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THE SYNTHESIS AND CHARACTERIZATION OF α- AND β-1,1-DIIODO-3,4-BENZO-1-TELLURACYCLOPENTANE, $C_8H_8TeI_2$

RONALD F. ZIOLO * and WOLFGANG H.H. GÜNTHER
Xerox Corporation, Webster Research Center, Xerox Square-114, Rochester, N.Y. 14644 (U.S.A.)

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Summary

Elemental tellurium reacts with α,α'-dichloro-*o*-xylene and NaI in 2-methoxyethanol to form 1,1-diiodo-3,4-benzo-1-telluracyclopentane in 83% yield. $C_8H_8TeI_2$ is molecular in acetone, methylene chloride and methyl ethyl ketone, but ionic in DMF. Two crystalline modifications of the compound have been isolated from 2-methoxyethanol. The yellow-orange or α form is monoclinic, space group $P2_1/c$; the orange-red or β form is also monoclinic, space group $I2/c$. Infrared, optical and mass spectral data, along with solution UV, NMR, molecular weight and conductivity data, suggest that the two crystalline modifications are polymorphs, possibly differing in the degree and type of heavy atom interaction. In 2-methoxyethanol the β form undergoes a solution phase transformation to the stable α form. Both forms are thermochromic.

Introduction

Dialkyltellurium diiodides, R_2TeI_2, were originally reported to exist in two isomeric forms [1]. X-ray structural analyses of α- and β-$(CH_3)_2TeI_2$ showed, however, that although the α form was indeed a compound of the type R_2TeI_2 [2], the β form was actually a telluronium salt of the type R_3TeX [3], where X is the complex anion $[CH_3TeI_4]^-$. The 1-telluracycloalkane 1,1-diiodides, I and II, have also been reported to exist in two forms, each differing in color and crystal morphology [4,5]. Information about the constitution of these forms, however, is not available.

Recently, we observed the simultaneous formation of at least two crystalline forms of 1,1-diiodo-3,4-benzo-1-telluracyclopentane * (III). These forms appeared particularly suitable for characterization studies because of their relative stability and ease of preparation. We report here the synthesis, isolation and

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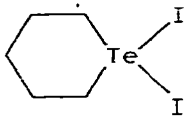
* Telluracyclopentane has also been called tetrahydrotellurophene, tellurolane and cyclotellurobutane.

characteristics of the two forms of the previously unreported compound, $C_8H_8TeI_2$.



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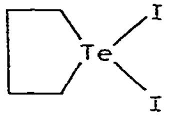

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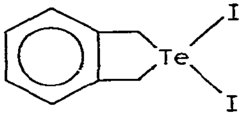

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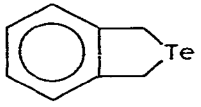
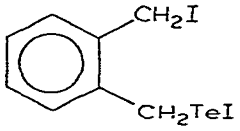


IV

Results and discussion

In the presence of sodium iodide, α,α′-dichloro-*o*-xylene reacts with elemental tellurium in 2-methoxyethanol to form 1,1-diiodo-3,4-benzo-1-telluracyclopentane (III) in 80 to 85% yield under the conditions cited. In addition to correct elemental analyses, compound III has ^1H magnetic resonance signals in DMF-d_5 (25°C) at δ 4.99 ppm (sharp singlet) and δ 7.0—7.5 ppm (multiplet) in 1/1 ratio. The methylene proton signal of III is downfield from the methylene resonances of α,α′-dichloro- and α,α′-dibromo-*o*-xylene (δ 4.67 and 4.60 ppm respectively) [6], consistent with the deshielding effect expected for tellurium(IV). Reduction of III in ethanol with $NaBH_4$ yielded IV [7] by comparison with reported properties [8]. The methylene proton resonance of IV (δ 4.59 ppm) [7,8] is upfield from that of III, consistent with less deshielding by tellurium(II). The above and subsequent data rule out the possible, although unlikely $C_8H_8TeI_2$ isomer, V. The mass spectrum of III shows no molecular ion. The major fragments observed, I_2^+, $C_8H_8Te^+$, Te^+, I^+, and $C_8H_8^+$ are consistent with structure III.



