_4\text{H}_2\text{Te}_2$  (50%),  $282 \text{ C}_2\text{H}_2\text{Te}_2$  (100%),  $256 \text{ Te}_2$  (60%), and  $130 \text{ Te}$  (45%). High-resolution mass spectrometry shows peaks in the molecular ion cluster at 595.6573 (calcd for  $\text{C}_6\text{H}_4^{130}\text{Te}_4^+$ , 595.6562) and in the  $\text{M} - \text{C}_2\text{H}_2$  cluster at 569.6439 (calcd for  $\text{C}_4\text{H}_2^{130}\text{Te}_4^+$ , 569.6406) and a peak corresponding to  $\text{C}_6\text{H}_4^{130}\text{Te}_3^{128}\text{Te}^+$  at 593.6570 (calcd 593.6545).

The electrochemical data, obtained by cyclic voltammetry, is shown in Table I. TTeF, as expected, shows two reversible one-electron oxidations. The value for the first oxidation potential ( $E_{1/2}(1)$ ) indicates an ionization potential for TTeF between TTF and TSF. With an ionization potential in this range it should be possible to form organic metals from TTeF. The other expected electrochemical result is that the  $\Delta E_{1/2}$  follows the trend  $\text{TTeF} < \text{TSF} < \text{TTF}$ , suggesting that the intramolecular Coulomb repulsion energy decreases in this series. It is interesting to note

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(12) <sup>1</sup>H NMR ( $\text{CS}_2/\text{C}_6\text{D}_6$ , relative to  $\text{Me}_4\text{Si}$ , 400 MHz) 8.48 ppm (s); UV ( $\text{Cl}_2\text{CHCH}_2\text{Cl}$ )  $\lambda_{\text{max}} = 324 \text{ nm}$ ; IR (KBr) 1498 (w), 1265 (s), 1210 (w), 810 (w), 647 (m), 641 (m), 600 (s), 596 (s), 586 (sh), 408 (w), 382 (w), 362 (w). Anal. Calcd for  $\text{C}_6\text{H}_4\text{Te}_4$ : C, 12.29; H, 0.69; Te, 87.03. Found: C, 12.27; H, 0.71; Te, 87.41.

that the  $\Delta E_{1/2}$  for BEDT-TTF is 0.24 V, making TTeF at 0.25 V one of the better donors in this respect.<sup>8b</sup>

The occurrence of an irreversible oxidation peak at 1.15 V in the crude TTeF suggests that the mixture contains some of the six-membered ring isomer **7**. This assignment is based on the similar electrochemical behavior of hexamethylenetetratellurafulvalene (HMTTeF) and its six-membered ring isomer, as well as the crystallographic structure of this compound.<sup>13,14</sup> Tetratellurafulvalene and **7** can be separated by HPLC and the components identified by using a stopped flow-UV scan method.<sup>15</sup> We estimate that the reaction product contains about 85% TTeF and about 15% **7**. A similar ratio was obtained by comparing anodic peak currents in the cyclic voltammogram.

While we are currently attempting to obtain single crystals of a variety of charge-transfer complexes and radical cation salts of TTeF, we believe it is desirable to make this synthesis available to the chemistry and physics community. This will ensure that the broadest range of solid-state properties is explored.

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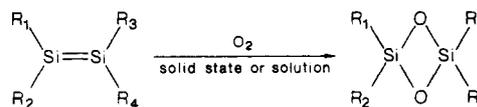
(15) TTeF was separated utilizing a C-18, reverse-phase column at  $25^\circ\text{C}$  with a 60%  $\text{CH}_3\text{CN}/40\% \text{H}_2\text{O}$  solution as the mobile phase. It has been noted that some decomposition of TTeF occurs during reverse and normal phase chromatography.

