# Tellurium-Centered Radical Cations. 1. The 1,3-Ditellurole Radical Cation by Chemical, Electrochemical, and Photochemical Oxidation

Michael R. Detty,* Neil F. Haley, Raymond S. Eachus, James W. Hassett, Henry R. Luss, M. Gary Mason, John M. McKelvey, and Alex A. Wernberg

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. Received April 11, 1985

Abstract: 1,3-Ditellurole was oxidized by chemical (nitrosyl fluoroborate, 96% sulfuric acid), electrochemical, and X-irradiation methods. The resulting species were examined by absorption, ESR, and ESCA spectroscopy. In solution, two different species were observed with λ_{max} at 560 and 610 nm. These species are the ditellurole radical cation and the dimer dication of the open-shell species, respectively. The species with λ_{max} at 610 nm was diamagnetic in both solution and the solid phase. Its formation in solution was favored by lower temperatures or higher concentrations of 1,3-ditellurole. The structure of 1,3-ditellurole was determined by X-ray crystallography. The experimentally determined geometry was used in CNDO/2 calculations, which predicted the gross features of the ESR spectrum of the radical cation, which were a Te-centered radical cation with slight spin density at methylene hydrogens and none at the vinylic hydrogens. Irradiated 1,1,2-trichloro-1,2,2-trifluoroethane glasses of 1,3-ditellurole gave a 1:2:1 triplet feature with $g = 2.2571$ and $a_H = 21.0 \pm 0.1$ G. An irradiated glass of [^{125}Te,^{125}Te]-1,3-ditellurole gave two doublets-of-triplets features with $g_\parallel = 2.2571$, $a_\parallel(^1H) = 21.0 \pm 0.1$ G, and $a_\parallel(^{125}Te) = 260.0 \pm 0.5$ G, and $a_\perp(^1H) = 25.0 \pm 0.1$ G. This suggested a localized radical-cation structure. Irradiated crystals of 1,3-ditellurole gave only the free spin of an electron ($g = 2.002$) with no evidence for a Te-containing radical cation. This was taken as evidence for hole transport and the formation of a dimer dication in the crystal lattice. ESCA spectra of thin films of 1,3-ditellurole showed two different Te $3d_{5/2}$ binding energies, consistent with the formation of the dimer dication.

The one-electron oxidation of cyclic molecules containing two nonadjacent sulfur atoms in the ring leads to radical cations in which the S–S interaction is a function of ring size. In medium-ring compounds such as 1,5-dithiacyclooctane radical cation (**1**),[1,2] a strong S–S interaction occurs to give a two-center, three-electron bond.[3] In 1,3- and 1,4-dithiacyclohexane radical cations (**2** and **3**), weaker S–S two-center, three-electron bonds are observed, but in 1,3-dithiolane radical cation (**4**) only intermolecular S–S interactions are observed.[1]
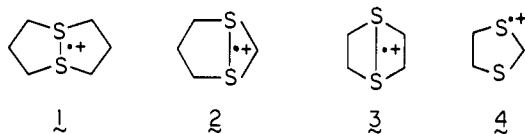
The addition of a carbon π framework linking the two sulfur atoms changes the nature of the resulting radical cations. Thus, ESR studies show that the radical cations of the 1,3-dithiole **5** and the 1,4-dithiacyclohexane **6** are π-delocalized with little evidence of direct S–S interaction.[4]
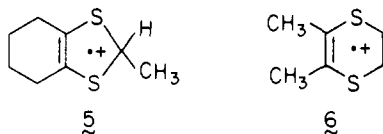
The dithia compounds are often quite different from their oxygen counterparts as well. Whereas **2** has a pronounced S–S interaction and little delocalization into the [–S–CH$_2$–S–]$^+$ unit, 1,3-dioxane and 1,3-dioxolane radical cations have π structures involving delocalization within the [–O–CH$_2$–O–]$^+$ unit with high spin density on the methylene groups.[5]

The radical-cation analogues of the heavier chalcogen elements (selenium and tellurium) have not been prepared. It is anticipated that the heteroatom–heteroatom interactions as well as heteroatom orbital overlap with a carbon π framework would be quite different with the larger (and more electropositive) elements. In support of this, differences in the modes of ionization and in the stabilization of the resulting radical cations between tetrathiafulvalenes and tetratellurafulvalenes have been suggested, based on the size, electronegativity, and polarizability differences between sulfur and tellurium.[6]
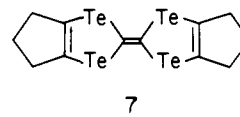
We have been interested in 1,3-ditelluroles as model systems for and precursors to tetratellurafulvalenes.[7] The two-electron oxidation of 1,3-ditellurole (**8**) to the 1,3-ditellurolylium cation **9** has been described,[7b] but the one-electron oxidation to radical cation **10** has not. Herein we report the chemical, electrochemical,
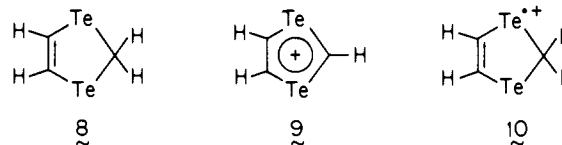
and photochemical (X-ray irradiation) oxidation of 1,3-ditellurole (**8**) to its radical cation **10** and dimerization products and analyses of these systems by absorption, ESCA, and ESR spectroscopy (including the preparation of ^{125}Te-labeled samples).

Experimental Section

1,3-Ditellurole (**8**) was prepared by the literature method.[7b] Dichloromethane was dried over activity I alumina before use. Acetonitrile was distilled from P$_2$O$_5$ and stored over 3A molecular sieves. 1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) and fluorotrichloromethane

(1) (a) Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* **1979**, *101*, 5322. (b) Asmus, K.-D. *Acc. Chem. Res.* **1979**, *12*, 436.

(2) (a) Musker, W. K.; Wolford, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3055. (b) Brown, T. G.; Hirschon, A. S.; Musker, W. K. *J. Phys. Chem.* **1981**, *85*, 3767.

(3) Baird, N. C. *J. Chem. Educ.* **1977**, *54*, 291.

(4) Russel, G. A.; Zaleta, M. *J. Am. Chem. Soc.* **1982**, *104*, 2318.

(5) (a) Rao, D. N. R.; Symons, M. C. R.; Wren, B. W. *Tetrahedron Lett.* **1982**, *23*, 46739. (b) Symons, M. C. R.; Wren, B. W. *J. Chem. Soc., Chem. Commun.* **1982**, 817.

(6) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154.

(7) (a) Bender, S. L.; Detty, M. R.; Fichtner, M. W.; Haley, N. F. *Tetrahedron Lett.* **1983**, *24*, 237. (b) Bender, S. L.; Detty, M. R.; Haley, N. F. *Ibid.* **1982**, *23*, 1531.