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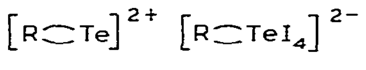

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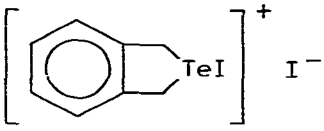

VII

Solution data for $C_8H_8TeI_2$ are given in Table 1. In acetone (37°C), III is non-conducting, and shows a small degree of association consistent with concentration-dependent molecular weights. Methylene chloride and methyl ethyl ketone (MEK) solutions of III are also non-conducting. In MEK (37°C), III gives approximately monomeric molecular weight values with little or no concentration dependence observed at about 10^{-2} *M*. These data rule out species VI and VII for $C_8H_8TeI_2$ in these solvents, and suggest the molecular species III. In DMF, III is ionic with molecular weight and conductivity data supporting formulation VII. The lower molar absorptivities for III (Table 1) in DMF, as compared to those in CH_2Cl_2, are consistent with the ionic formulation VII. In solution, III and I have nearly identical electronic absorption maxima [9] with III having higher molar absorptivities consistent with its aromaticity.

At least two crystalline forms of III appear upon recrystallization of III from 2-methoxyethanol. One form, henceforth referred to as the α modification, con-

TABLE 1

SOLUTION DATA FOR $C_8H_8TeI_2$ [a]

Conductivity (ohm^{-1} cm^2 mol^{-1}), 10^{-3} M, 23°C

Solvent	Observed value	Measured value, 1/1 electrolyte [b]	Literature range, 1/1 electrolyte [c]
CH_2Cl_2	<0.01	25	—
Acetone	<0.5	132	100—140
MEK	<3	105	—
DMF	70	61	65—90

Molecular weight (calcd.: 485.6 (conc. in mg/ml))

Acetone (37°C)	MEK (37°C)	DMF (65°C) [d]
520(1.088)	477(2.933)	222(5.468)
546(3.358)	474(3.434)	218(7.906)
566(5.134)	479(4.411)	224(9.943)

Optical absorption (λ_{max} nm ($\log_{10} \epsilon$)), 22°C, 1.30×10^{-3} M

CH_2Cl_2: 270(4.50), 339(4.25)
DMF: 273(4.14), 339(3.97)

[a] Reported values are averages of individual values obtained for α- and β-$C_8H_8TeI_2$ separately; no significant difference in values was observed. [b] As measured for tetrabutylammonium iodide. [c] Reference 10. [d] A sufficient amount of H_2O was present to cause further dissociation of $C_8H_8TeI^+ I^-$, resulting in the observed values being slightly less than one half the calculated value. Similarly, anomalously high conductivity values were reported for I in the presence of water [9].

sists of yellow to orange holohedral needles or hexagonal plates. The other form, or β modification, is orange to red, appears holohedral, but is more nearly isometric with some crystals approximating the shape of an octahedron. If a mixture of the crystals is kept for several days in 2-methoxyethanol, only the α form will remain, suggesting a solution phase transformation of the β modification to the α modification. Both forms may be obtained separately by change of solvent and conditions of crystallization. Each form gives correct elemental analyses, and is convertible by recrystallization to the other form. Within experimental error, solutions of both forms appear identical (Table 1).

The above data and observations suggest that the two crystalline forms of 1,1-diiodo-3,4-benzo-1-telluracyclopentane are polymorphs. In a series of X-ray structural investigations of $RTeI_2$, R_2TeI_2 and $RTeI_3$ type compounds, McCullough and co-workers demonstrated the existence of a variety of intermolecular bonding arrangements involving secondary Te ··· I and sometimes secondary I ··· I interactions [11—15]. Although polymorphism may occur for all compounds [16], this variety in intermolecular interactions displayed by these types of compounds would appear to enhance the possibility of there being several crystalline modifications of a given organotellurium iodide. 2-Biphenylyltellurium triiodide, for instance, has been isolated in three modifications [13—15]. Aside from the present case of 1,1-diiodo-3,4-benzo-1-telluracyclopentane, polymorphism in the many known $RTeI_2$ compounds has not been established. Its occurrence, however, may be quite common in these and other types of organotellurium iodides. The similarity of the physical and chemical properties of III

TABLE 2

CRYSTALLOGRAPHIC DATA (23° C) FOR $C_8H_8TeI_2$

α (Yellow-orange)	β (Orange-red)
Monoclinic, $P2_1/c$	Monoclinic, Ic
a 12.573(5) Å	a 8.703(3) Å
b 9.881(2) Å	b 14.965(5) Å
c 9.271(7) Å	c 8.703(3) Å
β 104.96(4)°	β 90.23(3)°
V 1112.7(5) Å^3	V 1133.5(5) Å^3
D_{calcd} 2.90 g/cm^3	D_{calcd} 2.84 g/cm^3
D_{obs} 2.89(2) g/cm^3 [a]	D_{obs} 2.85(2) g/cm^3 [b]
$Z = 4$	$Z = 4$

[a] By flotation in $CHBr_3$ before dissolving. [b] By flotation in a mixture of $CHBr_3$ and CCl_4.

to those reported for compounds I and II [4,5], suggests that the dimorphs of I and II are also each polymorphic systems *.

