(4-ring C=C stretching), 1712 (diene C=C stretching), 1441, 1416, 1364, 1227, 1094, 1057, 969, 853, 788, 765, and 733 cm^{-1}. A structureless maximum appeared at 241 nm (log ϵ = 3.3 (1)) in the ultraviolet spectrum of the triene, determined at −60 °C in 95% ethanol. The hypsochromic shift relative to dibromide **10a** is striking.

The first-order rate of valence isomerization of the bicyclic triene **2** to **1** was measured in methylene chloride at several temperatures between 0 and −25 °C. These activation parameters were determined: $E_a = 18.9 \pm 0.6$ kcal/mol, $A = 1.1 \times 10^{12}$, corresponding to a half-life of 14 min at 0 °C. Remarkably, these numbers are indistinguishable from the values reported by Vogel[14] for the ring opening of the parent hydrocarbon ($E_a = 18.7 \pm 0.8$ kcal/mol, $A = 9.1 \times 10^{11}$, $t_{1/2}$ = 14 min at 0 °C). In light of the fact that extensive fluorine substitution dramatically alters properties and behavior of unsaturated hydrocarbons, this result was hardly a foregone conclusion. Its implications will be discussed after efforts in progress to measure the equilibrium constant for the **1**–**2** interconversion have been completed.

Irradiation of a methylene chloride solution of **2** at −50 to −60 °C with a superpressure mercury arc at wavelengths >220 nm produced the *anti*-tricyclooctadiene **4**.[15] This finding lends strong support to our earlier surmise that **2** is an intermediate in the photochemistry of **1**, though it does not, of course, require that conclusion. Photoisomerization of **2** to **4** also took place in an argon matrix at 20 K.

Cyclooctatetraene itself has been reported to photocyclize to its bicyclic isomer,[16] but no tricyclo[4.2.0.0^{2,5}]octa-3,7-diene has been obtained by irradiation of either isomer.[17]

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Spectral Simplification and Improved Sensitivity in Magic Angle Sample Spinning NMR

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The magic angle sample spinning (MASS) NMR experiment[1-3] has become a popular approach for obtaining high-resolution spectra of dilute spins in solids. If the spinning speed (ν_R) is less than the breadth of the static chemical shift powder pattern $\Delta\sigma = \sigma_{11} - \sigma_{33}$, the pattern breaks up into a centerband at the isotropic frequency and sets of rotational sidebands spaced at integral multiples of the rotor frequency. However, this approach to high resolution suffers from two deficiencies. First, since the observed signal intensity is now shared among the centerband and sidebands, the sensitivity of the experiment is decreased. Second, sidebands of one resonance may overlap with those from another, making interpretation of the spectrum difficult. Two approaches have been reported for dealing with these problems,[4,5] but both partially fail when $\Delta\sigma/\nu_R$ is large. In this paper we document these shortcomings and introduce a new technique for attenuating sidebands without significant intensity losses.

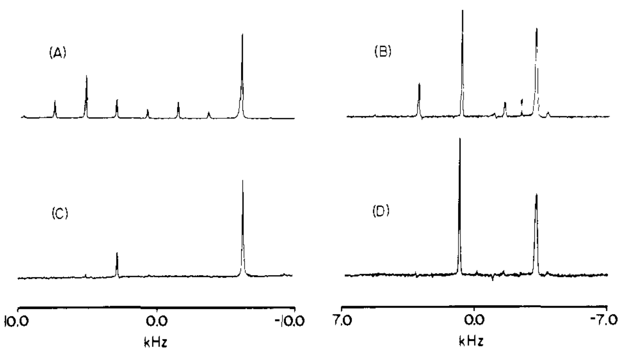

Figure 1. (A) MASS spectrum of HMB obtained at 79.9 MHz with ν_R = 2.27 kHz. The low-frequency line is due to the methyl carbons. The centerband of the aromatic resonance is denoted by an *, and contains 20% of the total integrated intensity. (B) HMB spectrum obtained with scaling (scale factor = 0.5) at ν_R = 2.27 kHz. The centerband of the aromatic resonance contains 70% of the total integrated intensity. Three weak sidebands are visible. The line denoted with a ‡ is a rotor frequency line. (C) HMB spectrum obtained with the same spinning speed by using TOSS. Sidebands are attenuated but the TOSS peak contains only 22% of the total integrated intensity. (D) HMB spectrum obtained with the same spinning speed using the new technique. The aromatic line contains 83% of the total integrated intensity.