### Bonding in 1,3-Cyclodisiloxanes: <sup>29</sup>Si NMR Coupling Constants in Disilenes and 1,3-Cyclodisiloxanes

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The nature of the bonding in 1,3-cyclodisiloxanes (**6–10**) has been the subject of considerable discussion in the chemical literature since their discovery in 1981.<sup>1</sup> In this class of compounds,



- 1  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{Mes}$  6
- 2  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Mes}$   $\text{R}_4 = \text{Xyl}$  7
- 3  $\text{R}_1 = \text{R}_2 = \text{Mes}$   $\text{R}_3 = \text{R}_4 = \text{Xyl}$  8
- 4  $\text{R}_1 = \text{Mes}$   $\text{R}_2 = \text{R}_3 = \text{R}_4 = \text{Xyl}$  9
- 5  $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{Xyl}$  10

Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl

the observed silicon-silicon internuclear distances are remarkably short, as determined by X-ray crystallographic studies.<sup>2</sup> In the

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**Table I.** Silicon-29 NMR Chemical Shifts and  $J(\text{Si}-\text{Si})$  for Unsymmetrical Disilenes and Disiloxanes<sup>a</sup>

disilene			$\delta$	$J(\text{Si}-\text{Si}), \text{Hz}$	disiloxane		
					$\delta$		$J(\text{Si}-\text{Si}), \text{Hz}$
1	(Mes) <sub>2</sub> Si=Si(Mes) <sub>2</sub>		63.68		6	-3.35 <sup>b</sup>	
2	(Mes) <sub>2</sub> Si=Si(Mes)(Xyl)		63.14, 64.42	158	7	-3.06, -2.33	
3	(Mes) <sub>2</sub> Si=Si(Xyl) <sub>2</sub>		62.56, 65.19	155	8	-3.63, -2.14	3.85
4	(Xyl) <sub>2</sub> Si=Si(Mes)(Xyl)		63.30, 64.63	156	9	-3.50, -2.76	4.02
5	(Xyl) <sub>2</sub> Si=Si(Xyl) <sub>2</sub>		64.06		10	-3.30	

<sup>a</sup> Mes = 2,4,6-trimethylphenyl, Xyl = 2,6-dimethylphenyl. <sup>b</sup> In CDCl<sub>3</sub>.

most extreme case, tetramesitylcyclodisiloxane (**6**), the silicon-silicon internuclear distance is only 230.6 pm, even shorter than that for a normal Si-Si single bond (~235 pm). In this communication we address from an experimental viewpoint the question of whether a transannular bond exists between the two silicon atoms.

Two extreme qualitative descriptions for the bonding in the 1,3-cyclodisiloxanes were originally considered.<sup>2</sup> One involves a localized  $\sigma$ -bond framework in which there is no bonding interaction between the silicon atoms (structure A). The second



(structure B) includes a  $\sigma$  bond between the silicon atoms, making the silicon-oxygen bonds necessarily electron deficient. In structure B, the addition of molecular oxygen to the disilene breaks only the  $\pi$  bond, leaving the  $\sigma$  component of the Si-Si double bond intact. The theoretical treatments published to date, though differing in details, favor structure A.<sup>3</sup> Silicon-29 NMR spectroscopy may provide a means for differentiating between structures A and B, since the silicon-silicon coupling constant,  $J(\text{Si}-\text{Si})$ , should be much larger in B than in A.

The unsymmetrically substituted 1,3-cyclodisiloxanes (**7-9**), each containing two chemically and magnetically nonequivalent silicon atoms, were generated by oxidation of the corresponding disilenes (**2-4**)<sup>4,5</sup> in benzene solution at 25 °C. Both the disilenes and their 1,3-cyclodisiloxane products were examined by <sup>29</sup>Si NMR spectroscopy in benzene solution,<sup>6-8</sup> with the results summarized in Table I. Representative spectra are shown in Figure 1.

In structure B, the coupling constant  $J(\text{Si}-\text{Si})$  should be within the range of values observed for directly bonded Si-Si couplings,  $^1J(\text{Si}-\text{Si})$ , for which typical values for organodisilanes range from 80 to 90 Hz.<sup>9</sup> The silicon-silicon coupling constant in structure A can be viewed as the super-position of two geminal couplings,

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(4) The unsymmetrical disilenes were generated photochemically by irradiation of their trisilane precursors in pentane solution at -60 °C. Disilenes **2** and **4** are new compounds, while disilenes **1**, **3**, and **5** have been reported previously.<sup>1,5</sup> Similarly, disiloxanes **7-10** are new compounds.