Table I. Positional and Thermal Parameters[a] of Ditellurole **8**[b]

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Te	0.16967 (4)	0.10366 (4)	0.24722 (9)	0.00643 (3)	0.00631 (3)	0.0425 (2)	-0.00080 (5)	-0.0010 (3)	-0.0018 (3)
C1	0.2311 (15)	0.2689	0.044 (2)	0.0078 (6)	0.0078	0.032 (4)	-0.001 (2)	-0.001 (3)	0.001
C2	0.3363 (7)	0.0781 (8)	0.453 (2)	0.0088 (7)	0.0077 (6)	0.057 (4)	0.003 (1)	-0.007 (3)	0.010 (3)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
H11	0.1709	0.3291	0.0554	5.0000	H2	0.3593	0.0008	0.5375	5.0000
H12	0.2471	0.2529	-0.1586	5.0000					

[a] The form of the anisotropic thermal parameter is: $\exp[-(B(1,1)*h2 + B(2,2)*k2 + B(3,3)*l2 + B(1,2)*hk + B(2,3)*hl + B(2,3)*kl)]$. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

(Freon 11) were distilled before use. UV–visible absorption spectra were recorded on Cary 17 and Perkin-Elmer 330 spectrophotometers.

X-ray Crystallographic Analysis of 8. The programs used were part of the Enraf–Nonius Structure Determination Package (SDP), Enraf-Nonius Delft, Holland, Version 18, 1981. A crystal $0.08 \times 0.10 \times 0.37$ mm was used for data collection. The crystal data are as follows: tetragonal, $P\bar{4}2_1m$, with $a = 11.048$ (1) Å, $c = 4.646$ (1) Å, $V = 567.1$ (2) Å^3, d(calcd) = 3.458 g cm^{-3}, $Z = 4$, and μ(Mo Kα) = 105.0 cm^{-1}. We chose $P\bar{4}2_1m$ over $P\bar{4}2_12$ after examining the vectors in the Patterson map. The molecule is located on a crystallographic mirror. A total of 529 independent reflections ($2\theta < 60°$) were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. A numerical absorption correction was applied.

The structure was solved by the heavy-atom method and refined by full-matrix least squares to $R = 0.0410$ and $R_w = 0.0465$ with the function minimized being $\sum_w ||F_o| - |F_c^*||^2$, $F_c^* = KF_c(1 + {_g}I_c)^{-1}$, $R = \sum ||F_o| - |F_c^*||/\sum|F_o|$, $R_w = [\sum_w ||F_o| - |F_c^*||^2/\sum_w|F_o|^2]^{1/2}$. The scale factor was $K = 2.584$ (14). An extinction parameter (g)[8] was included and refined to $2.8(7) \times 10^{-7}$. Hydrogen atoms were included in the structure factor calculations but were not refined. Refinement of the inverse configuration gave $R = 0.0413$ and $R_w = 0.0468$, and this configuration can be rejected at the 1% significance level by Hamilton's significance test.[9] Final atomic positional and thermal parameters are given in Table I.

Nitrosyl Fluoroborate Oxidations of 8. Ditellurole **8** (6.00 mg, 2.03 $\times 10^{-5}$ mol) was dissolved in 100 mL of dry dichloromethane. The resulting solution was deoxygenated by sonication under argon and then by a stream of argon bubbles. The resulting solution was cooled to –70 °C under a stream of argon and diluted to 100 mL with dichloromethane. The absorption spectrum of **8** at –70 °C was determined in a Dewar flask equipped with quartz windows: λ_{max} (ϵ) 346 (6500), 425 nm (440).

A solution of 24.0 mg (2.05 $\times 10^{-4}$ mol) of nitrosyl fluoroborate in 20 mL of 1:1 (v/v) dichloromethane–acetonitrile was deoxygenated by sonication and a stream of argon bubbles. A 2-mL portion (2.0×10^{-5} mol) of this solution was added to the ditellurole solution at –70 °C, giving a blue solution: λ_{max} (ϵ) 610 nm (4000). Addition of hydrazine (1 μL) to 5 mL of the blue solution regenerated the absorption spectrum of **8**.

The bulk of the blue solution was warmed to –10 °C, and the hue changed from blue to magenta: λ_{max} (ϵ) 560 nm (1800). Recooling the sample to –70 °C regenerated the blue species. The addition of hydrazine (1 μL) to 5 mL of the magenta solution regenerated the absorption spectrum of **8**.

The addition of nitrosyl fluoroborate (200 μL of a 1×10^{-3} M solution in 1:1 (v/v) dichloromethane–acetonitrile) to 10 mL of a 2×10^{-4} M solution of **8** in dichloromethane at ambient temperature generated a magenta solution: λ_{max} 560 nm. Cooling this solution gave a blue solution: λ_{max} 610 nm.

A 5×10^{-3} M solution of **8** in dichloromethane was prepared by dissolving 15 mg (5.1×10^{-5} mol) of **8** under argon in 10 mL of degassed CH$_2$Cl$_2$. Nitrosyl fluoroborate (6.0 mg, 5.1×10^{-5} mol) in 0.5 mL of acetonitrile was added, giving a blue (λ_{max} 610 nm) species that faded to yellow upon standing at ambient temperature.

Sulfuric Acid Oxidation of 8. The addition of degassed 96% sulfuric acid to crystals of **8** gave an intense magenta color that changed to yellow within seconds at either ambient temperature or 0 °C. The species was too short-lived for transfer to the sample chamber of an absorption or ESR spectrometer.

A 5×10^{-4} M solution of **8** in dry, deoxygenated dichloromethane was prepared and cooled to 0 °C. A drop of 96% sulfuric acid was added to a 5-mL sample of the solution of **8** contained in a 1-cm-wide quartz cell. Magenta globules of sulfuric acid formed and settled to the bottom of the cell. The cell was gently swirled, giving a magenta dichloromethane

(8) Stout, G. H.; Jensen, L. H. "X-ray Structure Determination"; Macmillan: New York, 1968; Chapter 17.
(9) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

solution with λ_{max} 552 nm. The magenta solution was cooled to –70 °C, where the magenta color (λ_{max} 556 nm) persisted for at least 6 h. When warmed to ambient temperature, the magenta solution became yellow within seconds after the addition of a drop of water.

ESCA Studies. The samples were prepared for ESCA by dissolving **8** in dichloromethane, coating the solution on a clean silicon substrate, and allowing the solvent to evaporate. This produced a uniform, thin film that gave no indications of sample charging. The sample did not appear to suffer X-ray-induced decomposition under normal operating conditions. The spectra were recorded on a Hewlett-Packard 5950A ESCA spectrometer with a monochromatic Al Kα source.

Electrochemical Studies. A Princeton Applied Research Model 173 potentiostat/galvanostat, a Model 179 current–voltage converter, and a Model 175 waveform generator were used for the electrochemical experiments. The working electrode for cyclic voltammetry was glassy carbon (Princeton Applied Research, Model 90021). The porous electrode used for the double-potential step chronocoulometry and for making some of the ESR and UV–visible measurements was similar to that reported by Miner and Kissinger[10] except that a reticulated glassy carbon (RVC) tube was substituted for the carbon particles used by those authors. In a nonflow mode, the porous electrode exhibited thin-layer behavior with the cell volume being obtained, with tritolylamine used as a known one-electron reversible oxidation. The RVC was obtained from Normar Industries and was of porosity 100, grade 4. A standard calomel reference electrode was used in all the measurements. Dichloromethane (HPLC grade) was obtained from J. T. Baker; it was further dried by storing it over 3A molecular sieves, previously activated at 180 °C in a vacuum oven for 15 h. Tetrabutylammonium fluoroborate was obtained from Southwestern Analytical Chemicals, Inc. and was dried at 80 °C for 15 h in a vacuum oven.