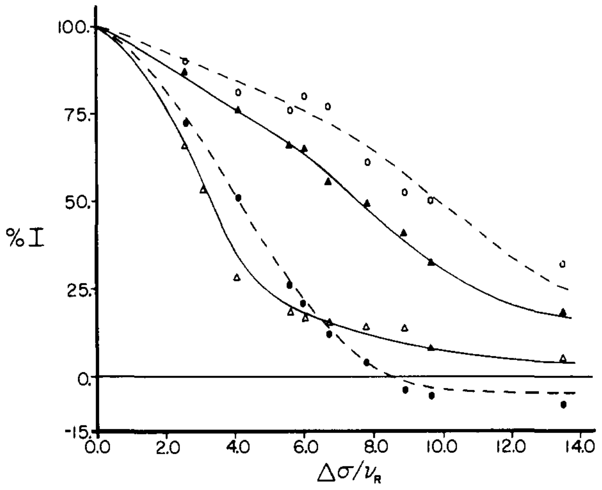

Figure 2. Experimental results showing the percentage of the total intensity contained in the centerband in the TOSS (●), MASS (△), scaled (▲), and new (○) experiment as a function of $\Delta\sigma/\nu_R$. The solid and dashed curves are the result of numerical calculations using a computer program described elsewhere.[8]

The first approach for dealing with rotational sidebands uses a multiple-pulse experiment to scale shift anisotropies by a predetermined factor.[5,6] If the anisotropies are reduced so that they are comparable to the rotor frequency, then any remaining sidebands will be very weak. Figure 1A shows a MASS spectrum of hexamethylbenzene (HMB) where the aromatic resonance consists of a centerband (*) and six sidebands. Figure 1B shows a spectrum obtained with the scaling experiment. Since the

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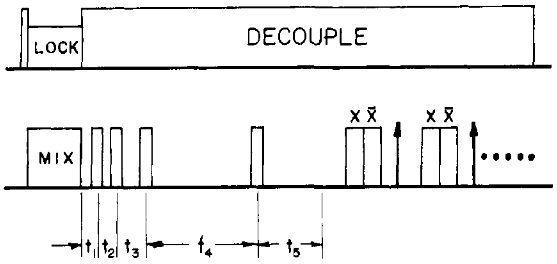

Figure 3. Pulse sequence for the new experiment. Timings for the spacing between the π pulses are given in fractions of a rotor period. $t_1 = 0.1314T_R$, $t_2 = 0.0353T_R$, $t_3 = 0.2666T_R$, $t_4 = 1.0222T_R$, $t_5 = 0.5445T_R$. Scaling pulses are 270° and the scaling duty cycle is adjusted to yield a 0.5 scale factor. Scaling begins at a rotor echo and sampling at the Hahn echo. A refocusing of resonance offset and isotropic chemical shift (Hahn echo) occurs at a $0.7745T_R$ after the last π-pulse.

