

2,4,6-Triphenylphenyltellurium(IV) triiodide – supramolecular self-assembling in organotellurium triiodides

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Abstract

2,4,6-Triphenylphenyltellurium(IV) triiodide, (2,4,6-Ph₃C₆H₂)TeI₃, can be obtained by the reaction of the corresponding ditelluride {(2,4,6-Ph₃C₆H₂)Te}₂ with iodine under an atmosphere of dry nitrogen in toluene. The apparent bisphenoidal coordination sphere of the central tellurium atom is extended by the presence of intermolecular Te···I and I···I secondary bonds which form chains along the crystallographic *a* axis. Weak intramolecular interactions with one of the phenyl rings of the (2,4,6-Ph₃C₆H₂) unit completes the pseudo-octahedral coordination geometry around each tellurium atom. A comparison of the structure of (2,4,6-Ph₃C₆H₂)TeI₃ with the bonding situations in other organotellurium(IV) triiodides suggests a strong dependence of the formation of supramolecular assemblies on the nature of the organic substituents.

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Keywords: Organotellurium triiodide; Secondary interactions; X-ray structure

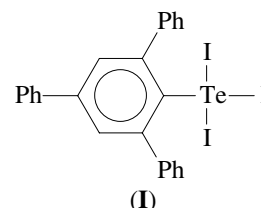
1. Introduction

The structural characteristics of several classes of organotellurium halides are known and especially for σ -tellanes R₂TeX₂ and RTeX₃ compounds, the VSEPR theory predicts a trigonal bipyramidal geometry in which the lone pair occupies an equatorial position. For most of the crystal structures reported for RTeX₃ species, the occurrence of intra- and intermolecular secondary bonding interactions, together with the nature of the organic groups binding to the tellurium atoms, exert an influence on the geometry around the tellurium(IV) centre and consequently define the structural motifs of these compounds [1].

Recently, as part of our research in the coordination chemistry of organotellurium compounds [2], the synthesis and the molecular structure of (α -naphthyl)TeI₃ has been reported [3]. It was assumed that the presence of intermolecular bonds in this and in other related

compounds allow them to be viewed as supramolecular assemblies.

In the light of these previous results and to extend our studies of the molecular structures and intermolecular bondings in organotellurium triiodides, we report the preparation, structural characterization and packing arrangement of the title compound (I), derived from a very bulky diarylditelluride.



2. Experimental

All manipulations were conducted under dinitrogen, using standard Schlenk techniques. The solvent was dried with sodium wires (benzophenone) and distilled

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prior to use. The ditelluride [(2,4,6-Ph₃C₆H₂)Te]₂ was prepared according to literature methods [4].

2.1. Synthesis of (2,4,6-Ph₃C₆H₂)TeI₃

[(2,4,6-Ph₃C₆H₂)Te]₂ (0.108 g, 0.12 mmol) was dissolved in 5 ml of dry toluene. The addition of iodine (0.095 g, 0.37 mmol) dissolved in toluene produced a dark blue solution. The resulting mixture was stirred for 3 h at room temperature and the volume was reduced to half in vacuo. The precipitated solid was separated by filtration. Crystals suitable for X-ray analysis were grown by slow cooling of a concentrated solution of the complex in toluene.

Dark blue, crystalline solid, yield 73% based on the ditelluride; m.p.: 95–97 °C. IR (cm⁻¹): 3440, 1639, 1492, 756, 729, 698. 526, 463, 317, 169, 150, 139, 61. Microanalysis calculated for C₂₄H₁₇I₃Te: C, 35.43; H, 2.11. Found: C, 35.85; H, 2.24%.

2.2. Structure analysis

Diffraction data of (2,4,6-Ph₃C₆H₂)TeI₃·toluene (C₃₁H₂₅I₃Te, irregular dark-blue block, 0.09 × 0.11 × 0.14 mm, triclinic, space group *P* $\bar{1}$, *a* = 10.297(2), *b* = 11.414(2), *c* = 13.476(3) Å, α = 79.72(1), β = 82.69(1), γ = 73.72(1)°, *Z* = 2) were collected on a Bruker SMART diffractometer, fitted with a CCD detector, with Mo K α -radiation (λ = 0.71073 Å at *T* = 193 K. 12,301 reflections were collected in the range 1.54–25.10 in θ from which 5270 were unique and 2809 have intensities *I* > 2 σ (*I*), μ = 4.121 mm⁻¹. The structure was solved by direct methods (SHELXS-97 [5]). Refinement was carried out with the SHELXL-97 [5] package and empirical absorption correction has been applied (SADABS, *T*_{min} = 0.787904, *T*_{max} = 1). All refinements were made by full-matrix least-squares on *F*² with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. *R*₁(observed data) = 0.0449, *wR*₂(all data) = 0.1109, GoF = 0.940. Maximum and minimum residual electron density: 0.667/–0.786 e/Å³. More details on the structural determinations have been deposited with the Cambridge Crystallographic Data Centre under the deposition number CCDC 220958.

