

Poly(methylene ditelluride)

C. W. Dirk, D. Nalewajek,¹ Graciela B. Blanchet,[†] Howard Schaffer, F. Moraes, R. M. Boysel, and F. Wudl*

Contribution from the Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106. Received February 21, 1984

Abstract: The title compound was prepared by reduction of bis(trichlorotelluro)methane. The latter was prepared by an improved procedure. The chemical and physical properties of the polymer are described, including electrical conductivity as a function of temperature and pressure.

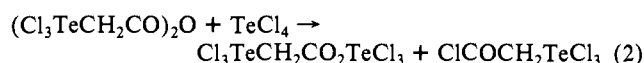
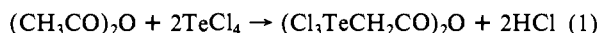
The natural evolution in research on organic conductors based on organochalcogen donors has been to move from sulfur to selenium heterocycles.² The next move further down the periodic table into organotellurium conductors was, and is, hampered by the relatively small number of synthetic reactions in organotellurium chemistry.^{3,4} It was not until 1982 that the first tellurafulvalene was reported,⁵ and to date only four organotellurium donors are known.⁴⁻⁸ So far no exotic properties associated with charge-transfer salts derived from these donors have been discovered.

In our search for synthetic intermediates for the possible preparation of tellurafulvalenes, we found Morgan and Drew's work⁹ on $\text{CH}_2(\text{TeCl}_3)_2$. In that early work, some of the properties of a reduction product (CH_2Te_2) were described. In this paper we present our most recent results with poly(methylenediteleuride) $[(\text{CH}_2\text{Te}_2)_n]$.

Results and Discussion

Preparation of Bis(trichlorotelluro)methane. Attempts to prepare this compound by the original procedure gave erratic results, and in all cases only very small amounts of pure material could be obtained. Since Morgan and Drew obtained bis(trichlorotelluro)methane as a side product in their synthesis of (trichlorotelluro)acetates, they had no reason to optimize the yield of the former. A more recent publication of Morgan and Drew's compound also did not address the synthetic problems.¹⁰

In an attempt to rationalize how $\text{CH}_2(\text{TeCl}_3)_2$ could be produced from acetic anhydride and tellurium tetrachloride, we arrived at the following sequence of reactions:

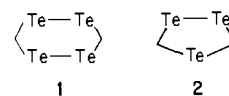


Equation 4 is just an addition of eq 1-3. Much to our gratification, we found that the stoichiometry of the left side of the eq 4 produced pure desired product in 50% isolated yield. While this result does not prove that the mechanism for product formation involves eq 1-3, it does support the notion that 3 equiv of tellurium tetrachloride is required for every molecule of acetic anhydride. The product obtained this way was a white, crystalline solid, soluble in hot chloroform and cold tetrahydrofuran (THF) without visible decomposition.

At room temperature and in a glovebox, the material slowly decomposed in the solid state, turning into a light gray solid. The latter could be purified by recrystallization from chloroform. Both NMR¹⁰ and IR spectra were in accord with the suggested structure. The infrared spectrum (cf. Experimental Section) exhibited relatively strong overtone and combination bands, which suggests further scrutiny by an infrared spectroscopist.

Poly(methylene ditelluride). Heterogeneous reduction of the above white solid near 0 °C with inorganic aqueous reducing agents (e.g., sodium metabisulfite) produced, as described earlier,^{9,10} a red powder. The red phase was thermally unstable and between 0 and 20 °C was converted to a gray solid.⁹

Elemental analysis showed the solid to be $(\text{CH}_2\text{Te}_2)_n$. Morgan and Drew had suggested a tetratelluracyclohexane (1) for the structure of $(\text{CH}_2\text{Te}_2)_n$, i.e., $n = 2$, although they also suggested that both red and gray forms may be "polymerides". Extraction



of the solid with dimethylformamide (DMF) gave an NMR spectrum consistent with this assignment.¹⁰ However, since the major constituent of gray $(\text{CH}_2\text{Te}_2)_n$ is insoluble in all known solvents, it probably consists of long chains or large rings. Long-term extraction of freshly prepared gray $(\text{CH}_2\text{Te}_2)_n$ with carbon disulfide produces a brownish red solution whose ¹H FTNMR shows single peaks at (ppm) 5.03 (relative intensity, 1), 3.67 (3), and 2.67 (1). Of these, the second peak probably corresponds¹¹ to $(\text{CH}_2\text{Te}_2)_2$ (1). The other singlets remain unassigned because of insufficient material available for characterization. However, from mass spectral evidence (see below) at least one of the peaks may be due to 2.