UV–visible absorption spectra were obtained with a Hewlett-Packard 8450A spectrophotometer, scanning 200–800 nm with a 1-s acquisition time. To obtain the UV–visible spectra of the products of electrolysis, we connected the exit of the electrochemical flow cell to the quartz spectral flow cell with Omnifit $^1/_{16}$-in. Teflon tubing and Tefzel connectors. All spectra were recorded while solutions were flowing through the electrolysis cell and the UV–visible cell.

Similarly, we examined ESR spectra of the electrooxidized solutions by connecting the exit of the electrolysis cell to a flat (0.5 mm) ESR cell (Wilmad Glass Co.). The ESR spectra of the oxidation products were examined on a Bruker ER200D-SRC 100-kHz spectrometer at ambient temperature.

ESR Studies. ESR spectra in rigid media were obtained on a standard Varian E-9 spectrometer fitted with an Air Products Heli-Tran continuous-transfer crystostat system. The latter allowed spectra to be measured at temperatures between 8 and 200 K. Spectra were calibrated with a Varian E 500 NMR gaussmeter and a Hewlett-Packard Model 5343A microwave frequency counter.

For generating radical cations of **8**, the material was first dissolved in purified Freon 113 (CF$_2$ClCCl$_2$F). This solvent was chosen because **8** was moderately soluble ($>10^{-4}$ M) in it, and its exposure to ionizing radiation at 77 K produced a matrix radical with a reasonably simple and narrow ESR spectrum centered at $g \simeq 2.0$. Small beads of the solution were prepared by spraying it into liquid nitrogen. They were transferred to a quartz tube, which was sealed and inserted into the nitrogen-filled Dewar system of an X-ray exposure apparatus. The samples were irradiated at 77 K for 7 h with the output of a Machlett 50T X-ray tube operating at 40 kV and 30 mA.

Identical substrate spectra were generated in Freon 11 (CFCl$_3$) with X-ray irradiation. However, the glass formed was not as easy to work with, and the matrix signal was broader and more intense.

A 10^{-4} M solution of **8** in dichloromethane was oxidized with nitrosyl fluoroborate at –70 °C (see above). The solution did not give an ESR signal at –70 °C. The sample was frozen in liquid nitrogen in a quartz ESR cell and slowly warmed to 163 K. No ESR signal was detected.

The oxidation of **8** with nitrosyl fluoroborate at ambient temperature gave a magenta species (see below), which did not give a detectable ESR

6300 *J. Am. Chem. Soc., Vol. 107, No. 22, 1985*

Detty et al.

Table II. Comparative Bond Angles and Distances for Tetratellurafulvalene **7** and Ditellurole **8**

distance or angle	7[a]	8
Te(1)–C(2)–Te(3)	115.2 (2)°	109.8 (5)°
C(2)–Te(3)–C(4)	90.2 (2)°	92.2 (5)°
Te(3)–C(4)–C(5)	122.1 (4)°	122.9 (5)°
Te(1)–C(2)	2.098 (5) Å	2.17 (2) Å
Te(1)–C(5)	2.090 (5) Å	2.094 (8) Å
C(4)–C(5)		1.34 (2) Å

[a] Reference 11.

signal. Attempts to quick freeze the sample in liquid nitrogen gave a blue diamagnetic solid.

The magenta species as prepared by sulfuric acid oxidation in dichloromethane was frozen in liquid nitrogen. The sample was paramagnetic between 77 and 200 K.

Preparation of [1,3-^{125}Te]-1,3-Ditellurole. A 95.67% enriched sample of ^{125}Te powder was obtained from Oakridge National Laboratories. *n*-Butyllithium (1.0 mL, 2.4 M) was added dropwise to a stirred solution of trimethylsilylacetylene (0.23 g, 2.4 mmol) in 5 mL of dry tetrahydrofuran (THF) cooled to –70 °C under argon. The ^{125}Te powder (0.20 g, 1.6 mmol) was added, and the mixture was warmed to room temperature. After 2 h, the reaction mixture was cooled to –70 °C, and a solution of iodochloromethane (0.35 g, 2.0 mmol) in 1 mL of dry THF was added. The mixture was stirred for 15 min and then quenched with 50 mL of water. The product was extracted with dichloromethane (3 × 15 mL). The combined extracts were washed with brine, dried over sodium sulfate, and concentrated to give 0.27 g (63%) of [^{125}Te]chloromethyltellurotrimethylsilylacetylene as a pale yellow oil: ^{1}H NMR (CDCl$_3$) δ 4.77 (d, 2 H, J = 30.8 Hz), 0.20 (s, 9 H); field-desorption mass spectrum (FDMS), m/e 271.

^{125}Te powder (0.125 g, 1.00 mmol) was added to 2 mL (2.0 mmol) of a 1 M solution of lithium triethylborohydride in THF with stirring under an argon atmosphere. After 2 h at ambient temperature, 2 mL of 1 M sodium ethoxide in ethanol was added, followed by 0.27 g (1.0 mmol) of [^{125}Te]chloromethyltellurotrimethylsilylacetylene in 2 mL of dimethylformamide. The reaction mixture was stirred for 2 h at ambient temperature. The reaction mixture was diluted with water (25 mL). The product was extracted with dichloromethane (3 × 5 mL). The combined extracts were dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel eluted with 1:1 (v/v) hexane–dichloromethane. The product fraction was concentrated and recrystallized from methanol to give 0.030 g (10%) of the ditellurole: mp 84–85 °C; ^{1}H NMR (CDCl$_3$) δ 8.90 (dd, 2 H, J = 87.9, 72.5 Hz), 4.77 (t, 2 H, J = 25 Hz); FDMS, m/e 290. The ^{1}H NMR spectrum is more complicated but reduces to d of d splitting for the olefinic protons as a first-order analysis. Actual couplings are J_{H-H} = 8.1 Hz, J_{Te-H} = 33.5 Hz, J_{Te-H} = 126.5 Hz. These values were determined from [mono-^{125}Te]ditellurole. The d of d splitting in the olefinic protons occurs from presumably a large and as yet undetermined Te–Te coupling.

Results and Discussion

X-ray Crystallographic Analysis. The suitability of 1,3-ditellurole (**8**) as a model system for tetratellurafulvalenes depends on similarities of bond distances and angles in the two systems. A comparison of the X-ray-determined structural parameters of tetratellurafulvalenes **7**[11] and 1,3-ditellurole (**8**) (Table II) shows that molecular geometries are similar in the two molecules.

