348 *Organometallics* 1994, *13*, 348–353

Conformational Polymorphism of Di(2-naphthyl) Ditelluride[†,1]

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Received October 13, 1993[•]

Di(2-naphthyl) ditelluride (1), synthesized by reaction of 2-chloronaphthalene with alkali metal ditelluride reagents in dipolar aprotic solvents, crystallizes in two polymorphic modifications. Single-crystal X-ray structure determinations show these to be *conformational polymorphs*. Polymorph **1a** is monclinic, space group $P2_1/c$, a = 8.406(3), b = 6.304(2), c = 32.323(9) Å, β = 99.92(3)°, V = 1687.2 Å^3, and Z = 4. Polymorph **1b** is also monoclinic, space group $C2/c$, a = 36.654(11), b = 7.840(2), c = 12.084(4) Å, β = 104.56(3)°, V = 3361.9 Å^3, and Z = 8. Polymorph **1a** has a C–Te–Te–C torsion angle of 105.2° and relatively long Te···Te contacts (4.13, 4.41 Å), while polymorph **1b** has a C–Te–Te–C angle of 78.6° and short intermolecular Te···Te contacts of 3.708 and 4.002 Å. Polymorphs **1a** and **1b** have also been characterized by differential scanning calorimetry and by infrared, Raman, and solid-state electronic spectroscopy. Raman shifted lines at 188 and 182 cm^{-1} in **1a** and **1b**, respectively, are assigned to the ditelluride stretching mode. Polymorph **1b** exhibits a shoulder near 510 nm in its solid-state electronic spectrum. This feature is not observed either in solution spectra or in the spectrum of solid **1a**. It is likely that the shoulder is associated with an extended electronic structure which arises from a continuous set of short Te···Te nonbonded contacts.

Introduction

In the course of our development of a direct approach to the synthesis of aromatic molecular[1,3,4] and polymeric[1,4,5] organoselenium and -tellurium materials, we isolated two forms of di(2-naphthyl) ditelluride (1). The polymorphic nature of these two forms was established by X-ray powder diffraction experiments, and single-crystal X-ray stuctural studies, detailed herein, firmly establish that the two forms are *conformational polymorphs*. Conformational polymorphism[6] may be defined as "the existence of different conformers of the same molecule in different polymorphic modifications".[7] Reported examples of compounds exhibiting conformational polymorphism include carbohydrates, nucleotide bases, Schiff bases, decaniobates, and nickel tris(2-cyanoethylphosphine) complexes.[7] Lattice energy calculations have been used to account for the relative stability of conformational polymorphs in Schiff base systems.[6] The present work provided[1] the first example of conformational polymorphism directly involving an atom as heavy as Te. Subsequent to our preliminary report,[1] the conformational polymorphism of bis(p-chlorophenyl) ditelluride was established.[8] We report here the isolation and X-ray structure determination of the two conformational polymorphs of 1, as well as their thermal and spectral properties. The lower-melting polymorph, **1a**, has a transoid conformation (C–Te–Te–C > 90°), while the higher melting polymorph **1b** has a cisoid conformation (C–Te–Te–C < 90°).

Experimental Section

General Techniques. Melting points taken in capillary tubes are uncorrected. Electronic spectra were recorded on a Varian

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[•] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

[†] The authors are pleased to dedicate this paper to Professor Kurt Mislow in the year of his 70th birthday with continued best wishes for his retirement.

(1) (a) Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Gagne, P. *Organometallics* **1983**, *2*, 549–551. (b) Sandman, D. J.; Stark, J. C.; Rubner, M.; Acampora, L. A.; Samuelson, L. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 293–305. (c) Sandman, D. J.; Stark, J. C.; Rubner, M.; Hamill, G. P.; Acampora, L. A.; Samuelson, L. A.; McGrath, M. A.; Allen, G. W. *Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium*, Birmingham, England, July 25–29, 1983; pp 637–670.

(2) On sabbatical leave at GTE Laboratories, 1980–81, 1988–89. Permanent address: Department of Chemistry, Eastern Nazarene College, Quincy, MA 02170.

(3) (a) Sandman, D. J.; Stark, J. C.; Foxman, B. M. *Organometallics* **1982**, *1*, 739–742. (b) Stark, J. C.; Reed, R.; Acampora, L. A.; Sandman, D. J.; Jansen, S.; Jones, M. T.; Foxman, B. M. *Organometallics* **1984**, *3*, 732–735.

(4) Sandman, D. J.; Stark, J. C.; Acampora, L. A.; Samuelson, L. A.; Allen, G. W.; Jansen, S.; Jones, M. T.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 1–17.

(5) (a) Sandman, D. J.; Rubner, M.; Samuelson, L., *J. Chem. Soc., Chem. Commun.* **1982**, *1133*–1134. (b) Acampora, L. A.; Dugger, D. L.; Emma, T.; Mohammed, J.; Rubner, M. F.; Samuelson, L.; Sandman, D. J.; Tripathy, S. K. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series No. 242; American Chemical Society: Washington, D.C., 1984; pp 461–472. (c) Sandman, D. J., Allen, G. W., Acampora, L. A.; Stark, J. C.; Jansen, S.; Jones, M. T.; Ashwell, G. J.; Foxman, B. M. *Inorg. Chem.* **1987**, *26*, 1664–1669.

(6) Corradini, P. *Chim. Ind.* (Milan) **1973**, *55*, 122–129. Pangiotoupoulis, N. C.; Jeffrey, G. A.; LaPlaca, S. J.; Hamilton, W. C. *Acta Crytallogr.*, Sect B: Struct. Sci. **1974**, *B30*, 1421–1430. Bernstein, J.; Hagler, A. T. *J. Am. Chem. Soc.* **1978**, *100*, 673–681.

(7) Bernstein, J. *In Organic Solid State Chemistry*; Desiraju, G. R., Ed.; Elsevier: Amsterdam, 1987; pp 471–518.