When the carbon disulfide extracts were evaporated, relevant groups of peaks centered at m/e 426 ($\text{CH}_2\text{Te}_2\text{CH}_2\text{TeCH}_2$), 412 ($\text{CH}_2\text{TeTeCH}_2\text{Te}$), 384 (Te_3), 270 (CH_2Te_2), 256 (Te_2), 142 (CH_2Te), and 128 (Te) were observed. This mass spectrum was much more complex than the one resulting from thermal decomposition of a freshly prepared gray sample (see below). The residue from the above, prolonged, extractions was in all respects very similar in thermal behavior to a freshly prepared sample. However, its electrical conductivity was different (see below).

Thermal analysis of the gray solid (heating rate; DTA, 10 °C/min; TGA, 20 °C/min) showed¹² one endothermic transition at 55 °C and several exothermic transitions at 100, 130, 175, 190, and 230 °C. The latter was the largest and corresponded to a decomposition reaction as determined by thermal gravimetric analysis (TGA).¹² At 55 °C, the sample becomes tacky and can

(1) Allied Corporation Research Laboratory, Buffalo, NY.

(2) Bechgaard, J. D. *Sci. Am.* **1982**, *247*, 52.

(3) "The Organic Chemistry of Tellurium"; Irgolic, K. J., Ed.; Gordon and Breach: New York, 1974.

(4) Cooper, W. C. "Tellurium"; Van Nostrand Reinhold: New York, 1971.

(5) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154.(6) Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739.(7) Shibaeva, R. P.; Kaminskii, V. F. *Cryst. Struct. Commun.* **1981**, *10*, 663.(8) Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T. O.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1982**, 336.(9) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1925**, 531.(10) Berry, F. J.; Smith, B. C.; Jones, C. H. W. *J. Organomet. Chem.* **1976**, *110*, 201.(11) There appears to be a strong solvent dependence on chemical shift¹⁰ so that it is reasonable to compare the reported values of 3.85 ppm in CHCl_3 ¹⁰ with 3.67 ppm in CS_2 for $(\text{CH}_2\text{Te}_2)_2$.

(12) Wudl, F. In "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: London, 1977; p 233.

*Present address: Central Research Department, E. I. du Pont de Nemours & Co., Wilmington, DE.