Figure 1 shows the molecular packing of **8** viewed approximately down the $\bar{4}$ axis. There are significant Te···Te intermolecular interactions, resulting in a three-dimensional "polymeric" array. The distances (3.864, 3.865 Å) are less than twice the van der Waals radius for Te (2.06 Å),[12] and the interacting atoms are in stereochemically significant positions, both criteria given by Alcock[13] for evidence of "secondary bonds". Such short intermolecular contacts were also observed for **7**.[11] The configuration about Te can be described as distorted tetrahedral with two lone pairs of electrons and the two Te–C bonds occupying the four sp^3-hybridized orbitals. The lone pairs are directed at neighboring Te atoms, resulting in a nearly linear arrangement of Te···Te—C
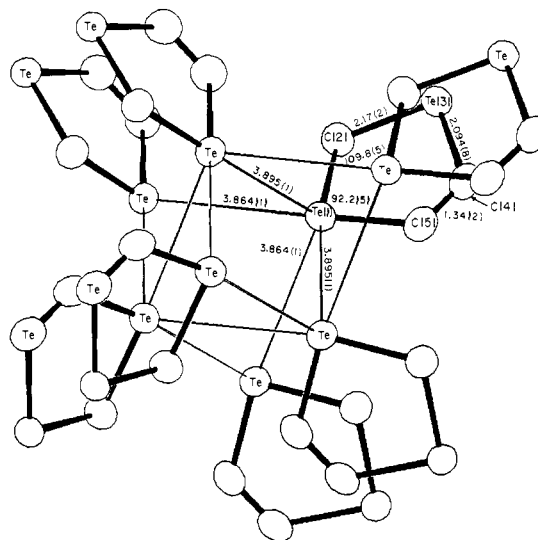
Figure 1. ORTEP plot of the molecular packing of ditellurole **8**.
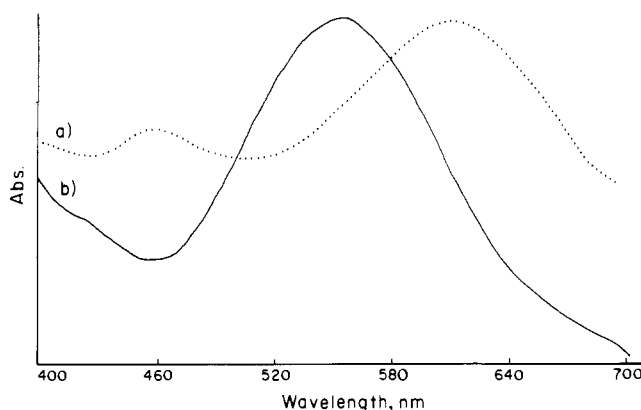
Figure 2. Absorption spectrum of the nitrosyl fluoroborate oxidation product of **8** at (a) –70 °C and (b) –10 °C.

atoms. The relevant angles are 169.8° for Te···Te(1)—C(5) and 167.4° for Te···Te(1)—C(2). The C–Te–C angles (92.2°, Table I) are reduced as predicted by VESPR theory[14] and to accommodate the five-membered ring.

Chemical Oxidations. Nitrosyl fluoroborate has been a useful oxidant for generating radical cations and dications from cyclic disulfides.[2,15] Ditellurole **8** was readily oxidized by nitrosyl fluoroborate in dichloromethane solution. At –70 °C, a 2 × 10^{-4} M solution of **8** gave a species with λ_{max} 610 nm (Figure 2a) upon addition of 1 equiv of nitrosyl fluoroborate. Warming this solution to –10 °C gave a new species with λ_{max} 560 nm (Figure 2b). Hydrazine reduction of either species regenerated **8**. Further warming of the 560-nm-absorbing species to ambient temperature gave a yellow solution (λ_{max} 440 nm) after several minutes, which showed small amounts of starting material (by HPLC) and no other characterizable products. The magenta solution upon recooling to –70 °C became blue (λ_{max} 610 nm).

A 5 × 10^{-3} M solution of **8** was oxidized by 1 equiv of nitrosyl fluoroborate at ambient temperature to give a short-lived 610-nm-absorbing species, which faded to yellow within 1 min. This species was longer lived at 0 °C.

The species absorbing at 610 nm was diamagnetic in solution at –70 °C, according to ESR spectroscopy. Frozen solutions of this species were diamagnetic between 77 and 200 K. The species absorbing at 560 nm was diamagnetic as well at ambient temperature. Attempts to quick freeze the 560-nm solution in liquid nitrogen gave diamagnetic blue solids.

(10) Miner, D. J.; Kissinger, P. T. *Biochem. Pharmacol.* **1979**, *28*, 3285.

(11) Carroll, P. J.; Lakshmikantham, M. V.; Cava, M. P.; Wudl, F.; Aharon-Shalom, E.; Cox, S. D. *J. Chem. Soc., Chem. Commun.* **1982**, 1316.

(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(13) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(14) Gillespie, R. J.; Nyholm, R. S. *Q. Rev. Chem. Soc.* **1957**, *11*, 339.

(15) (a) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416. (b) Musker, W. K.; Roush, P. B. *Ibid.* **1976**, *98*, 6745.
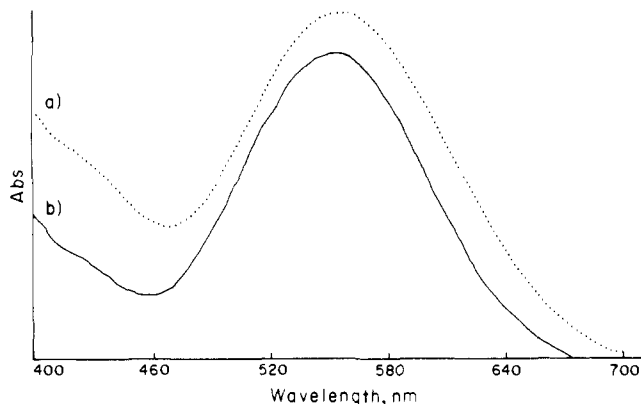
Figure 3. Absorption spectrum of the sulfuric acid oxidation product of **8** at (a) 25 °C and (b) -70 °C.
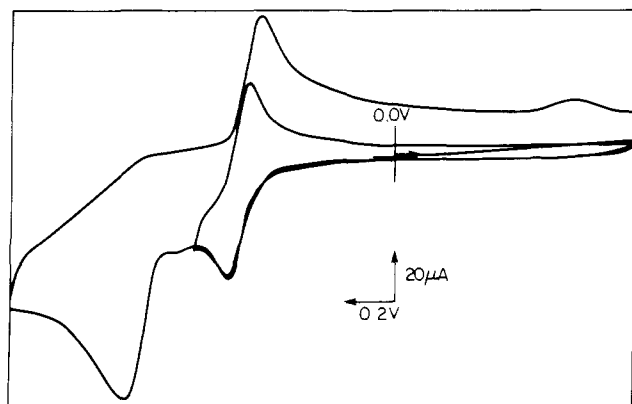

Figure 4. Cyclic voltammograms of 4.9 × 10^{-4} M 1,3-ditellurole in methylene chloride with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte and a sweep rate of 0.1 V/s.