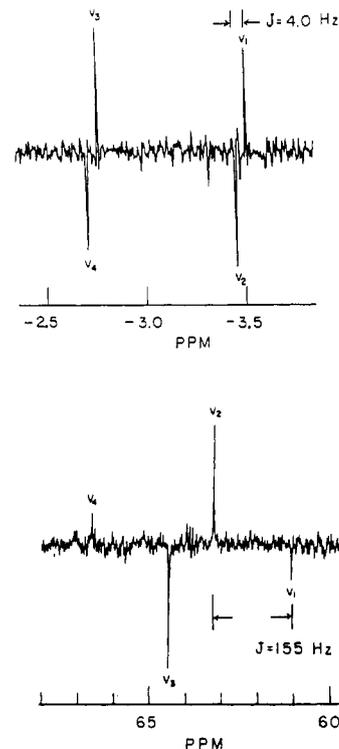
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(6) All spectra were recorded on a Bruker AM-360 (71.55-MHz) spectrometer using either INEPT<sup>7</sup> or INEPT-INADEQUATE<sup>8</sup> pulse sequences and complete proton decoupling. Chemical shifts are reported in parts per million downfield from a tetramethylsilane external reference. First-order spectra were obtained for disiloxanes **8** and **9**, while disilenes **2-4** gave non-first-order, AB spin systems (Figure 1).

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**Figure 1.** INEPT-INADEQUATE <sup>29</sup>Si NMR spectra (a, top) for disiloxane **9**,  $J = 4.02 \text{ Hz}$ ,  $\Delta\nu/J = 13.2$ ; and (b, bottom) for disilene **3**,  $J = 155 \text{ Hz}$ ,  $\Delta\nu/J = 1.2$ .

$^2J(\text{SiOSi})$ . Typical values for  $^2J(\text{SiOSi})$  range from 1 to 4 Hz.<sup>10</sup> The measured values of  $3.85\text{--}4.02 \pm 0.1 \text{ Hz}$  for the cyclodisiloxanes are consistent with structure A. However, a third model has recently been proposed by Schaefer and Grev.<sup>11</sup> In this treatment, bonding in cyclodisiloxanes is represented as a "dibridged  $\pi$  complex" in which the bonding between the silicons, if it exists, is described as an "unsupported  $\pi$  bond". Our observations, which indicate that there is little if any  $s$  orbital contribution to the bonding between the silicon atoms, are also entirely consistent with this new model.

In addition to the Si-Si coupling constants for the 1,3-disiloxanes, we report the first coupling constants  $^1J(\text{Si}=\text{Si})$  for the silicon nuclei in disilenes (Table I and Figure 1b). The measured values of 155–158 Hz for  $^1J(\text{Si}=\text{Si})$  represent an increase by a factor of ca. 1.8 over  $^1J(\text{Si}-\text{Si})$  normally observed for the silicon-silicon single bond in organodisilanes.<sup>9,12</sup> By comparison,  $J(\text{C}-\text{C})$  increases by a factor of 1.98 from ethane [ $J(\text{C}-\text{C}) = 34.6 \text{ Hz}$ ] to ethylene [ $J(\text{C}=\text{C}) = 67.6 \text{ Hz}$ ] in the carbon system, where it has been established that the carbon-carbon coupling constant is related qualitatively to the percent  $s$  character of the carbon orbitals involved in C-C bonding.<sup>13,14</sup> Thus, our measured values

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(12) Ab initio calculations on the unsubstituted disilene, H<sub>2</sub>Si=SiH<sub>2</sub>, predict a value slightly higher for  $J(\text{Si}=\text{Si})$ , +183.6 Hz. See: Galasso, V.; Fronzoni, G. *Chem. Phys.* **1986**, *103*, 29.

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for  $J(\text{Si-Si})$  in both the disilene and 1,3-disiloxane systems provide experimental verification for the proposed bonding descriptions.

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### Inelastic Neutron Scattering from Tetramethylammonium Cations Occluded within Zeolites