(8) Van den Bossche, G.; Spirlet, M. R.; Dideberg, O.; Dupont, L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1011–1012.

0276-7333/94/2313-0348$04.50/0

Cary 17 spectrophotometer with a diffuse reflectance attachment. Solid-state spectra were recorded using 1% dispersions (w/w) in sodium chloride. Differential scanning calorimetry (DSC) was performed on a DuPont 1090 analyzer using a DuPont 910 DSC module.

Fourier Transform (FT) Raman Spectroscopy. FT-Raman spectra were recorded on polycrystalline samples on a Perkin-Elmer 1760X FTIR spectrophotometer equipped with a FT-Raman accessory in a 180° optical collection geometry. Excitation was accomplished with a cw Nd:YAG laser at 1064 nm with a laser power of 500 mw. Scattered radiation from the sample was reflected into the spectrometer and was detected by an InGaAs detector cooled with liquid nitrogen. Spectra were recorded at a resolution of 2 cm^{-1} at a scan sped of 0.1 cm^{-1}/s; 32 scans were accumulated for all samples.

Synthesis of 1 Using Na_2Te_2 in HMPA. Sodium (0.34 g, 15 mmol), in small pieces, was added to a suspension of Te (1.9 g, 15 mmol) in hexamethylphosphoramide (HMPA, freshly distilled and stored over molecular sieves, 50 mL); the mixture was heated under argon at 110 °C for 1 h. To this reagent was added 2-chloronaphthalene (2.26g, 14 mmol), and the resultant mixture was heated under argon at 160–175 °C for 22 h, after which it was filtered and poured into brine (400 mL). Suction filtration gave a dark-brown solid which, after air drying, was vacuum sublimed to recover 2-chloronaphthalene (0.92 g). The residue was treated with hot benzene; the solution was filtered to remove a black solid and was chromatographed on silica gel. Benzene elution of a red-brown band, followed by evaporation and recrystallization from hexane–benzene (90:10), gave 1 (0.567 g, 27%) as copper-colored platelets, m.p. 118–119 °C (capillary). The melt is red and on cooling gives a deep red solid, mp 120–122 °C. Reported melting points for 1 are 117–118,[9] 120–122,[10] and 123 °C.[11] In dichloromethane solution (10^{-4} M), the following absorption spectrum was observed (λ_{max}(nm) ($\epsilon \times 10^{-3}$)): 400(1.6), 336(3.5), 303(20), 290(23), 258(52), 223(108). In hexane solution, an absorption maximum was noted at 395 nm (ϵ 1.5 × 10^3). In 10^{-3} M acetonitrile solution using 0.1 M tetraethylammonium perchlorate as support electrolyte, 1 exhibits an irreversible anodic wave at +1.01 V vs a saturated calomel electrode at a sweep rate of 100 mV-s^{-1}.

Synthesis of 1 from Triethylborohydride Using Li_2Te_2. Under argon atmosphere, $Li(C_2H_5)_3BH$ (20 mmol) in tetrahydrofuran (THF) was added via syringe to a suspension of Te (1.276 g, 0.01 mmol) in THF (10 mL).[12] After the initial reaction subsided, the mixture was stirred at reflux for 1 h to give a homogeneous purple reagent. This reagent was transferred via syringe to a solution of 2-chloronaphthalene (1.626 g, 10 mmol) in HMPA (50 mL) under argon. The mixture was heated at 140–145 °C for 16 h, followed by heating at 170–175 °C for 24 h. After cooling to room temperature, the mixture was suction filtered, the solid was washed with dry HMPA (10 mL), and the filtrate was slurried into brine (500 mL). The black precipitate was isolated by suction filtration and air-dried. The residue was extracted with dichloromethane (250 mL), followed by removal of the CH_2Cl_2 under reduced pressure. The residue was taken up in benzene (60 mL), chromatographed on silica gel packed in hexane, and eluted with hexane. The product 1 was recrystallized from hexane to give 0.446 g (17.5%), mp 121–123 °C (capillary), homogeneous by thin-layer chromatography on silica gel plates.

Polymorph 1a. The procedure for synthesis of 1 using Na_2Te_2 in HMPA given above produced a pure sample of **1a**. Diffraction-quality single crystals were obtained by allowing saturated solutions of 1 in hexane and benzene to diffuse at room temperature. The X-ray powder pattern of the diffraction sample exhibited the following peaks (*d*(Å), s = strong): 16.05(s), 8.01(s), 6.14, 5.91, 5.58, 5.34, 4.00, 3.20, 3.04, 2.95, 2.66(s). These *d*-spacings and intensities correspond well to those predicted from the unit cell of **1a** given below. The FTIR spectrum of **1a** dispersed in CsI was indistinguishable from that of **1b** under the same conditions between 4000 and 480 cm^{-1} and is that expected for a 2-naphthyl compound. Significant IR absorption was observed at 413, 386, 371, 359, 349, 335, 316, 299, 285, 266, 244, 231, and 224 cm^{-1}. The FT-Raman spectrum of **1a** exhibited the following shifted lines (cm^{-1}): 1619, 1576, 1497, 1454, 1426, 1377, 1144, 1054, 1016, 820, 764, 563, 515, 394, 265, 216, 202, 188.

Polymorph 1b. The procedure for the synthesis of 1 using Li_2Te_2 given above yielded **1b**. A diffraction-quality single crystal of **1b** was obtained from this sample. The X-ray powder pattern of this sample exhibited the following (d(Å), s = strong): 17.38(s), 15.71, 8.82(s), 7.91, 5.91(s), 5.73, 5.29, 4.43(s), 3.54(s), 2.95(s), 2.65, 2.53(s). Significant IR absorption for **1b** (CsI pellet) was noted at 389, 371, 336, 316, 304, 295, 264, 254, and 233 cm^{-1}. The FT-Raman spectrum of **1b** was indistinguishable from that of **1a** given above for shifts between 1619 and 265 cm^{-1}; additional shifts in **1b** are observed at 216, 195, and 182 cm^{-1}.