The oxidations of thianthrene (**11**)[16] and phenoxtellurine (**12**)[17] with 96% sulfuric acid have been reported. The addition of 96% sulfuric acid to crystals of **8** gave an intense purple color (wavelength not determined) that faded to a yellow-brown solution within seconds.
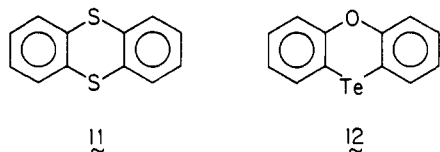
A longer-lived magenta solution was obtained by adding a drop of 96% sulfuric acid to a 5 × 10^{-4} M solution of **8** in dichloromethane cooled to 0 °C. The sulfuric acid droplets turned an intense purple color. This color was extracted into the dichloromethane solution to give λ_{max} at 552 nm. Simultaneously the sulfuric acid droplets turned yellow. Cooling the 552-nm-absorbing solution to -70 °C did not change hue or curve shape (Figure 3) even after 6 h. The CH_2Cl_2 solution from sulfuric acid oxidation of **8** gave a solid upon cooling, which was paramagnetic and gave an isotropic ESR spectrum with $g = 2.091$ and $\Delta H \simeq$ 180 G between 77 and 200 K. From these data, we conclude that the product of sulfuric acid oxidation is different from the product of nitrosyl fluoroborate oxidation. Further support for this conclusion was obtained from electrochemical studies of the oxidized species from sulfuric acid and from nitrosyl fluoroborate, in which the data were quite different for the two systems. The ESR spectrum of **1** generated by sulfuric acid oxidation is different from the ESR spectra of **1** in other solvents with other oxidants, which suggests solvent-dependent species.[2b]

(16) Shine, H. J.; Piette, L. *J. Am. Chem. Soc.* **1962**, *84*, 4798.
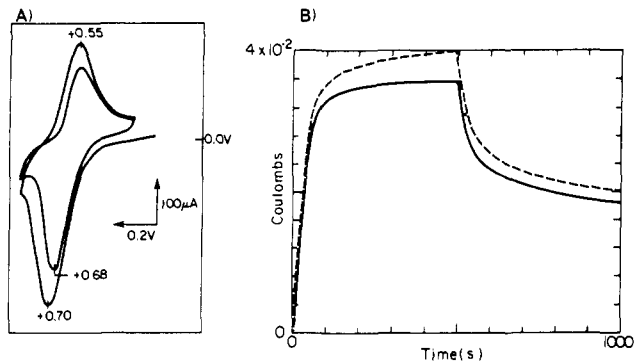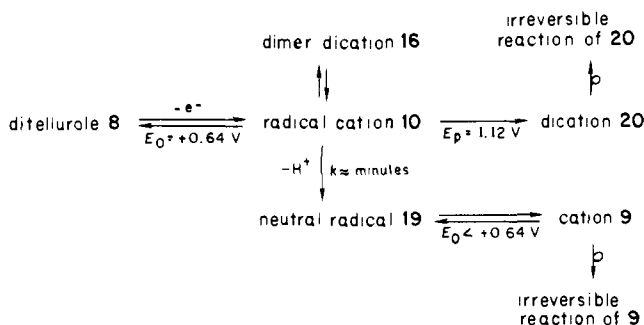(17) Drew, H. D. K. *J. Chem. Soc.* **1926**, 3054.

Figure 5. (a) Thin-layer cyclic voltammogram of 5 × 10^{-4} M 1,3-ditellurole in methylene chloride with 0.2 M tetrabutylammonium fluoroborate as supporting electrolyte and a sweep rate of 1 mV/s. (b) Double-potential step chronocoulometry of 2.6 × 10^{-4} M 1,3-ditellurole in RVC thin-layer cell: $E_{initial} = 0.2$ V, $E_1 = 0.85$ V, $E_2 = 0.2$ V; cell volume 0.78 mL.

Scheme I

Electrochemical Oxidations. Figure 4 shows the cyclic voltammogram of **8** in dichloromethane. The first reversible oxidation wave ($E_0 = 0.64$ V) suggests the formation of a relatively stable radical cation, whereas the second process occurring at $E_p = +1.12$ V is irreversible.

Controlled-potential electrolysis of **8** in a standard divided cell at ambient temperature gave a solution with λ_{max} 560 nm. A stirred-solution voltammogram of this solution, after the passage of 1.4 faradays/mol, showed essentially complete conversion of the oxidation wave to give the radical cation of **8** to a reduction wave occurring at the same potential to regenerate **8**, which is consistent with formation of a radical cation by one-electron oxidation. Consecutive voltammograms showed a steady decrease in the current response for the reduction wave with an increase in the oxidation current, suggesting a slow regeneration of the starting material through radical-cation disproportionation.

Controlled-potential electrolysis in the divided cell at -60 °C resulted in the loss of only 0.8 faraday/mol of starting material, with the resulting solution absorbing with λ_{max} 610 nm. On increasing the temperature to -30 °C, the solution gave λ_{max} 560 nm. Upon further warming to ambient temperature, the solution slowly became yellow, with no starting material being detectable.

Using an electrochemical thin-layer flow cell, we obtained the absorption spectrum of the oxidation product of **8** formed at +0.8 V at ambient temperature. The spectrum matched that shown in Figure 2 for the 560-nm species from nitrosyl fluoroborate oxidation of **8**. As in the chemical oxidation, no ESR signal was obtained for the 560-nm species under anaerobic conditions at ambient temperature. Upon cooling to -70 °C, the solution absorbed with λ_{max} 610 nm.

To determine the reversibility of the system to oxidation and rereduction, we used a thin-layer cell for the electrolysis and analyzed the results by double-potential chronocoulometry (Figure 5) and by HPLC analysis of the product. Complete oxidation of the solution at +0.85 V resulted in the passage of 2.0 faradays/mol, and the reduction of the oxidized product at +0.2 V required 0.8 faraday/mol. Complete oxidation at +1.28 V resulted

in the passage of 3.46 faradays/mol. HPLC analysis of the totally oxidized ditellurole solution showed complete loss of starting material, with no products being detectable at 254 nm by the HPLC detector. HPLC analysis of the rereduced solution showed the regeneration of ~40% starting material, consistent with the amount of reverse current observed in the chronocoulometric results. Any other products appeared to be polymeric in that they did not elute. The results described above suggest Scheme I as a mechanism for the electrochemical oxidation of **8**.