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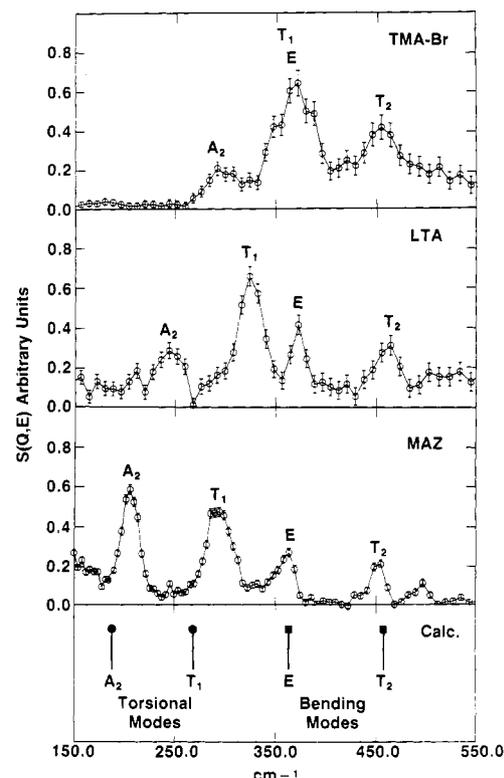
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The use of organic bases, for example, tetraalkylammonium hydroxides, and other organic reagents has greatly enhanced the scope of gel/solution synthesis routes to crystalline microporous materials such as zeolites.<sup>1,2</sup> The role of these organic components, however, continues to be the topic of considerable debate. The organic components first modify the gel structural chemistry. The presence of tetramethylammonium (TMA) hydroxide, for example, promotes the formation of double four-ring units in silicate solutions.<sup>3,4</sup> Occlusion of organic gel components in zeolite crystal structures, however, leads also to the concept of a "templating" effect<sup>5</sup> in which the organic component provides a basis around which the developing zeolite cages form. The mechanism of this templating process remains somewhat ill defined and must, at least, be of variable specificity. Thus a wide range of organic amines can be used to precipitate formation of ALPO-5 (AFI framework),<sup>6</sup> whereas in other systems such as TPA-ZSM-5 (MFI)<sup>7</sup> and SAPO-37 (FAU)<sup>8</sup> there appears to be a close correspondence between the conformation and/or amount of template(s) and the size, shape, and number of channel intersections or cages in the zeolite crystal structure. The occluded templates have been studied by powder X-ray diffraction,<sup>9</sup> <sup>13</sup>C NMR,<sup>10,11</sup> and Raman spectroscopy.<sup>12,13</sup> We describe here the use of inelastic neutron

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**Figure 1.** Inelastic neutron scattering spectra (energy loss mode) for TMA cations in TMA-Br (16 K, CAS, top), zeolite ZK-4 (14 K, CAS, middle), and zeolite omega (12 K, QENS, bottom). The assignments of the torsion and bending modes are shown. The bottom vertical lines indicate the scaled torsion and bending mode frequencies from the ab initio calculation for the free ion.

**Table I.** Torsion and Bending Mode Frequencies ( $\text{cm}^{-1}$ ) for Tetramethylammonium (TMA) Cations in Various Environments

environment	torsion		bending		ref
	singlet A <sub>2</sub>	triplet T <sub>1</sub>	doublet E	triplet T <sub>2</sub>	
TMA-Cl	301		371	456	17
TMA-Br	294	363		456	17
TMA-Br	290	370		455	this work (CAS)
TMA-I	265	344		451	17
LTA	245	325	372	460	this work (CAS)
MAZ	206	293	365	454	this work (QENS)
TMA (soln)			370	455	13
TMA (free ion calcd)	199	287	385	485	this work

scattering (INS) to measure TMA template torsional vibrations, vibrations that prove to be sensitive to the strength of the interaction between the template cation and the enclosing zeolite cage.

Samples of zeolites ZK-4 (LTA) and omega (MAZ) of respective compositions  $\text{Na}_{9.66}\text{TMA}_{0.96}\text{Al}_{10.62}\text{Si}_{13.38}\text{O}_{48}\cdot n\text{H}_2\text{O}$  and  $\text{Na}_{6.93}\text{TMA}_{1.92}\text{Al}_{8.85}\text{Si}_{27.15}\text{O}_{72}\cdot m\text{H}_2\text{O}$  were prepared by using literature procedures<sup>14,15</sup> and characterized by inductively coupled plasma emission spectroscopy (ICPES), powder X-ray diffraction, <sup>29</sup>Si NMR, and thermogravimetric analysis (TGA). The samples were dehydrated under flowing Ar at 350 (LTA) and 400 °C (MAZ), respectively, for 2 h and loaded into 0.005-in.-walled, 7/16-in. outside diameter vanadium sample cans fitted with vacuum-tight end caps. The INS spectra were recorded at 14 K on the CAS (LTA) and at 12 K on the QENS (MAZ) spectrometers

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