Structure Determination of 1a and 1b. Single crystals of **1a** and **1b** were obtained as described above. The crystals were mounted on Pyrex fibers affixed to brass pins, transferred to a Supper No. 455 goniometer, and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[13] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for all atoms were included in the calculations.[14] All computational work was carried out on either the Syntex/XTL structure determination system on a Nova 1200 computer (**1b**) or a VAX 6420 computer using the Enraf–Nonius MolEN package (**1a**).[15] Data for polymorph **1a** were originally collected in a different setting of the unit cell (space group $P2_1/n$);[1] owing to problems which occurred during the data collection, the data were recollected in space group $P2_1/c$ at a later date. Details of the structure analyses, in outline form, are given in Table 1, while atomic coordinates for **1a** and **1b** appear in Tables 2 and 3, respectively.

Results and Discussion

We have synthesized the samples of 1 used in the present investigations either by our previously reported[1] method or by the extension of the approach of Gladysz and coworkers to aromatic displacements, as described in the Experimental Section. Bulk and single-crystal samples of **1a** and **1b** were obtained as noted in the Experimental Section. While bulk samples of **1a** are often coppery in color and samples of **1b** appear dark red-orange, the colors of the single crystals used for diffraction were not noticeably different. X-ray powder diffraction is useful for distinguishing **1a** and **1b**, but our experience is that the powder pattern of the samples of **1b** typically reveal reflections assignable to **1a**. For example, the reflection at 15.71Å in the powder pattern of **1b** given in the Experimental Section is not in the pattern for the unit cell of **1b** given below. Another sample of **1b**, mp 122–124 °C (capillary), exhibited a strong reflection at 14.77 Å which is not in the calculated patterns of **1a** or **1b**. The existence

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[9] Bergman, J.; Engman, L. *Tetrahedron* **1980**, *36*, 1275–1276.

[10] Petragnani, N.; deMoura Compos, M. *Tetrahedron* **1965**, *21*, 13–17.

[11] Vicentini, G.; Giesbrecht, E.; Pitombo, L.R.M. *Chem. Ber.* **1959**, *92*, 40–46.

[12] Gladysz, J. A.; Hornby, J. L.; Garbe, J. E. *J. Org. Chem.* **1978**, *43*, 1204–1208.

[13] Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932–1938. Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113–116.

[14] Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101. Cromer, D. T.; Ibers, J. A. *Ibid.* pp 148–150.

[15] *MolEN, An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990. Johnson, C. K. *ORTEP-II: A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, ORNL*-5138, 1976. Sparks, R. A. et al. *Operations Manual, Syntex XTL Structure Determination System*; Syntex Analytical Instruments: Cupertino, CA, 1976.

Table 1. Data for the X-ray Diffraction Study of $C_{20}H_{14}Te_2$

	1a	**1b**
	(A) Crystal Data at 21(1) °C	
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ [C_{2h}^5; No. 14]	$C2/c$ [C_{2h}^6; No. 15]
a, Å	8.406(3)	36.654(11)
b, Å	6.304(2)	7.840(2)
c, Å	32.323(9)	12.084(4)
β, deg	99.92(3)	104.56(3)
V, Å^3	1687.2(17)	3361.9(34)
Z	4	8
crystal size, mm	0.042 × 0.21 × 0.63	0.021 × 0.13 × 0.90
formula wt	509.53	509.53
ρ_{calc}, g-cm^{-3}	2.006	2.014
ρ_{obs}, g-cm^{-3}	2.02(1)[a]	2.02(1)[a]
μ, cm^{-1} (Mo K$\bar{\alpha}$)	34.6	34.7
cell constant determination:	12 (6 for **1a**) pairs of ● (*hkl*) and refined 2θ, ω, χ values in the range 23° ≤ |2θ| ≤ 25° (λ(Mo K$\bar{\alpha}$) = 0.71073 Å)	
	(B) Measurement of Intensity Data	
radiation	Mo K$\bar{\alpha}$, graphite monochromator	
reflections measd	+*h*, +*k*, ±*l* (3.5° ≤ 2θ ≤ 45°)	+*h*, +*k*, ±*l* (2θ ≤ 45°)
scan type, speed	ω, vble, 2.44–6.51°/min	θ–2θ, vble, 1.95–6.51°/min
scan range	1.1°, 1.0° bkgd offset in ω	symmetrical, [1.8 + $\Delta(\alpha_2 - \alpha_1)$]°
no. of reflections measd	2375; 2199 in unique set	2259; 2214 in unique set
stand reflections; period	023, 2,1,14, 2,0,$\overline{10}$; 100	110, 21,1,0, 51$\bar{7}$; 60
absorption correction	empirical	empirical
transmission factor range	0.644–1.00	0.706–1.00
data reduction: as before[b]	*p* = 0.040	*p* = 0.035
R_{av}	0.031 (0*kl* reflections)	0.017 (0*kl* reflections)
no. data used in refinement	1649 [$I > 1.96\sigma(I)$]	1830 [$I > 1.96\sigma(I)$]
no. of refined parameters	199	199
weighting of reflections: as before[c]	*p* = 0.04	
solution	Patterson, difference-Fourier	Patterson, difference-Fourier
refinement[d]	full-matrix least-squares	full-matrix least-squares
anisotropic disp params	all non-hydrogen atoms	all non-hydrogen atoms
isotropic disp params	fixed H atoms	fixed H atoms
R	0.036	0.026
R_w	0.038	0.038
SDU	1.18	0.90
R (*all* reflections)	0.070	0.036
final difference map	two peaks, 0.69 and 0.75 e$^-$/Å^3 at (x, $^1/_2 + y$, z) from Te atoms; five peaks at 0.42–0.52 e$^-$/Å^3 near Te atoms; other peaks random and ≤0.42 e$^-$/Å^3	five peaks 0.36–0.55 e$^-$/Å^3 near Te; other peaks random and <0.31 e$^-$/Å^3

