Note

Crystal and molecular structure of (α-naphthyl)TeI₃

Ernesto Schulz Lang [a,*], Gelson Manzoni de Oliveira [a,*], Edson Tarabal Silveira [a],
Robert Alan Burrow [a], Ezequiel M. Vázquez-López [b]

[a] *Departamento de Quimica, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, Campus-Camobi, 97105-900 Santa Maria RS, Brazil*
[b] *Departamento de Química Inorgánica, Facultade de Ciencias-Química, Universidade de Vigo, Vigo, Galicia, Spain*

Abstract

(α-Naphthyl-Te)₂ reacts with iodine in toluene to give deep brown crystals of (α-naphthyl)TeI₃. The structure of the new organotellurium trihalide has been studied by means of single crystal X-ray diffractometry. (α-Naphthyl)TeI₃ crystallizes in the monoclinic space group $P2_1/c$. The primary coordination sphere about the Te atom is bisphenoidal. The secondary bonds among the heavy atoms hold the (α-naphthyl)TeI₃ molecules into chains along the lattice; the Te–I primary bonds show additionally different lengths. The compound can be considered as a supramolecular array comprised of tectonic charge-transfer complexes.
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organotellurium triiodides; Intermolecular bonds; Polymeric superstructures; Supramolecular self-assembly

1. Introduction

The chemistry of organotellurium compounds—especially organotellurium trihalides—is also the chemistry of the secondary bonds. Intermolecular bonding effects of the type Te⋯X and X⋯X of various strengths lead to the formation of polymeric chains, dimeric structures or monomers with fairly strong intermolecular interactions. Thus, while compounds of the series R₃TeX were reported [1] to occur essentially as ionic species R₃Te⁺X⁻ and phenyl dihalides R₂TeX₂ (X = F, Cl or Br) are present as monomers linked by secondary Te⋯X bonds [2–4], the isomorphous PhTeCl₃ and PhTeBr₃ form infinite chains with bridging halides, but with no Te⋯X secondary bonds [3,5]. In contrast to the polymeric chlorides and bromides, PhTeI₃ was reported to exist as dimers, having either *cis* or *trans* oriented phenyl groups [6].

It has been assumed that among RTeX₃ compounds there is a tendency for the chlorides to be polymeric, the bromides either polymeric or dimeric, the iodides to be dimeric, and, if R is particularly bulky monomeric structures would be the rule. Here the size of the halogen should be the other determining factor, with dimeric structures preferred as halogen size increases [5,6]. In fact, these concepts can be applied for many cases, like for example the occurrence of (4-ethoxyphenyl)TeCl₃ as a chlorine-bridged polymer [7], while (4-EtOPh)TeBr₃ and (4-EtOPh)TeI₃ are dimers which present square pyramidal coordination at tellurium with the halogen atoms in the basal positions and the organic group apical, the dimers being further associated, base to base, in pairs. Otherwise, if the intermolecular interactions occurring in 2-biphenylyltellurium triiodide [8] and its β modification [9], so if the packing arrangements are carefully examined, both compounds should not be contemplated [6] as monomers. The secondary, intermolecular bonds (two sets) in 2-biphenylyltellurium triiodide are all of the I⋯I type. One set links the molecules into chains along 2₁ screw axes which consist of two molecules per cycle, with a I⋯I distance of 3.239 Å, a value of 1.06 Å less than the van der Waals radii of 4.30 Å. The second set is weaker (I⋯I distance of 3.772 Å), and in this case linear chains are formed parallel to the face-diagonal lattice-row line (101). The β modification of 2-biphenylyltellur-

* Corresponding authors. Fax: +55-55-2208031
E-mail address: manzoni@quimica.ufsm.br (G. Manzoni de Oliveira).

ium triiodide shows a quasi dimeric structure, with I···I and Te···I intermolecular bonds. The main differences between the two structures (α and β) are in the systems of secondary bonds among the heavy atoms. In the β structure, the strongest intermolecular bonds are again between I atoms (I···I, length: 3.337 Å) along 2_1 screw axes. In this case, however, atoms from four different molecules are involved in a ring which also includes weaker intermolecular bonds between I and Te atoms (3.703 Å), the latter bonds also serving to hold pairs of molecules in dimeric relationships across centers of symmetry in the crystal lattice.