Characteristics of α- and β-$C_8H_8TeI_2$

Unit cell data (23 ± 1°C) for each modification are given in Table 2. α-$C_8H_8TeI_2$ is denser than β-$C_8H_8TeI_2$ by approximately 2%. Both forms are monoclinic with four formula units per unit cell, although the unit cell dimensions of the β form define a nearly tetragonal system. The systematic extinctions for α-$C_8H_8TeI_2$ ($h0l$: $l \neq 2n$; $0k0$, $k \neq 2n$) uniquely determine its space group as $P2_1/c$ Systematic extinctions for β-$C_8H_8TeI_2$ ($h + k + l \neq 2n$; $h0l$: $l \neq 2n$) and inspection of the Patterson map [15] indicate space group Ic **.

At 22°C (1 atm) solid α-$C_8H_8TeI_2$ in Nujol shows two very broad bands centered approximately at 280 and 385 nm. The β form also shows a very broad band centered approximately at 425 nm with small broad shoulders at higher frequencies. Neither α- nor β-$C_8H_8TeI_2$ appears pleochroic in contrast to the dimorphs of I which are reported to be dichroic [4]. Marked thermochromic behavior for both forms of $C_8H_8TeI_2$, however, is observed. At —195°C and below (1 atm), the α form in bulk is a light, bright yellow, whereas the β form in bulk is a light, bright orange. Upon slow heating above these temperatures, both forms continue to darken to deep brown until they decompose. One possible explanation for the color change upon warming, at least to temperatures well below the decomposition temperature, is the broadening of the near ultraviolet absorption band. Other mechanisms or combinations are, of course, possible. Although no solid—solid transformation was observed for either modification upon heating or cooling, the possibility of its occurrence has not been ruled out. A similar observation was reported for II [5]. The dimorphs of I apparently form an enantiotropic system [4,9].

In a sealed capillary, the β form decomposes with melting at 222°C and the α form at 225°C. Differential scanning calorimetry confirmed the three degree

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[*] A second modification of 1-oxa-4-telluracyclohexane 4,4-diiodide is also known [15].

[**] Body centering was the preferred choice for intensity data collection; X-ray structural analysis of both forms is in progress [17].

difference in melting points, and confirmed α as the stable form. Both thermograms appeared similar with a decomposition exotherm immediately following the melting endotherm. Thermal gravimetric analyses indicate that decomposition (mass loss) for both modifications occurs over the temperature range of about 225 to about 400°C. Reaction with the platinum boat was observed. Partial decomposition of both forms also occurs well below 225°C at pressures less than one atmosphere.

As expected, the solid state infrared spectra of the two modifications between 4000 and 200 cm^{-1} were nearly identical, but showed major differences below 200 cm^{-1} in the region associated with Te—I and I—I vibrational stretching modes and lattice modes. In α-$C_8H_8TeI_2$ three bands occurred at 180 m, 158 s and 138 s (sh 142) cm^{-1}, while in β-$C_8H_8TeI_2$ two bands occurred at 171 m and 141 s (sh 150) cm^{-1}. Low frequency Raman data also showed major differences between the two modifications [18].

The above optical and infrared spectroscopic differences observed between α- and β-$C_8H_8TeI_2$ suggest differences in the heavy atom interaction in the two modifications consistent with the structural findings of McCullough and co-workers for organotellurium iodides in general [11—15]. It is likely that α- and β-$C_8H_8TeI_2$ possess structures similar to those found in other $RTeI_2$ compounds studied to date [11,12], and that differences between the interaction in the two modifications are of both type and degree. This is particularly suspect in view of the correlation between color and the type and degree of intermolecular bonding in organotellurium iodides as discussed by McCullough [12]. Since color differences are ascribed to differences in intermolecular interaction, the polymorphic systems are particularly important for elucidating the electronic nature of the organotellurium iodides. Precise differences between the present modifications await the X-ray structural analysis results.

Experimental

Elemental analyses and osmometric molecular weight measurements were done by Galbraith Labs, Inc., Knoxville, Tennessee 37921. Crystal data were obtained by Molecular Structure Corp., College Station, Texas 77840, on an Enraf-Nonius CAD4 automated diffractometer. Cell constants (23 ± 1°C) were obtained by computer-centering of 25 reflections, followed by least squares refinement of the setting angles. Space groups were determined by systematic extinctions. X-ray powder patterns, and scans obtained on a Phillips diffractometer were compared with calculated patterns for compound identification.