[a] Measured by neutral bouyancy in 1,2-$C_2H_4Br_2$–CCl_4. [b] Foxman, B. M.; Goldberg, P. L.; Mazurek, H. *Inorg. Chem.* **1981**, *20*, 4368. All computations in the present work were carried out using the ENRAF-NONIUS Structure Determination Package. [c] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197. [d] $R_{av} = \sum|I - I_{av}|/\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = \{\sum[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$; SDU = $\{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$ where *m* is the number of observations and *n* is the number of parameters.

of additional polymorphs of **1** cannot be ruled out. The infrared spectra of **1a** and **1b** show observable differences between 480 and 220 cm^{-1} as noted in the Experimental Section. An earlier report[16] noted that **1** became yellowish on storage for 1 year. Our samples of both **1a** and **1b** retain their original color on standing under ambient conditions for more than 8 years.

FT-Raman spectroscopy also provides a means of distinguishing **1a** and **1b**. As noted in the Experimental Section, the FT-Raman spectra of the polymorphs are indistinguishable between shifts of 1619 and 265 cm^{-1}. However, as displayed in Figure 1, three lines near 200 cm^{-1} reveal a difference between the polymorphs. For **1a**, shifts of 215, 202, and 188 cm^{-1} are observed, while for **1b**, shifts of 215, 195, and 182 cm^{-1} are noted. The shifts of 188 cm^{-1} in **1a** and 182 cm^{-1} in **1b** are assigned to the ditelluride stretching mode, by analogy to earlier work.[16] For both polymorphs, the line at 1377 cm^{-1} and the ditelluride stretching mode are the strongest shifted lines. Attempts to record the Raman spectra of **1a** and **1b** using 514.6 and 632.8 nm as wavelengths of excitation led only to sample decomposition even at the lowest laser powers attempted. These observations serve to emphasize the

Table 2. Atomic Coordinates for $C_{20}H_{14}Te_2$, Polymorph 1a[a,b]

atom	*x*	*y*	*z*	*B* (Å^2)
Te(1)	0.06583(7)	0.1438(1)	0.21529(2)	3.91(1)
Te(2)	0.34606(7)	0.09730(9)	0.27012(2)	3.73(1)
C(1)	0.1623(9)	0.342(1)	0.1721(3)	3.2(2)
C(2)	0.173(1)	0.263(1)	0.1332(2)	3.3(2)
C(3)	0.2429(9)	0.389(1)	0.1046(3)	3.9(2)
C(4)	0.257(1)	0.314(2)	0.0641(3)	4.7(2)
C(5)	0.327(1)	0.439(2)	0.0374(3)	5.9(3)
C(6)	0.387(1)	0.644(2)	0.0498(3)	5.9(3)
C(7)	0.370(1)	0.719(2)	0.0878(3)	4.6(2)
C(8)	0.2990(9)	0.597(1)	0.1164(3)	3.3(2)
C(9)	0.280(1)	0.673(1)	0.1563(3)	4.2(2)
C(10)	0.212(1)	0.551(1)	0.1828(3)	3.7(2)
C(11)	0.3013(9)	0.300(1)	0.3196(2)	3.0(2)
C(12)	0.2169(9)	0.222(1)	0.3490(2)	3.3(2)
C(13)	0.1973(9)	0.350(1)	0.3840(3)	3.4(2)
C(14)	0.112(1)	0.275(2)	0.4156(3)	4.1(2)
C(15)	0.098(1)	0.397(2)	0.4490(3)	5.6(3)
C(17)	0.166(1)	0.598(2)	0.4531(3)	5.7(3)
C(17)	0.247(1)	0.675(2)	0.4240(3)	5.2(2)
C(18)	0.2633(9)	0.554(1)	0.3887(3)	3.4(2)
C(19)	0.348(1)	0.629(1)	0.3564(3)	4.0(2)
C(20)	0.364(1)	0.509(1)	0.3231(3)	3.4(2)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as: $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] Numbers in parentheses in this and following tables are estimated standard deviations in the least significant digit.

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(16) McWhinnie, W. R.; Thavornyutikarn, P. *J. Organometal. Chem.* **1972**, *35*, 149–154.

Table 3. Atomic Coordinates for $C_{20}H_{14}Te_2$, Polymorph 1b[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Te(1)	0.47385(1)	0.30227(6)	0.01457(4)	3.72(1)
Te(2)	0.45642(1)	0.00228(5)	0.10170(4)	3.63(1)
C(1)	0.4309(2)	0.4480(7)	0.0618(5)	3.2(1)
C(2)	0.3949(2)	0.4401(7)	−0.0027(5)	3.0(1)
C(3)	0.3655(2)	0.5283(7)	0.0275(5)	2.9(1)
C(4)	0.3272(2)	0.5155(8)	−0.0362(5)	3.7(2)
C(5)	0.2999(2)	0.597(1)	−0.0002(6)	4.4(2)
C(6)	0.3078(2)	0.6975(9)	0.0976(7)	4.7(2)
C(7)	0.3442(2)	0.7165(9)	0.1619(6)	4.4(2)
C(8)	0.3739(2)	0.6291(7)	0.1292(5)	3.0(1)
C(9)	0.4118(2)	0.6391(8)	0.1918(5)	3.9(2)
C(10)	0.4397(2)	0.5506(8)	0.1620(5)	3.6(2)
C(11)	0.4091(2)	−0.0604(8)	−0.0345(5)	3.2(1)
C(12)	0.3737(2)	−0.0078(7)	−0.0313(5)	3.3(2)
C(13)	0.3418(2)	−0.0532(7)	−0.1198(5)	3.1(1)
C(14)	0.3047(2)	0.0041(8)	−0.1211(6)	3.9(2)
C(15)	0.2751(2)	−0.044(1)	−0.2061(7)	4.9(2)
C(16)	0.2804(2)	−0.1497(9)	−0.2950(6)	4.8(2)
C(17)	0.3152(2)	−0.2031(9)	−0.2980(6)	4.4(2)
C(18)	0.3469(2)	−0.1545(7)	−0.2105(5)	3.4(2)
C(19)	0.3838(2)	−0.2051(8)	−0.2112(5)	3.8(2)
C(20)	0.4139(2)	−0.1609(8)	−0.1273(6)	3.9(2)