The observation of different species upon oxidation of ditellurole **8** at different temperatures and concentrations has considerable precedent in the chemistry of sulfide radical cations (**13**). Sulfide radical cations generated by pulse radiolytic,[1,18] chemical,[2,15] and electrochemical[19] oxidation have been observed to react with unoxidized sulfide to give dimer radical cations (**14**). A second
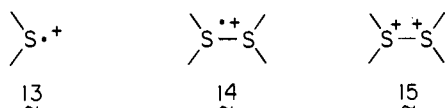
pathway available to sulfide radical cations is dimerization to give dimer dications (**15**), which can be isolated in some cases.[2,15,18] The formation of intermolecular sulfide/radical-cation/sulfide complexes does not occur in systems in which intramolecular complexes are possible, most notably in 1,5-dithiacyclooctane radical cation (**1**).[1,2] Intermolecular Se–Se interactions have been observed in the dimethyl selenide dimer radical cation as well.[20]

The second-order rate constant for the reaction of 1,4-dithiacyclohexane radical cation (**3**) with unoxidized 1,4-dithiacyclohexane to give complex **17** has been calculated to be 5.8×10^9 M^{-1} s^{-1}, or nearly diffusion controlled.[1a] If paramagnetic species such as **10** were in rapid equilibrium with other diamagnetic and/or paramagnetic species, spin pairing and spin inversion might broaden the ESR signal to the point that it would not be detectable.[21] One such process with **10** would be dimerization to give the dimer dication **16** as shown in eq 1.
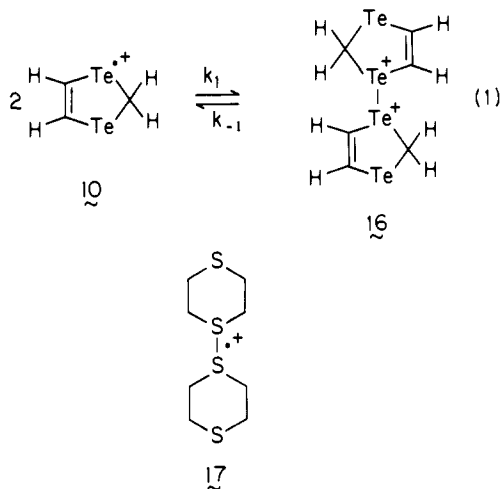
The dication **16** would be a diamagnetic species. The 610-nm-absorbing species, generated by nitrosyl fluoroborate and electrochemical oxidation of **8**, is diamagnetic between 77 and 200 K. Increasing the concentration of the radical cation **10** should favor dimer dication formation. Consistent with this, oxidation of a 5×10^{-3} M solution of **8** at ambient temperature gives the 610-nm species, not the 560-nm species observed at 2×10^{-4} M concentrations. For these reasons we have assigned the structure

of the dimer dication **16** to the oxidation product of **8** that absorbs at 610 nm (ϵ 4000).

The 560-nm species observed upon oxidation of **8** could be either the radical cation **10** or the dimer radical cation **18**. The latter species could form by reaction of the radical cation **10** with ditellurole **8** as shown in eq 2. However, in the electrochemical
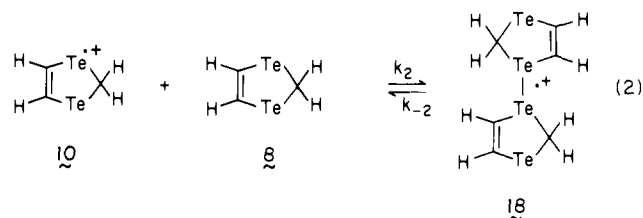
oxidations, the optical density at 560 nm at ambient temperature increases as more current is passed up to 1 faraday/mol. This observation is inconsistent with the dimer radical cation **18** as the major magenta species, since this species would require only 0.5 faraday/mol to reach maximum optical density. However, a small equilibrium concentration of **18** cannot be ruled out.

The magenta species from nitrosyl fluoroborate oxidation and electrochemical oxidation can most probably be assigned to the radical cation structure **10**. Although this species should give an ESR signal, rapid spin pairing and resulting spin inversion[21] or spin–orbit coupling[22] between two tellurium atoms in the molecule could explain the absence of a detectable ESR signal at ambient temperature.

The radical cations of 1,8-chalcogen-bridged naphthalenes have been examined by ESR spectroscopy.[22] All of the species gave a detectable ESR signal except the ditelluro-bridged species. Broadening due to spin–orbit coupling was invoked to account for the lack of signal.

XY = SS, SSe, STe, SeSe, SeTe
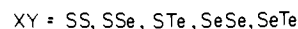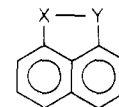
A third and less likely possibility to explain the lack of an ESR signal from **10** is shown in eq 3. The deprotonation of radical
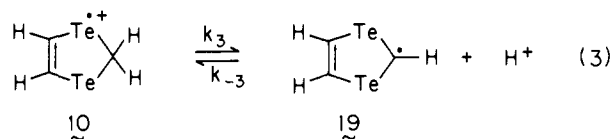
cation **10** to give the carbon-centered radical **19** has precedent in the electrochemical oxidative dimerization of 1,3-dithioles to tetrathiafulvalenes.[23] Should the proton loss be reversible, the interconversion of two radicals with quite different *g* anisotropies would lead to a very broad ESR signal, which might not be easily detected. However, **19** would be expected to be quite reactive toward dimerization and tetratellurofulvalene formation.

Further electrochemical oxidation of the radical cation **10** can occur at more positive potentials (+1.12 V) to give a product of 2e oxidation that is unstable, presumably owing to traces of nucleophilic impurities in the solvent. At ambient temperature and presumably because of water in the solvent, the radical cation **10** can also deprotonate (minutes) to give the neutral radical **19** (eq 3). This neutral radical would be expected to oxidize at the potential applied for oxidation of the ditellurole starting material, and the resulting 2e oxidation product formed is cation **9**. A slow, irreversible rearrangement–decomposition of **9**[7b] results in only

(18) (a) Bahnemann, D.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1975**, 238. (b) Asmus, K.-D.; Gillis, H. A.; Teather, G. G. *J. Phys. Chem.* **1978**, *82*, 2677.

(19) Wilson, G. S.; Swanson, D. D.; Klug, J. T.; Glass, R. S.; Ryan, M. D.; Musker, W. K. *J. Am. Chem. Soc.* **1979**, *101*, 1040.

(20) (a) Wang, J. T.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1981**, 1184. (b) Wang, J. T.; Williams, F. *Ibid.* **1983**, 980.

(21) Symons, M. C. R. "Electron-Spin Resonance Spectroscopy"; Wiley: New York, 1978.

(22) Bock, H.; Brühler, G., Dauplaise, D.; Meinwald, J. *Chem. Ber.* **1981**, *114*, 2622.

(23) Saeva, F.; Morgan, B.; Fichtner, M.; Haley, N. *J. Org. Chem.* **1984**, *49*, 390.

partial reversibility for the overall 2e oxidation with proton loss of **8**.

A second 2e oxidation path for **8** that cannot be rigorously excluded includes a 1e oxidation of radical cation **10** to give dication **20**. If **20** were formed, then deprotonation would lead

20
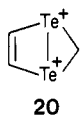
to **9**. However, it is not likely that the oxidation of the radical cation **10** to the dication **20** would occur at the same potential as the oxidation of **9** to **10**, owing to simple electrostatic considerations. Cyclic dications with two sulfur atoms have ample precedent.[15b]

We investigated the viability of such a dication by CNDO/2 calculations,[24] using Burn's exponents and Te β-parameters chosen to reproduce the experimental geometry of **8** by gradient search techniques.[25] We found in going from **8** to **10** to **20**, using the geometry of **8**, an increase in the Wiberg indices (0.027, 0.091, and 0.384, respectively) between the two Te atoms, with the largest increase between **10** and **20**. Therefore, the dication **20** could lead to significant shortening of the Te–Te distance, implying formation of a Te–Te bond. This could lead to significant geometry changes from the parent and will be the focus of future study.