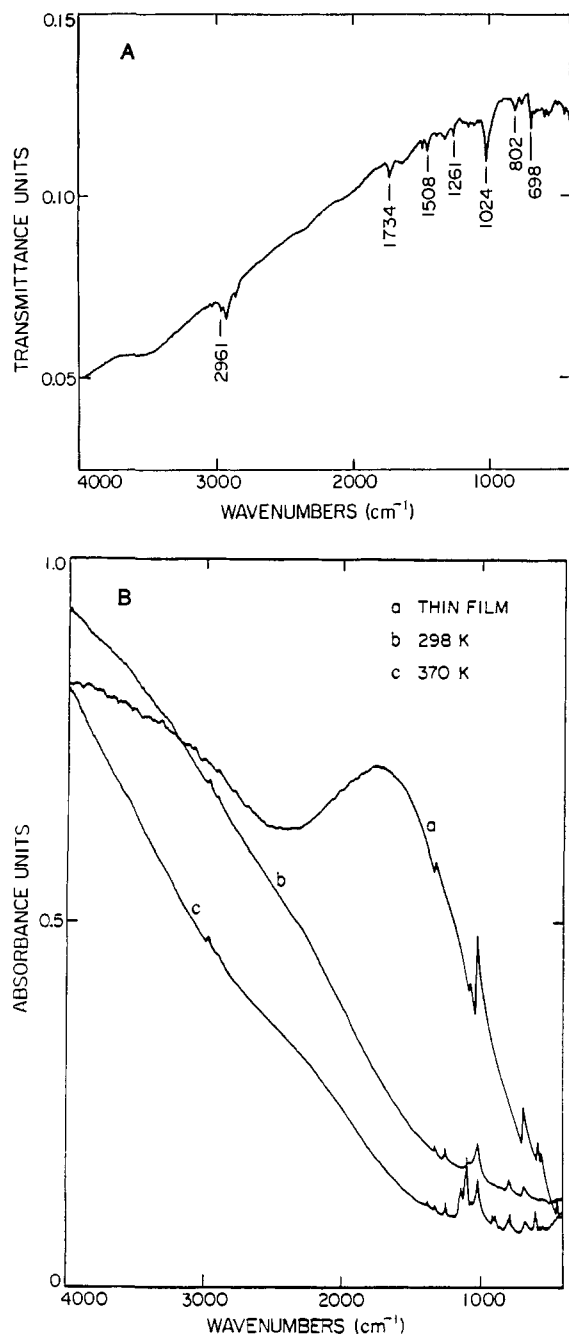


Figure 1. (A) KBr suspension FTIR spectrum of $(\text{CH}_2\text{Te}_2)_n$. (B) FTIR spectra of vapor deposited $(\text{CH}_2\text{Te}_2)_n$ plotted as absorbance vs. wavenumbers.

be drawn into fibers or rolled into sheets. If the sample is not heated above 55°C , it remains pliable. Fibers drawn at 45°C or the original red or gray powder show no X-ray powder pattern, indicating that $(\text{CH}_2\text{Te}_2)_n$ is amorphous, contrary to the statement made in ref 10 that red "crystals" of the red form can be isolated from the reduction procedure of Morgan and Drew. When a pellet of $(\text{CH}_2\text{Te}_2)_n$ was heated above 60°C (60 – 150°C), it appeared to expand and became brittle. Microscopic examination of the heated "swollen" pellet revealed craters and blisters, as if a gas had evolved. When the experiment was repeated several times in a sublimator at 150°C under ~ 10 - μtorr dynamic vacuum, a red film formed on various thin substrates (KBr, polyethylene, quartz) attached to the cold finger with a small amount of vacuum grease. Fourier transform infrared spectroscopy of the films revealed that they were very similar to, but not superimposable with, the unheated bulk polymer (cf. Figure 1). Heating the films converts them to uniform gray with concomitant changes in infrared spectra. Mass spectroscopy (20–600 amu) of the gases evolved

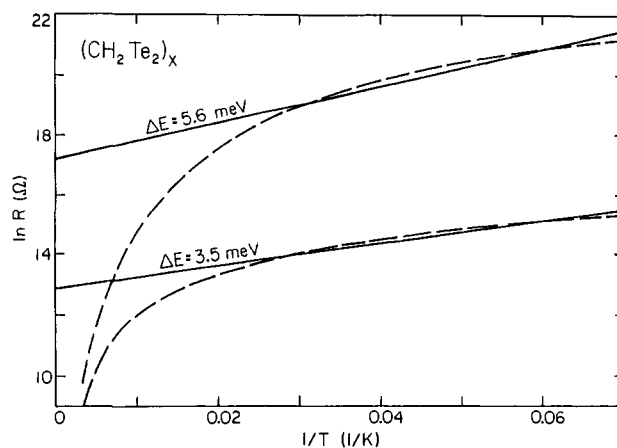


Figure 2. Natural log of resistivity vs. inverse temperature for 100°C heat-treated sample (top curve) and 150°C heated sample (lower curve).

during heating of a pellet directly into the inlet of a mass spectrometer showed typical organotellurium multiplets of m/e 272 (TeCH_2Te) and 412 ($\text{TeCH}_2\text{TeTeCH}_2$) and no peaks assignable to polymethylenes, e.g., $(\text{CH}_2)_3$, $(\text{CH}_2)_4$, etc. The 412 peak may be due to **2**.