[a] Atoms refined using anisotropic displacement parameters are given in the form of the isotropic equivalent displacement parameter defined as: $1.33[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

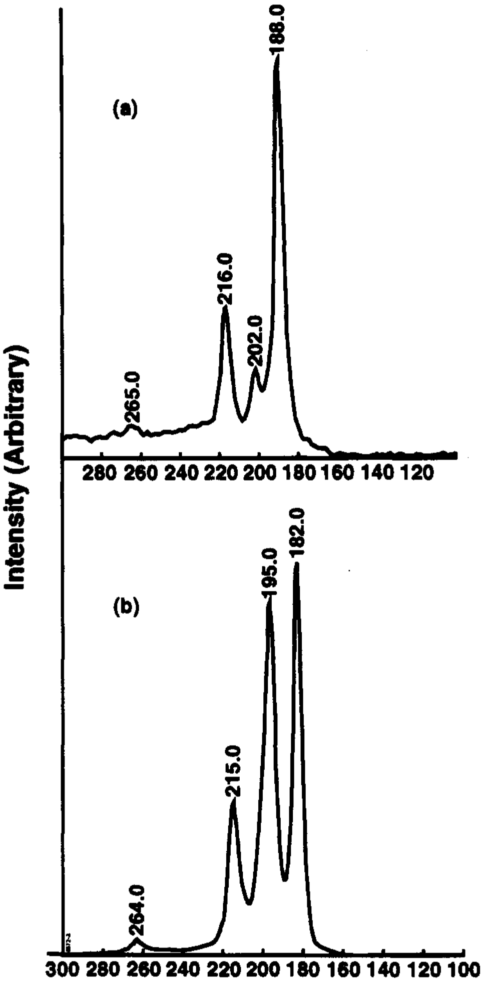

Figure 1. Low frequency FT-Raman spectra of (a) **1a** and (b) **1b**, recorded at 2-cm^{-1} resolution.

utility of FT-Raman spectroscopy for samples decomposed by visible-light lasers. The utility of the FT-Raman technique for obtaining routine vibrational spectra of organotellurium compounds has recently been noted by others.[17]

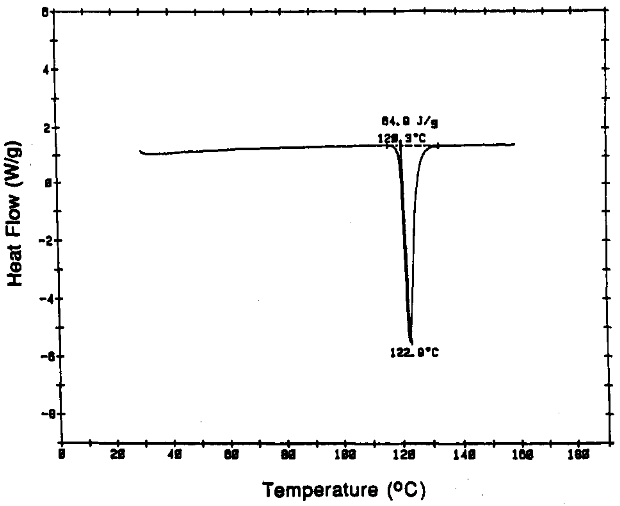

Figure 2. DSC curve for **1b**.

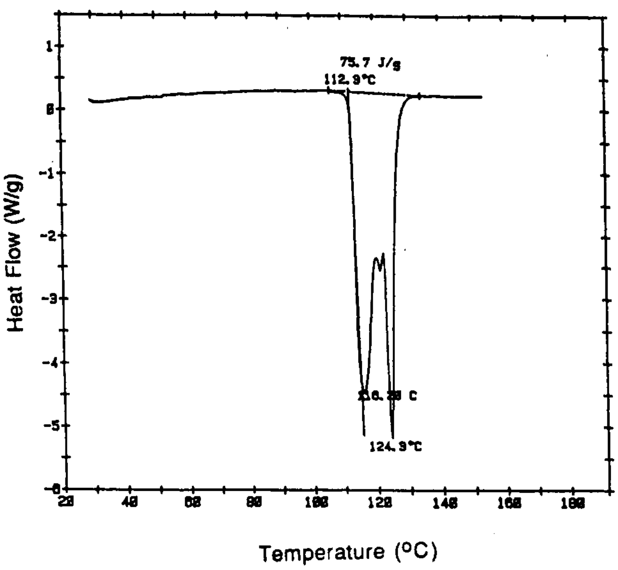

Figure 3. DSC curve for **1a**.

An initial hint of possible polymorphism of **1** came from the capillary melting behavior of **1a** noted above in the Experimental Section. Hence, we opted to study the melting behavior of **1a** and **1b** by DSC. Figure 2 displays the DSC curve for a sample of **1b** for its first scan where mp 120.3 °C is observed. The second heating of this sample exhibited mp 121.1 °C and a heat of fusion of 67.2 J/g. The DSC curve for the first heating of **1a** is given in Figure 3. The second heating of this sample exhibited a DSC curve similar to that of Figure 2 with mp 120.9 °C. On the basis of DSC behavior, **1b** is the more stable of the two polymorphs. The structure of the DSC curve shown in Figure 2 is attributed to the following. The initial melting of **1a** gives a mixture of **1a** and liquid **1**. The latter, at equilibrium, crystallizes as **1b**. As all of **1a** is converted to liquid **1**, which crystallizes as **1b**, the melting of **1b** is observed. A solid-state conversion of **1a** to **1b** has not been observed to date.