ESR Studies. The monomeric radical cation **10** has a variety of electronic states available to it. In one extreme, the radical-cation center could be quite localized on one Te atom, as in i, with little intramolecular Te–Te interaction. In such a radical cation, π delocalization might be important. In the other extreme, a

i　　　　　　　　　ii
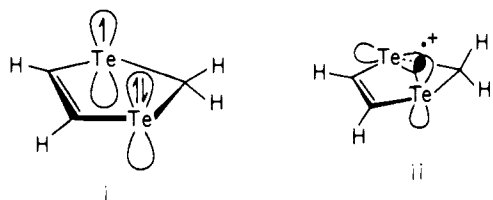
strong Te–Te interaction, as in ii, should give diminished π delocalization and high spin density on the Te atoms. Furthermore, a strong Te–Te interaction might be reflected in a shorter Te–Te distance as a result of σ bonding.

To this point, observation of the radical cation **10** was complicated by the intervention of either spin–orbit coupling or more than one oxidized species, as perhaps represented by **16** and **18**. We sought methods of observing **10** where competing second-order processes should be eliminated or diminished. Ditellurole **8** was readily oxidized by irradiation with X-rays. Irradiated crystals of **8** gave a strong, narrow ESR signal at free spin ($g = 2.002$), suggesting the formation of electrons from radiation damage and presumably a paramagnetic substrate radical cation as well. However, no structural information for **10** could be obtained from the crystal data. The irradiation of substrate molecules isolated in a frozen matrix of fluorotrichloromethane (Freon 11) has given matrix-isolated organic radicals, which have been examined by ESR spectroscopy.[5] Therefore, we next attempted to examine the ESR spectra of radical cation **10** generated by ionizing X irradiation in several Freon matrices.

The preferred solvent for matrix formation and irradiation has been fluorotrichloromethane (Freon 11).[5] We found that this solvent was mechanically difficult to work with and gave a broad, complex signal upon X irradiation. A better solvent in our hands was 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). Compound **8** was moderately soluble in this solvent ($>10^{-4}$ M). Mechanically, Freon 113 formed spherical beads when sprayed into liquid nitrogen. The signal produced upon irradiation of Freon 113 was

(24) Pople, J. A.; Santry, D. P.; Segal, G. A. *J. Chem. Phys.* **1965**, *43*, 5129.

(25) The program used was GEOMORV: Schmidling, D. *QCPE* **1978**, *11*, 350.

Table III. Magnetic Resonance Data for **10**

$g_{\parallel} = 2.2571 \pm 0.0005$
$a_{\parallel}(^{125}\text{Te}) = 260.0 \pm 0.5$ G
$a_{\parallel}(^1\text{H}) = 21.0 \pm 0.1$ G
$a_{\perp}(^1\text{H}) = 25.0 \pm 0.1$ G

narrower and less complex than the signal produced from Freon 11.

Figure 6 includes ESR spectra obtained from X-irradiated beads of a 10^{-4} M solution of ditellurole **8** in Freon 113. The samples were irradiated at 77 K, and the spectra were measured at 10 K, where line width and Boltzman advantages should be realized. The well-resolved 1:2:1 triplet absorption centered at 2882 G in Figure 6a ($g = 2.2571 \pm 0.0005$) was observed only from Freon 113 beads containing **8**. The triplet splitting was 21.0 ± 0.1 G. The intensity of this feature varied monotonically with the concentration of **8** in the Freon solution and with the X-irradiation dosage. It was clearly the low-field component of the ESR spectrum, originating from a radiation-damage product of **8** (**10**). The strong matrix signal and line widths made the determination of spin concentrations imprecise.

The CNDO/2 calculations[24,25] on **10** predict a π radical in which the spin density is in the Te $5p_z$ orbitals (0.37 on each tellurium) and in the methylene hydrogens (0.066 on each hydrogen). The calculations show no spin density on the ethylene hydrogens or on the carbon atoms. The observed triplet features of the ESR spectrum are consistent with the predicted features from the CNDO/2 calculations although structures i and ii should give similar spectra.

We had hoped that the ESR spectrum of **10** would distinguish radical cations of structures i and ii. To assign the triplet spectrum, we prepared ditellurole **8** from tellurium enriched to $>95\%$ in the magnetic 125 isotope (^{125}Te; $I = ^1/_2$). Figure 6b shows the spectrum produced by irradiating the enriched material in Freon 113. Two new triplet features appear in the low-field region of this spectrum as a result of the enrichment. One has the absorption-like shape characteristic of a parallel feature, but the other has the derivative shape expected for a perpendicular signal. There is also a trace of the original $g = 2.2571$ triplet originating from the nonmagnetic isotopes of tellurium that contaminated the enriched sample of the metal. No other new signals were detected as a result of the enrichment.

The parallel triplet at 2882 G in Figure 6a is assumed to correspond to the low-field g feature of a Te-containing radical whose symmetry is D_{4h} or lower. The 1:2:1 triplet structure can most reasonably be assigned to hyperfine splitting from two equivalent protons. In the ^{125}Te-enriched sample, this triplet is split into two sets of triplets as a result of the interaction of the unpaired electron with a single ^{125}Te nucleus. The high-field set overlaps the tail of the strong matrix signal and cannot be resolved.

The derivative signal observed at 2955 G in the spectrum of the enriched material (Figure 6b) either is a perpendicular feature from an axially symmetric tellurium radical or is associated with the central g feature of an anisotropic center. In the absence of any detectable high-field g features, we assume that the radical is axially symmetric and that the triplet at 2955 G is the $m_1 = -^1/_2$ transition of a ^{125}Te perpendicular hyperfine splitting (note $g_n = -1.765$). In this model, the corresponding $m_1 = +^1/_2$ triplet is obscured by the matrix signal. The 1:2:1 triplet splitting is assigned to a 25.0-G hyperfine interaction with two equivalent protons. The magnetic resonance data obtained from this analysis are summarized in Table III.

We tried to obtain isotropic magnetic resonance data for the Te-containing radical by carefully warming the irradiated frozen solution above 77 K. With these data it would have been possible to calculate $g_{\perp}$ and $a_{\perp}$ (^{125}Te). Unfortunately, both the matrix and solute radicals decayed or underwent secondary, irreversible reactions before the Freon matrix softened enough to allow their free rotation.

The paucity of information on organotellurium radical cations generated by irradiation makes difficult the comparison of the paramagnetic species generated by the irradiation of **8** with other
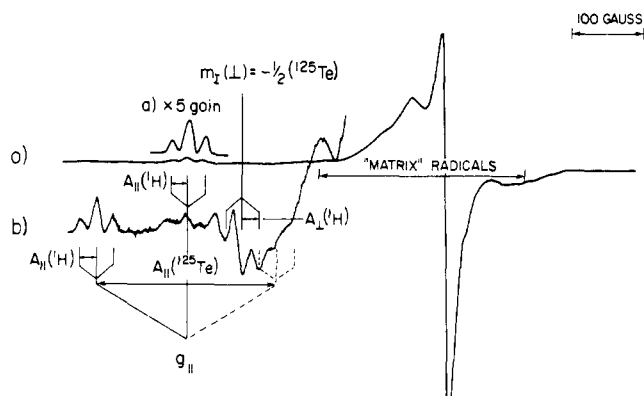
Figure 6. (a) ESR spectrum of 1,3-ditellurole in a Freon 113 matrix at 10 K. (b) ESR spectrum of [^{125}Te,^{125}Te]-1,3-ditellurole in a Freon 113 matrix at 10 K. In these spectra, the features associated with $g_{\parallel}$ are centered at 2882 G.