When a freshly prepared sample of $(\text{CH}_2\text{Te}_2)_n$ was Soxhlet extracted with carbon disulfide for 7 days, placed in a sublimator, and heated to 150°C under vacuum, the same red films could be deposited on the cold finger of the sublimator, indicating that film formation is not due to evaporation of small (extractable) fragments but due either to thermal depolymerization or¹⁵ greater mobility of low molecular weight, CS_2 -insoluble fragments resulting from "opening" of the structure as a result of exhaustive extraction.

Results of elemental analyses of samples that were heat-treated (H-T) in a sublimator for ~ 14 h were the same, within experimental error, as those of freshly prepared $(\text{CH}_2\text{Te}_2)_n$. This was a surprising result in view of the fact that both infrared spectra (Figure 1) and physical properties change drastically upon heating.

It was reported⁹ that suspensions of $(\text{CH}_2\text{Te}_2)_n$ in chloroform could be converted with chlorine gas to $\text{CH}_2(\text{TeCl}_3)_2$. When we repeated this experiment on pristine, gray $(\text{CH}_2\text{Te}_2)_n$, moderate reaction with chlorine at room temperature was observed. Infrared spectroscopy of the isolated product revealed that it consisted mostly of $\text{CH}_2(\text{TeCl}_3)_2$ but that TeCl_4 as well as an unknown ($\text{ClCH}_2\text{TeCl}_3?$) compound was also produced. When this chlorolysis reaction was attempted on H-T samples, it was found that even after 48 h of exposure, $>50\%$ of the sample still remained unreacted. Under these conditions, amorphous tellurium reacts readily to produce TeCl_4 .

Powder X-ray diffraction ($\text{Cu K}\alpha$) investigation of pellets (10×0.5 mm) of pristine and H-T samples revealed no reflections between 3° and 35° ($2/\pi$), suggesting that all samples were amorphous.

Solid-State Properties. Freshly prepared $(\text{CH}_2\text{Te}_2)_n$ was an insulator ($R > 10^{10} \Omega \text{ cm}$). As samples were heated above 60°C , their resistance dropped dramatically and irreversibly (65°C , $10^5 \Omega \text{ cm}$; 110°C , $10^4 \Omega \text{ cm}$; 150°C , $10^2 \Omega \text{ cm}$). Measurement of resistivity as a function of temperature of a 100°C treated sample showed it to be a semiconductor between room temperature and ca. 50 K where a transition to a very small band gap semiconductor (E_g 0.006 eV) was observed (cf. Figure 2). As seen in Figure 3, application of moderate pressure decreased both the resistivity and band gap of a 100°C treated sample. This behavior is much unlike that of tellurium itself.⁴ The latter is a semiconductor ($E_g = 0.33$ eV) between room temperature and ca. 280 K where it

(13) There is ample analogy in the case of depolymerization of polymeric sulfur to S_8 and other cycles (S_6 , etc.) and the poly(dichlorophosphazenes) (Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972).

(14) Adams, D. M.; Lock, P. J. *J. Chem. Soc. A* 1967, 145.

(15) We thank a referee for this suggestion.

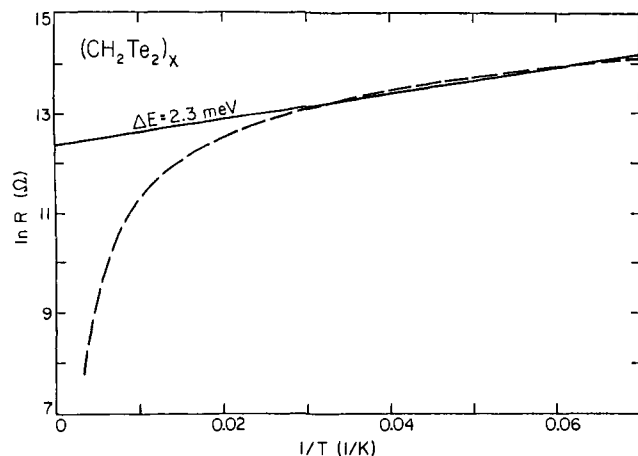


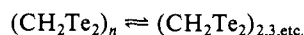
Figure 3. Natural log of resistivity vs. inverse temperature at 8 kbar of pressure of a 100 °C heat-treated sample.

undergoes a *semiconductor to metal transition*. At ca. 140 K it becomes a semimetal ($E_g \sim 0$) and remains a semimetal down to 77 K. Since the measurements were performed on compressed pellets, they were obviously dominated by interparticle resistance. A more realistic, intrinsic value of the semiconductor gap at room temperature could be obtained from spectroscopy. As can be seen in Figure 1, the infrared absorptions are only minor perturbations ("fine structure") on the overwhelming electronic absorption which gives a gap at room temperature of ca. 0.2 eV on a sample that was highly reflectant (silver) and yet was an insulator by dc measurements. Reflectance spectroscopy showed that a 150 °C H-T sample was more reflectant than the nonheated samples.