In solution, **1** exhibits its lowest energy maximum at 395 nm (hexane) and at 400 nm (dichloromethane). A

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(17) Greaves, M. R.; McWhinnie, W. R.; McWhinnie, S. L. W.; Waters, D. N. *J. Organometal. Chem.* **1992**, *430*, 37–41.

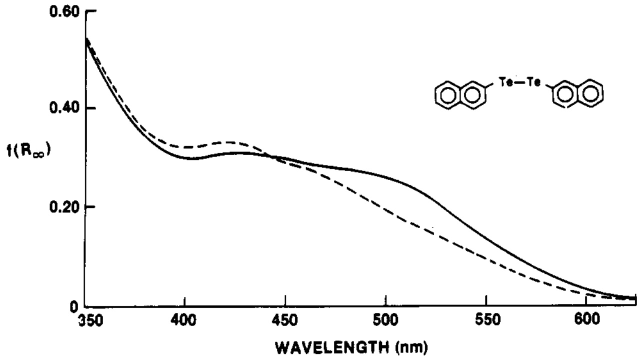

Figure 4. Diffuse reflectance spectra of **1a** (dashed line) and **1b** (solid line).

molar extinction coefficient of the order of 10^3 is noted in each solvent. Similar data for the analogous transition, primarily attributed to a localized ditelluride excitation as it appears at the same wavelengths in simple dialkyl ditellurides,[18] have been reported for diphenyl ditelluride in chlorinated solvents.[16] The molar extinction coefficients for **1** and diphenyl ditelluride[16] are higher than those observed in studies of dialkyl ditelluride by Laur and coworkers.[18] While extinction coefficients comparable to those observed for the diaryl ditellurides have been reported[19] for diethyl ditelluride, they were not reproduced in the more recent extensive study.[18]

The diffuse reflectance spectra of solid **1a** and **1b** are shown in Figure 4. Both solids exhibit broad maxima near 410 nm. Compared to the solution spectrum of **1**, this feature near 410 nm in the solid-state spectra represents the usual[20] solid-state spectral shift. Additionally, **1b** exhibits a broad shoulder near 510 nm which is *not* observed in the spectrum of **1a** or in solution spectra. Hence, this low-energy feature in **1b** is a solid-state effect, and we associate it with a solid-state electronic structure which has its origin in the relatively short intermolecular Te···Te contacts found in the crystal structure (*vide infra*).

2,2′,5,5′-Tetramethyldistibolyl (**2**) provides an additional example of a compound whose solid-state spectrum reveals low-energy absorption not found in either the solution spectrum or the spectrum of the melt; the crystal structure exhibits short intermolecular contacts involving a *collinear chain* of heavy atoms, namely, Sb.[20] A one-dimensional electronic band structure, with the assignment of the low-energy absorption of the solid-state spectrum of **2** to a $\sigma \rightarrow \pi^*$ transition, has been described.[21] The Bi analog exhibits a solid-state transition similar to that for **2** at slightly lower energy.[22]

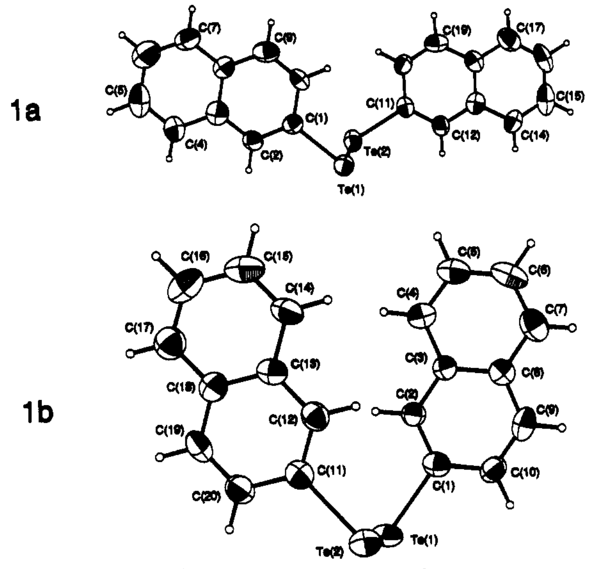

Figure 5. Molecular structures of **1a** and **1b**, showing 50% probability ellipsoids and atomic numbering schemes.

Table 4. Bond Lengths (Å) and Angles (deg) for $C_{20}H_{14}Te_2$, Polymorph 1a

Te(1)–Te(2)	2.7089(7)	C(9)–C(10)	1.35(1)
Te(1)–C(1)	2.134(8)	C(11)–C(12)	1.37(1)
Te(2)–C(11)	2.132(8)	C(11)–C(20)	1.41(1)
C(1)–C(2)	1.37(1)	C(12)–C(13)	1.42(1)
C(1)–C(10)	1.41(1)	C(13)–C(14)	1.43(1)
C(2)–C(3)	1.42(1)	C(13)–C(18)	1.40(1)
C(3)–C(4)	1.42(1)	C(14)–C(15)	1.35(1)
C(3)–C(8)	1.42(1)	C(15)–C(16)	1.39(2)
C(4)–C(5)	1.38(1)	C(16)–C(17)	1.34(1)
C(5)–C(6)	1.42(2)	C(17)–C(18)	1.40(1)
C(6)–C(7)	1.35(1)	C(18)–C(19)	1.44(1)
C(7)–C(8)	1.42(1)	C(19)–C(20)	1.34(1)
C(8)–C(9)	1.41(1)		
Te(2)–Te(1)–C(1)	96.1(2)	Te(1)–C(1)–C(10)	121.2(6)
Te(1)–Te(2)–C(11)	100.4(2)	Te(2)–C(11)–C(12)	119.0(6)
Te(1)–C(1)–C(2)	118.6(6)	Te(2)–C(11)–C(20)	120.3(6)