In the light of these experiments and results, and also to provide informations about the influence of the α-naphthyl group on the intermolecular bonding effects in RTeI$_3$, we report the synthesis and the molecular structure of (α-naphthyl)TeI$_3$.

2. Experimental

All manipulations were conducted under nitrogen by use of standard Schlenk techniques. The solvents were dried with Na–benzophenone and distilled before use.

2.1. (α-Naphthyl)TeI$_3$

In a 100-ml two necked flask equipped with a nitrogen inlet and stirring bar, 0.255 g (0.5 mmol) of (α-naphthyl-Te)$_2$ was dissolved in 50 ml of $C_6H_5CH_3$. The addition of 0.381 g (1.5 mmol) of iodine dissolved in $C_6H_5CH_3$ produces a black precipitate. The reaction mixture was filtered and the black solid was dissolved in warmed CH_2Cl_2, occurring recrystallization after a few days at room temperature.

Properties: deep brown, crystalline substance; $C_{10}H_7TeI_3$ (635.466).

Yield, quantitative based on (α-naphthyl-Te)$_2$ taken. M.p.: 128 °C.

3. Results and discussion

X-ray diffraction studies of (α-naphthyl)TeI$_3$ were performed with a Bruker SMART CCD1000 area detector diffractometer [10] with Mo–K$_α$ radiation at 293(2) K. Crystal data and experimental conditions are given in Table 1. The structure was solved using direct methods [11] and difference Fourier techniques, refined by a full-matrix least-squares procedure on F^2 [12]. Multi-scan absorption corrections were applied [13]. Anisotropic thermal parameters were used to refine the position of the non-hydrogen atoms. The positions of the hydrogen atoms were calculated based on the geometry of the molecule, and the thermal displacement parameters were refined isotropically on a groupwise

Table 1
Crystal data and structure refinement parameters of (α-naphthyl)TeI$_3$

Empirical formula	$C_{10}H_7I_3Te$
Formula weight	635.466
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	7.3334(15)
b (Å)	8.1632(17)
c (Å)	23.217(5)
$α$ (°)	90
$β$ (°)	100.087(7)
$γ$ (°)	90
V (Å^3)	1368.4(5)
Z	4
D_{calc} (mg m^{-3})	3.085
Absorption coefficient (mm^{-1})	8.907
$F(000)$	1112
Crystal size (mm^3)	0.12 × 0.09 × 0.09
Theta range for data collection (°)	1.78–28.00
Index ranges	$-9 \le h \le 8$, $-10 \le k \le 10$, $-24 \le l \le 30$
Radiation, $λ$ (Å)	Mo–K$_α$, 0.71073
Reflections collected	7909
Independent reflections	3147 [R_{int} = 0.0536]
Completenes to theta = 28.00	94.9%
Final R indices [$I > 2σ(I)$]	R_1 = 0.0544; wR_2 = 0.1379
Absorption correction	SADABS, multi-scan
Goodness-of-fit on F^2	1.094

basis. An ellipsoid [14] representation of the molecule of (α-naphthyl)TeI$_3$—which corresponds also to the asymmetric unit—is shown in Fig. 1. The intra and intermolecular bond distances and angles about the iodine atoms are listed in Table 2.