effective shift anisotropy has been reduced by 0.5, more signal intensity is transferred to the centerband, which now dominates the sidebands. Figure 2 illustrates the substantial increase in sensitivity obtained with scaling. Here we have plotted the centerband intensity of an $\eta = 0$ shift tensor as a function of $\Delta\sigma/\nu_R$, and the centerband intensity in the scaling experiment (▲) is always greater than that in a MASS experiment (△). The principal drawback to scaling is that with presently available techniques it is difficult to obtain small scale factors and most work has used factors in the range of 0.35–0.5, which will strongly reduce but do not always eliminate sidebands. The second approach is due to Dixon[4] and has been christened TOSS. It uses four π-pulses to suppress sidebands, but it does not efficiently transfer signal intensity from sidebands to the centerband. This is shown in the experimental spectra in Figure 1, parts A and C. The intensity of the aromatic centerband is only 1.1 times larger than in the MASS experiment and a factor of 3 less than the centerband intensity in the scaling experiment (Figure 1B). The intensity of the centerband is determined by the average magnetization vector of each spin packet over a signal rotor period. The pulses in TOSS align the magnetization paths of different spin packets, causing the centerbands of each packet to be in (or 180° out of) phase while sidebands have phase shifts which cause their elimination when a powder average is performed.[7] The intensity of the centerband in TOSS as a function of $\Delta\sigma/\nu_R$ is also shown in Figure 2 for an $\eta = 0$ tensor. For $\Delta\sigma/\nu_R$ between 2 and 6 the TOSS peak is more intense than the centerband in the MASS spectrum, but is always less than the centerband of the scaled spectrum, and actually passes through zero and inverts for $\Delta\sigma/\nu_R \simeq 9$. The large intensity losses in TOSS can be avoided by increasing ν_R, thus decreasing $\Delta\sigma/\nu_R$. This approach is limited by current spinner technology with "routinely available" spinner speeds of 1–4 kHz.

Our approach to controlling sidebands is based on a hybrid experiment involving a new four π-pulse sequence in conjunction with scaling (Figure 3). After a four π-pulse sequence, scaling is initiated at a rotor echo and sampling begins at the normal Hahn echo position. Figure 1D shows an HMB spectrum obtained with this technique for $\Delta\sigma/\nu_R \approx 6.0$. The sidebands are absent, and the centerband intensity for the new experiment as a function of $\Delta\sigma/\nu_R$ is shown in Figure 2. Even at $\Delta\sigma/\nu_R \approx 10$, 50% of the intensity is retained while TOSS yields a weak inverted line. If one combines scaling with TOSS, sidebands will not cancel and the centerband intensity is reduced. TOSS aligns the average magnetization vectors but the scaling pulse train, by decreasing the effective anisotropy, then misaligns the vectors. The timing of the pulses in the hybrid experiment ensures alignment of the average magnetization vectors of different packets after scaling starts. The timings are thus dependent on the scale factor chosen. A table of pulse timing for scale factors from 0.3 to 0.5 will be published elsewhere.[8]

We have shown that TOSS and scaling suffer from deficiencies when $\Delta\sigma/\nu_R$ is large, and we have quantified intensity losses in the TOSS experiment. We believe the alternative technique described here will be generally useful but will be particularly important for nuclei with large shift anisotropies.

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Synthesis, Structure, and Physical Properties of a Novel Tetratellurafulvalene Electron Donor

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The realization of superconductivity in the family of salts, (TMTSF)$_2$X,[1] where TMTSF is tetramethyltetraselenafulvalene and X is any one of a number of complex inorganic anions, has renewed widespread interest in organic charge-transfer compounds.

It was recognized early that the structure adopted by the (TMTSF)$_2$X salts plays an important role in determining the physical properties of these materials.[1] In particular, the network of interdonor interactions in these systems is dominated by Se···Se contacts which are often shorter than the expected van der Waals separation; the presence of the chalcogen-dominated interdonor network has been strongly linked[2,3] to the electronic dimensionality and the achievement of bulk superconductivity in these materials.

The search for new organic electron donors of the heterofulvalene type whose salts exhibit superconductivity has followed predominantly along two molecular design strategies. First, the logical, but chemically demanding, step of synthesizing tetratellurafulvalene analogues has met with some success. Wudl[4] has reported the synthesis of HMTTeF (hexamethylenetetratellurafulvalene), and the synthesis of DBTTeF (dibenzotetratellurafulvalene) has been reported from these laboratories.[5] Second, the incorporation of several chemically inequivalent chalcogen sites within the donor framework should both increase the molecular polarizability and allow for interdonor interactions along several alternate, chalcogen-dominated pathways. Success along this second design strategy has followed from the syntheses of bis(ethylenedithiolo)tetrathiafulvalene (BEDT-TTF)[6] and

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