Table 5. Bond Lengths (Å) and Angles (deg) for $C_{20}H_{14}Te_2$, Polymorph 1b

Te(1)–Te(2)	2.7179(6)	C(9)–C(10)	1.36(1)
Te(1)–C(1)	2.135(6)	C(11)–C(12)	1.371(9)
Te(2)–C(11)	2.127(5)	C(11)–C(20)	1.417(9)
C(1)–C(2)	1.356(8)	C(12)–C(13)	1.417(8)
C(1)–C(10)	1.421(8)	C(13)–C(14)	1.428(9)
C(2)–C(3)	1.403(9)	C(13)–C(18)	1.402(9)
C(3)–C(4)	1.427(8)	C(14)–C(15)	1.349(9)
C(3)–C(8)	1.428(8)	C(15)–C(16)	1.41(1)
C(4)–C(5)	1.35(1)	C(16)–C(17)	1.35(1)
C(5)–C(6)	1.39(1)	C(17)–C(18)	1.411(8)
C(6)–C(7)	1.37(1)	C(18)–C(19)	1.41(1)
C(7)–C(8)	1.43(1)	C(19)–C(20)	1.341(8)
C(8)–C(9)	1.406(9)		
Te(2)–Te(1)–C(1)	95.7(2)	Te(1)–C(1)–C(10)	120.5(4)
Te(1)–Te(2)–C(11)	97.2(2)	Te(2)–C(11)–C(12)	120.2(4)
Te(1)–C(1)–C(2)	119.9(4)	Te(2)–C(11)–C(20)	120.1(4)

The molecular structures of polymorphs **1a** and **1b** are shown in Figure 5. Selected bond lengths and angles for **1a** and **1b** appear in Tables 4 and 5, respectively. Bond lengths and angles in the two polymorphs lie within normal ranges. The C–Te–Te–C torsion angles for **1a** and **1b** are 105.2(3)° and 78.6(2)°, respectively. The C–Te–Te–C torsion angles for 10 acyclic Te_2 molecules extracted from version 5.04 of the Cambridge Structural Database[23] lie in the range −72.4° to −91.5° and +85.8° to +92.2°.[8,24–32] Additionally, the structures of dimesityl ditelluride (**3**);

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(18) (a) Laur, P.H.A. *Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds*, Metz, France, July 9–12, 1979; Cagniant, D., Kirsch, G., Eds.; pp 217–301. (b) Bendix, D. Doctoral Dissertation, Technische Hochschule, Aachen, Germany, 1981; pp 58–61.

(19) Cross, R. J.; Millington, D. *J. Chem. Soc., Chem. Commun.* **1975**, 455–456.

(20) Ashe, A. J., III; Butler, W.; Diephouse, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 207–209.

(21) Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* 104, 3876–3879.

(22) Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495–496.

(23) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Info. Comp. Sci.* **1991**, *31*, 187–204.

(24) Ludlow, S.; McCarthy, A. E. *J. Organometal. Chem.* **1981**, *219*, 169–176. R_2Te_2, R = *p*-methoxyphenyl; CSD refcode: BAJHAV; C–Te–Te–C, −81.1° and 86.8° (two independent molecules); shortest Te···Te 3.553 Å.

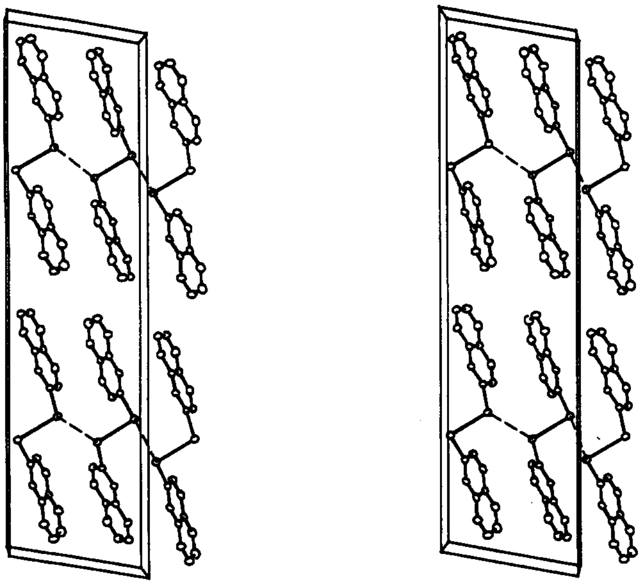

Figure 6. Stereoscopic view of the unit cell of **1a** (*a*, horizontal; *c*, vertical). The Te···Te contacts within the cell borders are 4.414 Å; those crossing the cell borders are 4.129 Å.

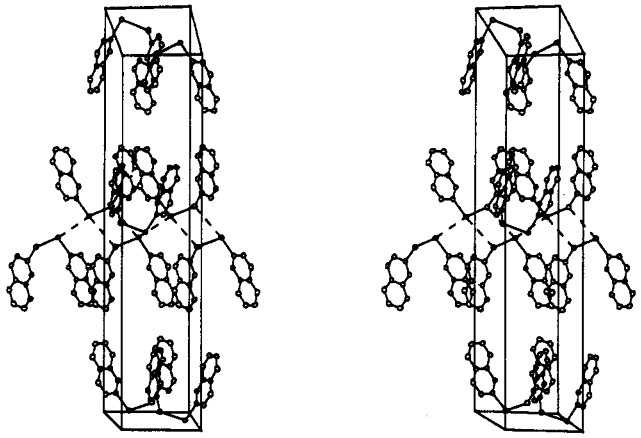

Figure 7. Stereoscopic view of the unit cell of **1b** (*b*, horizontal; *a*, vertical). The leftmost Te···Te contact and translation-related contacts are 4.002 Å; the rightmost Te···Te contact and translation-related contacts are 3.708 Å.

