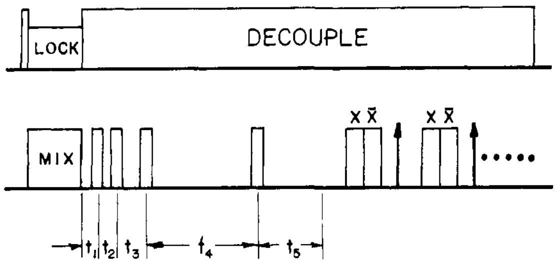

Figure 3. Pulse sequence for the new experiment. Timings for the spacing between the π pulses are given in fractions of a rotor period. $t_1 = 0.1314T_R$, $t_2 = 0.0353T_R$, $t_3 = 0.2666T_R$, $t_4 = 1.0222T_R$, $t_5 = 0.5445T_R$. Scaling pulses are 270° and the scaling duty cycle is adjusted to yield 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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Registry No. HMB, 87-85-4.

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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, $(TMTSF)_2X$,[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 $(TMTSF)_2X$ 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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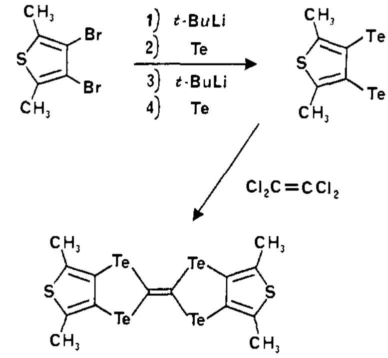
Scheme I



dithienotetrathiafulvalene (DTTTF)[7] and has culminated with the realization of superconductivity in the 2:1 ReO_4^- and I_3^- salts of BEDT-TTF.[8,9]

In this report, we describe a convenient synthetic pathway to and the molecular structure and physical properties of a novel electron donor, bis(dimethylthieno)tetratellurafulvalene (BDMT-TTeF, I), which combines the advantages of both molecular design strategies. The presence of the tetratelluraethylene core offers a distinct increase in molecular polarizability and bandwidth while the exterior dimethylthieno rings in conjunction with the tetratelluraethylene core offers the possibility of either homoatomic or heteroatomic intermolecular, interchalcogen interactions.

BDMT-TTeF was prepared in 75% yield via a procedure similar to those used to prepare DBTTeF and HMTTeF; this method is shown in Scheme I. 3,4-Dibromo-2,5-dimethylthiophene in THF was treated with 2 equiv of *t*-BuLi at -78 °C (2 h); then 1 equiv of elemental tellurium was added and the mixture warmed slowly to 0 °C. The reaction was allowed to proceed at 0 °C until all of the tellurium had reacted, and then the entire procedure was repeated. The reaction mixture was then cooled to -78 °C, $^1/_2$ equiv of tetrachloroethylene was added, and the mixture was stirred for 18 h while the temperature was allowed to reach room temperature. A brown solid was isolated by filtration, which upon extraction with CS_2 gave CS_2-soluble BDMT-TTeF in 75% yield. Recrystallization of this solid from 1,1,2-trichloroethane produced shiny, bronze-colored (reflected light), blood-red (transmitted light), leaflike crystals melting with decomposition at 295–298 °C.

The mass spectrum of BDMT-TTeF shows a molecular ion M^+ (m/z 756, relative intensity 62%) with an isotope pattern closely resembling a computer simulation. Other fragments are 500, M - 2Te (20%), 376, M^{2+} (2%), 390, $C_8H_6STe_2$ (8%), 366, $C_6H_6STe_2$ (48%), 134, C_8H_6S (52%), and 110, C_6H_6S (100%).

Cyclic voltammetry was performed on BDMT-TTeF in CH_2Cl_2 with Bu_4NBF_4 as the electrolyte using platinum button working and standard calomel reference electrodes. The compound shows two single electron oxidation potentials at 0.78 and 1.20 V, respectively. Only the first step was entirely reversible.

Finally, the molecular and crystal structure of BDMT-TTeF has been determined by X-ray diffraction methods.[10] In its crystalline environment, BDMT-TTeF is nonplanar, exhibiting an unusual[11] and very asymmetric boat conformation (see Figure 1). Quantitatively, the dihedral angles between the tetratelluraethylene core and the exterior dimethylthienoditellural planes are dramatically different at 47.1 (3)° and 16.0 (3)°. Some of the deviation from planarity is surely related to the presence in the solid of "dimers" (see Figure 1), which are coupled together through short intermolecular Te···Te contacts at 3.666 (1) and 3.758 (1) Å—the former of which is some 0.73 Å shorter than twice the van der Waals radius (2.20 Å) of Te.[12] These intermolecular Te···Te contact distances are similar to those displayed in the crystalline structure of HMTTeF[4] (with intermolecular Te···Te contacts at 3.583 and 3.743 Å).

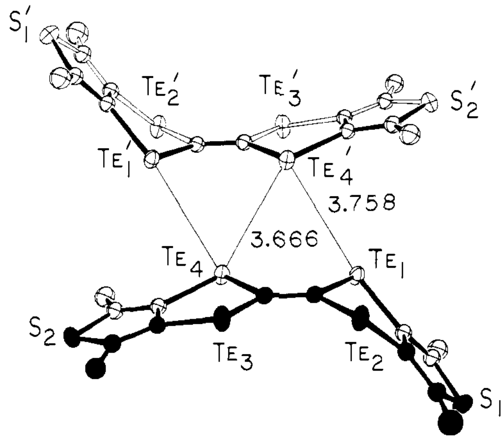


Figure 1. Molecular structure of BDMT-TTeF and the association into "dimers" in the crystal via short intermolecular Te···Te contacts. The two molecules shown are related through the inversion center at ($^1/_2$,$^1/_2$,$^1/_2$).

Collectively, these two results strongly suggest that interdonor Te···Te interactions are dominant forces in determining the mode and strength of intermolecular interactions in tetratellurafulvalenes, even more so than in tetraselenafulvalenes.[13,14] If the dominance of these interdonor Te···Te interactions, or their replacement by Te···S interactions, carries over to the charge-transfer salts of BDMT-TTeF, then the heteroatom-dominated interaction network which plays such an important[2,3] role in the achievement of bulk superconductivity in the $(TMTSF)_2X$ salts may also play an important role in these materials. In this regard, the preparation and physical characterization of both inorganic and organic charge-transfer salts utilizing BDMT-TTeF as the electron donor are under active investigation.

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Supplementary Material Available: Table of atomic positional and thermal parameters for BDMT-TTeF (1 page). Ordering information is given on any current masthead page.

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(10) X-ray analysis. Diffraction-quality, blood-red crystals of BDMT-TTeF were obtained by evaporation from CS_2. The crystal system is triclinic, space group $P\bar{1}$, with crystal data for the Friedel-reduced cell as follows: a = 9.589 (2) Å, b = 11.232 (2) Å, c = 8.635 (1) Å, α = 94.08 (2)°, β = 102.12 (1)°, γ = 89.41 (1)°, V = 907.0 Å^3, one independent molecule per cell with no required symmetry. Least-squares refinement (based on 5914 absorption-corrected X-ray data, Mo Kα radiation (λ = 0.7107 Å), $2\theta_{max}$ = 65°, T = 297 K) has led to an R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.049.

(11) In accord with data on thia-, selena-, and other tellurafulvalene systems, it is assumed that the "free" BDMT-TTeF molecule is nominally planar, with the dihedral angle between the tetratelluraethylene core and the dimethylthienoditellural planes on the order of only a few degrees.

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