Infrared spectra were obtained using KBr (4000—400 cm^{-1}) or polyethylene (600—200 cm^{-1}) pellets, or Vaseline mulls on polyethylene (200—33 cm^{-1}) on Perkin—Elmer spectrophotometers, models 283 and 180. TGA and DSC data were determined on a DuPont 900 thermal analyzer using open platinum boats and hermetically sealed sample holders, respectively. Mass spectra were obtained on a Nuclide 1290G at 70 eV and 80°C by direct insertion of the sample into a temperature programmed source.

UV-vis measurements were recorded on a Cary Model 17D using spectra grade solvents and 0.1 mm pathlength quartz cells or Nujol mulls on white filter paper. NMR spectra were recorded on a Jeol C-60H instrument and are reported in parts per million from internal tetramethylsilane. Solution conductivities were measured with a Radiometer Conductivity Meter, Type CDM2b and a CDC104 platinized platinum electrode cell calibrated with a standard aqueous KCl solution. All reagents and solvents used were analytically pure; 2-methoxyethanol was Eastman practical grade.

Compound preparation

A mixture of α,α'-dichloro-*o*-xylene (3.5 g; 0.02 mol), finely powdered (<100 μm) elemental tellurium (2.55 g; 0.02 g-atom) and sodium iodide (12.0 g; 0.08 mol) in 2-methoxyethanol (~100 ml) was stirred and heated to a gentle boil in an open Fleaker beaker. After one hour the mixture contained a heavy orange precipitate and a small amount of unreacted tellurium. After the addition of 200 ml of deionized water, which caused additional precipitation, the precipitate was collected by filtration, washed with water, rinsed with acetone, and air dried. Unreacted tellurium comprised 5% of the filtrant (8.5 g) giving a yield for $C_8H_8TeI_2$ of 83% *.

Recrystallization of the initial reaction product from hot methoxyethanol yielded both yellow-orange and orange-red crystalline forms, which could readily be distinguished by inspection. Crystals suitable for single crystal X-ray diffraction analysis were obtained by slowly cooling a hot, dilute 2-methoxyethanol solution of once recrystallized product. Anal. Found: C, 19.77; H, 1.65; I, 52.21; Te, 26.26. $C_8H_8TeI_2$ calcd.: C, 19.79; H, 1.66; I, 52.27; Te, 26.28%.

α-$C_8H_8TeI_2$, pure by inspection at 70× and by X-ray powder patterns, was obtained by slowly cooling an *N,N*-dimethylformamide solution of the recrystallized product. Anal. found: C, 19.74; H, 1.66; I, 52.16; Te, 26.26. Similar treatment of the reaction product in methyl ethyl ketone produced pure β-$C_8H_8TeI_2$. Anal. found: C, 19.79; H, 1.64; I, 52.19; Te, 26.27. In bulk, between approximately 10 and 30° C, α-$C_8H_8TeI_2$ is orange and β-$C_8H_8TeI_2$ is red. Both forms decompose with melting in sealed capillaries at approximately 225°C (α) and 222° C (β).

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References

1 R.H. Vernon, J. Chem. Soc., 117 (1920) 86.
2 L.Y.Y. Chan and F.W.B. Einstein, J. Chem. Soc. Dalton Trans., (1972) 316.
3 F.W.B. Einstein, J. Trotter and C. Williston, J. Chem. Soc. A, (1967) 2018.
4 G.T. Morgan and H. Burgess, J. Chem. Soc., (1928) 321.
5 G.T. Morgan and H. Burstall, J. Chem. Soc., (1931) 180.
6 Sadtler Standard Spectra, NMR Nos. 497 and 1882.
7 J. Lewicki, personal communication.
8 S. Cuthbertson and D.D. MacNicol, Tetrahedron Lett., (1975) 1893.
9 F.L. Gilbert and T.M. Lowry, J. Chem. Soc., (1928) 2658.

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* Small amounts of NaI may be occluded in the precipitate.

10 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
11 J.D. McCullough, Inorg. Chem., 12 (1973) 2669, and ref. therein.
12 J.D. McCullough, Inorg. Chem., 14 (1975) 1142.
13 J.D. McCullough and C. Knobler, Inorg. Chem., 15 (1976) 2728.
14 J.D. McCullough, Inorg. Chem., 16 (1977) 2318.
15 C. Knobler and J.D. McCullough, personal communication.
16 W.C. McCrone in D. Fox, M.M. Labes and A. Weissberger (Eds.), Physics and Chemistry of the Organic Solid State, Vol. II, Interscience, New York, 1965, pp. 725—767.
17 C. Knobler and R.F. Ziolo, to be published.
18 M. Slade, unpublished results.