$[2\text{-Me}_2\text{N-4,6-(CF}_3)_2\text{C}_6\text{H}_2\text{Te}]_2$ (**4**); and TTFTe$_2$, $(\text{C}_6\text{H}_3\text{S}_4)_2\text{Te}_2$ (**5**); have recently been reported.[33,34] The torsion angles are 93.9(2)°, 145.1(3)°, and −80.9° for **3**, **4**, and **5**, respectively; it appears that steric effects are responsible for the large torsion angle in **4**. Thus, **1a** is the only compound with a C–Te–Te–C angle much greater than 90° in which steric effects play no obvious role; there are no unusual intramolecular contacts or intermolecular contacts for **1a**. The Te–Te–C–C torsion angles in **1a** (84.0°, 111.8°) show a greater deviation from 90° than do those in **1b** (91.6°; 99.0°). Stereoscopic views of the unit cells for **1a** and **1b** are shown in Figures 6 and 7, respectively. In **1a**, the molecules pack along the crystallographic *a* direction; the shortest Te···Te contacts (4.129 and 4.414 Å) occur along these chains and are shown in the figure. In Figure 7, chains of **1b** molecules are shown packed along the crystallographic *b* direction. The Te···Te contacts connecting these molecules are much shorter (3.708 and 4.002 Å). The chain of Te···Te contacts is not linear (*cf.* the linear chain of Sb atoms in **2**); the Te-Te···Te angles associated with these contacts are 159.7° and 81.5°. The 3.708-Å contact is among the shorter contacts observed for acyclic Te$_2$ compounds; there are two very short Te···Te contacts (3.553 and 3.578 Å) in *p,p'*-bis(dimethoxydiphenyl) ditelluride.[24,35]

Acknowledgment. We are grateful to the National Science Foundation for partial support of this work (Grants SP1-8160202 [to GTE Laboratories in support of J.C.S.] and DMR-9221487 [B.M.F.]). S.T. acknowledges partial support from the Office of Naval Research for the purchase of the FT-Raman instrumentation. The authors thank J. Mullins and F. Kochanek for furnishing X-ray powder diffraction patterns and FTIR spectra, respectively. D.J.S. thanks Professor P. Laur for furnishing a copy of the doctoral dissertation of D. Bendix.[18b] Drs. S. H. W. Hankin and J. E. Saunders attempted to record Raman spectra of **1a** and **1b** using visible light lasers as excitation sources.

Supplementary Material Available: Tables S-I through S-IV, listing all bond lengths and angles, anisotropic displacement parameters, H atom coordinates, and torsion angles for **1a**, and Tables S-V through S-VIII, listing the same information for **1b** (8 pages). Ordering information is given on any current masthead page.

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(25) Kruse, F. H.; Marsh, R. E.; McCullough, J. D. *Acta Crystallogr.* **1957**, *10*, 201–209. R$_2$Te$_2$, R = *p*-chlorophenyl, monoclinic form; CSD refcode: CLPHTE; C–Te–Te–C, −72.4°; shortest Te···Te 4.219 Å.

(26) Reference 8. R$_2$Te$_2$, R = *p*-chlorophenyl, orthorhombic form; CSD refcode: CLPHT01; C–Te–Te–C, −88.8°; no Te···Te ≤ 4.4 Å.

(27) Llabres, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr., Sect B: Struct. Sci.* **1972**, *B28*, 2438–2444. R$_2$Te$_2$, R = phenyl; CSD refcode: DPHDTE; C–Te–Te–C, −91.5°; shortest Te···Te 4.254 Å.

(28) Spirlet, M. R.; Van den Bossche, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr., Sect. B: Struct. Sci.* **1979**, *B35*, 1727–1729. R$_2$Te$_2$, R = *p*-tolyl; CSD refcode: DPTOTE; C–Te–Te–C, −85.8°; shortest Te···Te 4.377 Å.

(29) Zingaro, R. A.; Herrera, C.; Meyers, E. A. *J. Organomet. Chem.* **1986**, *306*, C36–C40. R$_2$Te$_2$, R = *N,N'*-dimethylaminoformyl; CSD refcode: *FEKGIL*; C–Te–Te–C, −88.5°; shortest Te···Te 4.188 Å.

(30) du Mont, W.-W.; Lange, L.; Karsch, H. H.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Chem. Ber.* **1988**, *121*, 11–14. R$_2$Te$_2$, R = 2, 4, 6-tri-*tert*-butylphenyl; CSD refcode: FOZSIW; C–Te–Te–C, 92.2°; no Te···Te ≤ 4.4 Å.

(31) Abid, K. Y.; Al-Salim, N. I.; Greaves, M.; McWhinnie, W. R.; West, A. A.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1697–1703. R$_2$Te$_2$, R = 2-hydroxyiminomethyl(phenyl); CSD refcode: JATSEC; C–Te–Te–C, −77.5°; shortest Te···Te 3.777 Å.

(32) Kumar, S. K.; Singh, H. B.; Das, K.; Sinha, U. C. *J. Organomet. Chem.* **1990**, *397*, 161–167. R$_2$Te$_2$, R = 2-benzo(b)thienyl; refcode: VIBNEZ; C–Te–Te–C 88.5°; shortest Te···Te 3.939 Å.

(33) Edelmann, A.; Brooker, S.; Bertel, N.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Z. Naturforsch.* **1992**, *47b*, 305–309. Shortest Te···Te, 4.770 Å for **3**; 4.125 Å, 4.170 Å for **4**.

(34) Becker, J. Y.; Bernstein, J.; Dayan, M.; Shahal, L. *J. Chem. Soc., Chem. Commun.* **1992**, 1048–1049. Shortest Te···Te, 4.800 Å.

(35) Mundt, O.; Becker, G.; Roessler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1983**, *506*, 42–58.