The Te···I primary bonds in (α-naphthyl)TeI$_3$ have different distances. The Te1–I3 distance [3.0530(16) Å] can be viewed as a charge-transfer (CT) interaction [15], when compared to the lengths of the Te1–I1 and Te1–I2 bonds, respectively 2.8689(17) and 2.7438(15) Å, and to the sum of the van der Waals radii of the two atoms (4.35 Å). The Te1–I3 distance is very similar to the Te–I bond length of Ph$_3$PTe(Ph)I, 3.0930(9) Å, and this compound was described [16] as a T-shaped CT com-

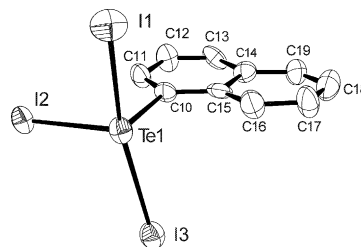
Fig. 1. ORTEP-3 [14] plot of the (α-naphthyl)TeI$_3$ molecule with thermal ellipsoids at the 30% probability level, showing the bisphenoidal geometry. Hydrogen atoms are omitted for clarity.

Table 2
Intra- and intermolecular bonding: distances (Å) and angles (°) about iodine atoms in $C_{10}H_7I_3Te$

Bond distances			
Te(1)–I(1)	2.8689(17)	Te(1)···I(3)′	3.9791(15)
Te(1)–I(2)	2.7438(15)	I(2)···I(3)″	3.4463(16)
Te(1)–I(3)	3.0530(16)	I(2)···I(2)‴	3.860(2)
Bond angles			
I(2)–Te(1)–I(1)	94.33(5)	I(3)–Te(1)···I(3)′	76.11(4)
I(2)–Te(1)–I(3)	97.85(5)	Te(1)–I(2)···I(3)″	173.84(5)
I(1)–Te(1)–I(3)	167.39(5)	Te(1)–I(2)···I(2)‴	114.45(5)
I(2)–Te(1)···I(3)′	76.71(3)	I(3)″···I(2)···I(2)‴	71.52(4)
I(1)–Te(1)···I(3)′	103.74(4)	C(10)–Te(1)···I(3)′	161.4(4)

Symmetry transformations used to generate equivalent atoms: (′) $-x$, $-y+1$, $-z$; (″) $x-1$, y, z; (‴) $-x-1$, $-y+1$, $-z$.

plex, with the P1–Te1–I1 angle essentially linear (179.45(5)°).

Two kinds of intermolecular bonds—Te···I and I···I interactions—can be distinguished in the crystalline structure of (α-naphthyl)TeI$_3$. The strongest are the bonds between I2 atoms and the iodine atoms I2 and I3 from different (α-naphthyl)TeI$_3$-units, which do not interact with the Te atom from I2: in decrease of the bond order, I2···I3″ (3.4463 Å) and I2···I2‴ (3.860 Å). Weaker (with a length of 3.979 Å) secondary bonds between Te and I3′ are important to hold the molecules into chains along 2$_1$ screw axes—located in the middle of the I2···I2‴ bonds—which consist of rings involving atoms from four different molecules. The reciprocal intermolecular bonds Te···I3′ are responsible for the retaining of pairs of (α-naphthyl)TeI$_3$ molecules in dimeric association across centers of symmetry in the crystal lattice, allowing to conceive a square pyramidal configuration about each tellurium center, with I2 atoms in the apical positions. These assignments can be visualized in the projection of Fig. 2.

The molecular structures of (α-naphthyl)TeI$_3$ and the β modification of 2-biphenylyltellurium triiodide [9] are very similar, as well as the secondary interactions in their lattices. Nevertheless, although the secondary bonds Te···I3′ are also common to both structures, the short intramolecular contact Te–C12, described in 2-biphenylyltellurium triiodide—and also explaining an octahedral coordination about tellurium—could not be observed in (α-naphthyl)TeI$_3$. Otherwise, the intermolecular bonds I2···I2‴ of (α-naphthyl)TeI$_3$ are not present in the lattice of 2-biphenylyltellurium triiodide, on account of the stereochemistry of the biphenyl group, and this represent probably the main reason for the differences in the packing arrangement of the two compounds.