Electron spin resonance spectroscopy on both freshly prepared and H-T samples revealed that the latter had a broad, ~ 800 G wide line, whereas the former, not unexpectedly, exhibited no resonance signals.

Summary and Conclusions

When the stoichiometry of the reaction of tellurium tetrachloride with acetic anhydride is changed, moderate yields of pure $\text{CH}_2(\text{TeCl}_3)_2$ can be achieved. Reduction of the latter at low temperature produces a red solid that turns irreversibly to gray upon warming to room temperature. The gray solid behaves like a typical organic polymer (ductility, malleability, TGA, and DTA). Removal of low molecular weight fragments by extended Soxhlet extraction causes the resistance of a sample to drop from 10^{10} to $\sim 10^6 \Omega \text{ cm}$. Heat treatment also causes evolution of small fragments with concomitant, dramatic drop in resistivity, cross-linking, and generation of unpaired spins. The low molecular weight fragments generated upon heat treatment are probably the result of ring-chain tautomerization concomitant with depolymerization:¹³



As heating proceeds, a competing cross-linking reaction may prevent further depolymerization. Support for this notion stems from the mass spectrum of the fragments resulting from depolymerization. Whenever a 412-amu fragment ($\text{CH}_2\text{TeTeCH}_2\text{Te}$) is produced, enough defects (free-radical sites) are generated to give rise to cross-linking with the attendant embrittlement of the sample. When the gaseous fragments impinge on a cold surface they produce a red (gray upon warming) film that is indistinguishable from the original $(\text{CH}_2\text{Te}_2)_n$.

Morgan and Drew's polymer is therefore a unique material because it may be used not only to produce a new organometallic conductor with an unusual semiconductor to semimetal transition, but it may also be used for the generation of organometallic films containing fissionable C-Te bonds for the deposition of tellurium metal.

Experimental Section

General. All melting points were uncorrected. Spectral data were recorded on the following instruments: NMR, Varian EM360L; IR, Perkin-Elmer 1330 and IBM IR/98; X-ray powder diffraction, Diano powder diffractometer; MS, Zab 2F micromass high-resolution mass spectrometer. Electrical conductivity measurements were made on a locally constructed instrument.

Reagent chemicals and solvents were used without further purification unless otherwise specified.

Bis(trichlorotelluro)methane. In a dry N_2 -purged 300-mL Schlenk flask affixed with condenser and N_2 bubbler, 30.21 g (0.112 mol) of TeCl_4 (Alfa, 99%) was dissolved as well as possible in 100 mL of hot CHCl_3 (dry, ethanol free; purified by extracting with H_2SO_4 and H_2O drying over CaCl_2 , and distilling from P_2O_5 under dry N_2 ; alternatively, drying overnight over alumina has been successful). Acetic anhydride (3.53 mL; 3.82 g; 0.037 mol) (Mallinckrodt, 97%) was added by syringe against a N_2 purge. The mixture was stirred magnetically and refluxed for 27–28 h. After this period 1–2 cm^3 of activated charcoal was added, and the mixture was refluxed for 10 min and then hot Schlenk filtered through a medium frit. Upon cooling, the yellow filtrate produced copious amounts of fine white needles. Further cooling to -15 °C (MeOH/ice) produced more crystals; however, this second batch may be occluded with a gray impurity. The crystals were Schlenk filtered, washed with CHCl_3 , and then oil pump vacuum-dried. The product was recrystallized from CHCl_3 (3 times recrystallized gave 9.293g; 52%), mp 168–171 °C (lit.^{9,10} 173, 168–172 °C). Small amounts of the gray impurity could be removed with activated charcoal. The product was moisture sensitive, though apparently not air sensitive. The product was stored under argon at -30 to -40 °C, though even at this temperature, it tended to gray somewhat over several weeks.