Figure 7. Te $3d_{5/2}$ binding energies of an ESCA spectrum of 1,3-ditellurole.

similar radicals. In particular, we were concerned about the possibility of ring cleavage, although the data seemingly rule that out. The ESR spectrum of dithiole radical cation **5** has been reported after oxidation of the appropriate dithiole with sulfuric acid.[4] The value of $a_H = 21$ G for the methylene hydrogens in **10** is similar to $a_H = 24.2$ G for the methine hydrogen in **5**.[4] The similarity of a_H in both systems suggests (but does not prove) that the ring remains intact after X irradiation of **8**.

The observed ESR spectrum for the ^{125}Te-labeled sample of **10** requires a localized unpaired electron on one Te. Asmus and co-workers[1] have argued that sulfides are oxidized to give π-type radicals, which coordinate with another sulfur atom through interaction of the unbound p-electron pair of the latter with the unpaired electron of the radical. The intramolecular S–S radical cation complex **1** is unsymmetrical by ESR, owing to conformational nonequivalence of the methylene protons adjacent to S, although the two S atoms are equivalent.[2b] Conformational arguments do not differentiate the two Te atoms in ditellurole radical cation **10**.
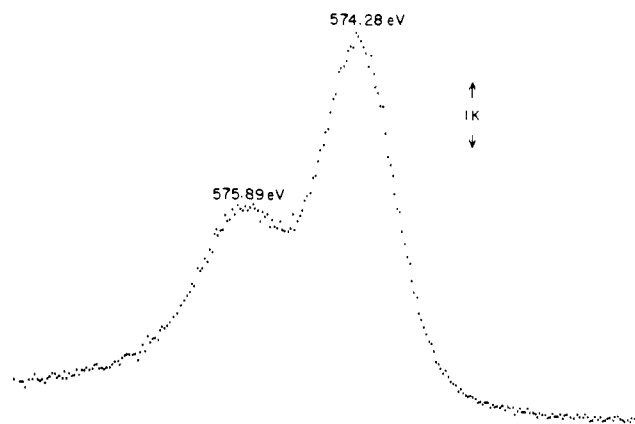
In ditellurole radical cation **10**, the interpenetration of Te lone pairs of electrons might be so extensive that electron transfer from one Te to the other would resemble a two-center, three-electron bond in which the odd electron is more antibonding than the bonding energy of the bonding pair.[3] In this case, a substantial barrier to electron transfer would exist, and a localized unpaired spin would be energetically favored. This feature was not predicted by the CNDO/2 calculations.

The ESR spectrum of irradiated crystals of **8** showed only the signal for free electrons. No signal was detected for radical cation **10**. An interesting possibility for this lack of signal is that hole transport is possible in the crystal lattice. Since the Te atoms of adjoining molecules in the crystal are less than their van der Waals radii apart, hole transport to give adjacent radical-cation centers could lead to formation of the diamagnetic dimer dication **16** in the crystal lattice. Only the spin of free electrons would be observed in such a system. An ESCA analysis of a thin film of **8** was undertaken to examine further this possibility.

ESCA Studies. Ditellurole **8** undergoes radiation damage upon exposure to X-rays to give, presumably, radical cation **10** and free electrons. In the ESCA studies, it is reasonable to assume that a large radical-cation population is being produced during X-ray exposure of a 100-Å-thick film.[27] If the radical-cation centers

were to dimerize to give **16**, the photoemission spectrum would show two distinct peaks. On the other hand, electron exchange between the two telluriums in **10** might be rapid at 300 K and only one peak would be seen.

The Te $3d_{5/2}$ spectra of 1,3-ditellurole (**8**) show two well-defined peaks, as would be expected from a structure like **16** (Figure 7). The binding energies are greater than that of elemental tellurium and suggest that both tellurium atoms have some positive charge. The 1.6-eV splitting between the two peaks shows that the charges are not equivalent and that charge has significantly localized, as in **16**. The spectra were resolved into two Gaussian components (fwhm = 1.3 and 1.85 eV) by using the Du Pont 310 curve resolver. The area ratio was 1:0.8, with the narrower, low-binding-energy component being the more intense. This ratio was independent of the radiation flux over a factor of 8.

The ESCA studies suggest that, under the conditions of the experiment, the dimer cation **16** is produced. Alternatively, the radical cation **10** may be produced, in which both of the Te atoms may be positively charged, but the dominant charge and unpaired spin are localized on just one of the Te atoms. The time frame of the ESCA measurement is usually estimated at $<10^{-16}$ s.[26] The measurements show that the charge is localized within this time frame, but it may well be fluctuating between the two Te atoms at some slower rate.

If the ditellurole **8** is an appropriate model system for tetratellurafulvalenes, then some interesting properties may emerge in single-crystal, radical-cation complexes of the latter. A localized radical-cation center on Te with close intermolecular Te–Te contacts might allow electron and hole transport along Te stacks at both ends of tetratellurafulvalene molecules with minimal intervention of the π framework and with mixed stacks of dication, radical cation, and neutral donor. The difference in the first and second oxidation potentials of **7** of 0.29 V is markedly less than for tetrathiafulvalenes (~ 0.5 V) and tetraselenafulvalenes (~ 0.4 V) and suggests that charge localization on Te (and not in the π framework) is important.[6]

Furthermore, the ESR spectrum of the radical cation **5**[4] shows significant spin density in the allylic hydrogens, consistent with π delocalization. The ESR spectrum of tetrathiafulvalene radical cation shows a well-resolved five-line pattern from the four olefin hydrogens.[28] This argues for decreased spin density at sulfur (and between sulfurs) and increased spin density at carbon, which is also consistent with suggestions of Wudl and Aharon-Shalom.[6]

(26) Gadzuk, J. W. In "Photoemission and the Electronic Properties of Surfaces"; Feurerbacher, B., Fitton, B., Willis, R. F., Eds.; Wiley: New York, 1978.

(27) The mass attenuation coefficients for the Te atom increase in the order Mo Kα (X-ray structure) $<<$ Co Kα (ESR) $<$ Al Kα (ESCA), suggesting that the number of ionized species from **8** should increase in this order as well: "International Tables for X-ray Crystallography", Vol. 4; Kynoch Press: Birmingham, 1974; and "ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy"; Almquist and Wiksells Boktryckeri AB: Uppsala, 1965. For example, the absorption coefficient of 1,3-ditellurole (**8**) is 105 cm^{-1} for Mo Kα, 1300 cm^{-1} for Co Kα, and ~ 7800 cm^{-1} for Al Kα.

(28) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.