Recently, it has been reported [17] that many similar organotellurium compounds, in addition to secondary Te···halogen bonds, show intermolecular bonds of the type Te···π-aryl and can be considered as self-assembled
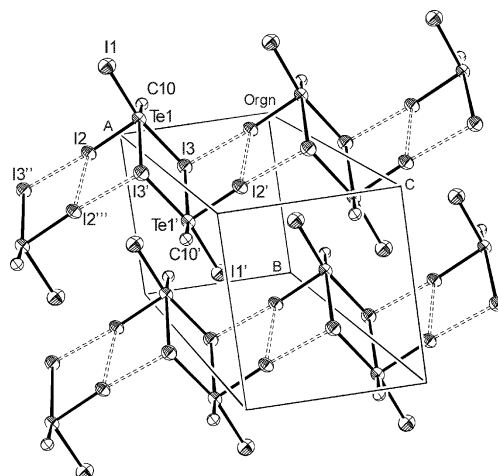

Fig. 2. Projection of a segment of the crystallographic cell of (α-naphthyl)TeI$_3$, showing the packing arrangement of the molecules. For clarity, the α-naphthyl groups are represented only as C10. Intermolecular bonds are indicated by means of dotted lines with exception of the Te···I3′ bonds; 2$_1$ screw axes are located in the middle of the I2···I2‴ bonds and are parallel to the b axis. (The coordinates of the beheld section are: $x = -0.9/1.9$; $y = -0.3/1.3$; $z = 0.3/0.7$.)

supramolecular arrays through tellurium π-C$_6$H$_5$ interactions [18,19] or as supermolecules formed through Te···X secondary bonds with intra-chain Te···π-aryl interactions [20,21], among others classifications, depending on the type of the molecular aggregate and secondary interactions.

Even if in our case no tellurium···π-aryl interactions have been observed, it can be easily recognized that the intermolecular bonds in (α-naphthyl)TeI$_3$ and in the related compounds discussed here are essential in the managing of the crystalline gathering of these substances, allowing them to be viewed as supramolecular assemblies.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 192637. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] R.F. Ziolo, J.M. Troup, Inorg. Chem. 18 (1979) 2271.
[2] F.J. Berry, A.J. Edwards, J. Chem. Soc. Dalton Trans. (1980) 2306.
[3] N.W. Alcock, W.D. Harrison, J. Chem. Soc. Dalton Trans. (1982) 251.

[4] G.D. Christofferson, J.D. McCullough, Acta Crystallogr. 11 (1958) 249.

[5] N.W. Alcock, W.D. Harrison, Acta Crystallogr. Sect. B 38 (1982) 2677.

[6] N.W. Alcock, W.D. Harrison, J. Chem. Soc. Dalton Trans. (1984) 869.

[7] P.H. Bird, V. Kumar, B.C. Pant, Inorg. Chem. 19 (1980) 2487.

[8] J.D. McCullough, C. Knobler, Inorg. Chem. 15 (1976) 2728.

[9] J.D. McCullough, Inorg. Chem. 16 (1977) 2318.

[10] SMART and SAINT, Bruker AXS Inc., Madison, WI, USA.

[11] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

[12] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[13] G.M. Sheldrick, SADABS, Multi-scan Program for Absorption Correction, University of Göttingen, Germany, 1996.

[14] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.

[15] S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarwar, J. Chem. Soc. Dalton Trans. (1997) 1031.

[16] P.D. Boyle, W.I. Cross, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarwar, J.M. Sheffield, Angew. Chem. Int. Ed. Engl. 39 (2000) 1796.

[17] J. Zukerman-Schpector, I. Haiduc, Cryst. Eng. Commun. 4 (2002) 178.

[18] G. Llabres, O. Dieberg, L. Dupont, Acta Crystallogr. Sect. B 28 (1972) 2438.

[19] M.R. Detty, J.M. Mc Kelvey, H.R. Luss, Organometallics 7 (1988) 1131.

[20] J. Zukerman-Schpector, J.V. Comasseto, H.A. Stefani, Acta Crystallogr. Sect. C 51 (1995) 861.

[21] J. Zukerman-Schpector, E.E. Castellano, G. Oliva, J.V. Comasseto, H.A. Stefani, Acta Crystallogr. Sect. C 47 (1991) 960.