¹H NMR (CDCl_3) δ 5.9 (s) (lit.¹⁰ δ 5.88 (s)); IR (KCl pellet; compound appeared to react slowly with KBr) 3990, 3747, 3020 (C-H) 2933 (C-H), 2398, 2136, 2046, 1993, 1733, 1624, 1468, 1330, 1165, 1064, 816, 727 (Te-C-H?), 674, 603 (Te-C) 557 (Te-C), 337 (Te-Cl) cm^{-1} . Many relatively strong overtones and combination bands were evident.

Poly(methylene ditelluride). $\text{Cl}_3\text{TeCH}_2\text{TeCl}_3$ (1.78 g; 3.69 mmol) was rapidly poured from an argon-filled vial into 50 mL of a 0 °C aqueous solution of 4.24 g (22.29 mmol) of $\text{Na}_2\text{S}_2\text{O}_5$ (Aldrich, 97%). The solid turned from white to red in seconds. After the mixture was stirred for 20–30 min, the reaction was apparently complete. As the mixture warmed to room temperature, the solid turned from red to gray. The solid was washed several times with water followed by decantation. A small amount of the more buoyant solid was lost in the process. The remaining solid was dried to give 910 mg (91%) of gray $(\text{CH}_2\text{Te}_2)_n$.

Anal. Calcd for $(\text{CH}_2\text{Te}_2)_n$: C, 4.46; H, 0.75; Te, 94.79. Found: C, 4.63; H, 0.81; Te, 94.06.

Elemental analyses of residues from heat treatment indicated only slight changes from the room-temperature materials.

Anal. Found for $(\text{CH}_2\text{Te}_2)_n$: heated to 110 °C, C, 4.55; H, 0.68; Te, 93.78; heated to 150 °C, C, 4.43; H, 0.67; Te, 93.82.

Chlorinolyses. In a dry 25-mL two-neck flask, equipped with stirring bar, was weighed 123.1 mg (0.457 mmol) of $(\text{CH}_2\text{Te}_2)_n$ (sample previously kept at ≤ 25 °C). Dry, purified CHCl_3 (7 mL) was added, and the flask was equipped with a Cl_2 gas inlet T-connected to a N_2 source and a N_2 bubbler T-connected to a N_2 source. The flask was flushed with N_2 and then with Cl_2 . Within 3 min of the initial Cl_2 exposure, all of the dark solid reacted to produce a clear solution. The CHCl_3 was removed under a N_2 stream. In an argon glovebox, the remaining white solid was scraped out to give 173 mg of crude product.

(Some of the solid remained in the flask.) IR investigation (KCl pellet and Nujol mull on polystyrene) indicated the presence of $\text{Cl}_3\text{TeCH}_2\text{TeCl}_3$ ($\nu(\text{Te-Cl})$ 337 cm^{-1}) and TeCl_4 ($\nu(\text{Te-Cl})$ 350 cm^{-1} ; lit.¹⁴ 353 cm^{-1}) as well as perhaps $\text{ClCH}_2\text{TeCl}_3$.

A freshly prepared $(\text{CH}_2\text{Te}_2)_n$ sample converted much more cleanly to $\text{Cl}_3\text{TeCH}_2\text{TeCl}_3$ than one that was ~ 10 days old.

Exposure of heat-treated samples of $(\text{CH}_2\text{Te}_2)_n$ to Cl_2 in the same manner resulted in incomplete (>50% dark solid remaining) reaction after 36–48 h. Amorphous tellurium itself reacted completely after 36 h to give TeCl_4 .

Acknowledgment. This research was partially supported by the Institute for Polymers and Organic Solids and by a grant from Grace and Co. We are indebted to Dr. Hugh Webb for mass spectroscopy.

Registry No. TeCl_4 , 10026-07-0; $\text{Cl}_3\text{TeCH}_2\text{TeCl}_3$, 61002-75-3; $(\text{CH}_2\text{Te}_2)_n$, 94111-12-3; acetic anhydride, 108-24-7.