3. Results and discussion

The reaction of the ditelluride [(2,4,6-Ph₃C₆H₂)Te]₂ with iodine, under an inert atmosphere, leads to the formation of the crystalline 2,4,6-triphenylphenyltellurium(IV) triiodide, (2,4,6-Ph₃C₆H₂)TeI₃. Single crystals of the compound were obtained by slow cooling of a hot concentrated solution of the complex in toluene. Its

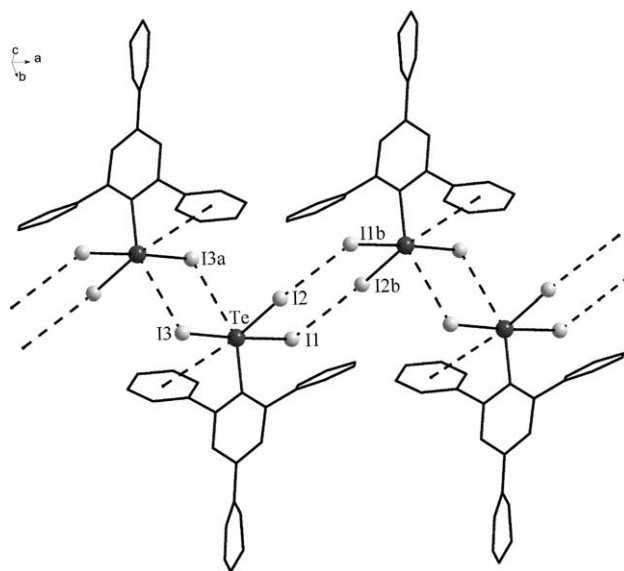


Fig. 1. Projection of a continuous zig-zag chain in the crystal packing of 2,4,6-Ph₃-C₆H₂TeI₃ along the crystallographic axis *a*. The interactions Te···I and I···I and Te···(C61–C66) are indicated by dotted lines.

solid-state structure is shown in Fig. 1. Selected bond lengths and angles are shown in Table 1.

To a first approximation, the geometry around the tellurium atom may be described as bisphenoidal, being bonded to three iodine atoms (I1, I2 and I3) and to one aromatic carbon atom (C1). The Te–I2 bond distance of 2.716(1) Å is much shorter than the Te–I1 and Te–I3 distances (2.978(1) and 2.7160(1) Å). Atoms I1 and I3 are *trans* to each other, while I2 is *trans* to the lone pair. The longest bond (Te–I1) clearly represents a charge-transfer (CT) interaction [6], when compared with the sum of van der Waal's radii of the two atoms, 4.35 Å. The Te–I1 distance is similar to that found in (α -naphthyl)TeI₃, 3.053 Å [3] and in Ph₃PTe(Ph)I, 3.093 Å [7]. Also, the bond angles I1–Te–I2 and the essentially linear I1–Te–I3, appear to be characteristic of a charge transfer complex.

Table 1
Selected bond lengths (Å) and angles (°) for 2,4,6-Ph₃C₆H₂TeI₃

Bond lengths		Bond angles	
Te–I1	2.9782(11)	I1–Te–I3	177.23(3)
Te–I2	2.7160(11)	I1–Te–I2	88.13(3)
Te–I3	2.9033(11)	I2–Te–I3	90.89(3)
Te–C1	2.166(8)	I1–Te–C1	93.7(3)
Te···C62	3.201(9)	I2–Te–C1	110.8(2)
Te1···I3 ^a	3.7437(11)	I3–Te–C1	89.1(3)
I1···I2 ^b	3.5854(13)	I3 ^a –Te–C1	155.21(25)

^a –*x*; –*y*; 2 – *z*.

^b 1 – *x*; –*y*; 2 – *z*.

try leading to either square-based pyramidal or octahedral coordination at tellurium atoms. In the structures of *cis*- and *trans*-PhTeI₃, the square-pyramidal, pseudo octahedral geometry, prohibits the formation of secondary bonds to the central tellurium atom, because the vacant position is already occupied by the lone pair. However, in all the other examples, such bonding constitutes an essential contribution for intermolecular association.

An analysis of the structures of RTeI₃ compounds suggests a strong dependence of the formation of supramolecular assemblies on the nature of the organic substituents. The organic substituents can induce simultaneously intramolecular and intermolecular secondary interactions between the heavy atoms and, in addition to Te···I and I···I secondary bonds, intramolecular bonds of the type Te···η⁶-π-aryl can be formed. Usually secondary bonds are not strong enough to survive in solution, especially in coordinating solvents, but they can have spectacular effects in the building of a crystal by creating the secondary structure which defines the supramolecular arrangement in the solid state [10,11] and in some cases this leads to the formation of tectonic charge-transfer complexes [3].

With the structure of (2,4,6-Ph₃C₆H₂)TeI₃ another member of the series of RTeI₃ compounds is now known. A comparison of the known structural motifs of these compounds in dependence on the steric requirements of the organic substituents bonded to tellurium allows an estimation of the supramolecular self-assemblies in this class of tellurium compounds which results in the formation of dimeric or polymeric architectures.

References

- [1] (a) C. Knobler, J.D. McCullough, *Inorg. Chem.* 16 (1977) 612; (b) J. Novosad, K.W. Törnroos, M. Necas, A.M.Z. Slawin, J.D. Woollins, S. Husebye, *Polyhedron* 18 (1999) 2861; (c) R.K. Chadha, J.E. Drake, *J. Organomet. Chem.* 293 (1985) 37; (d) M. Necas, J. Novosad, S. Husebye, *J. Organomet. Chem.* 623 (2001) 124; (e) H.B. Singh, N. Sudha, R.T. Butcher, *Inorg. Chem.* 31 (1992) 1431; (f) H. Fleischer, B. Mathiasch, D. Schollmeyer, *Organometallics* 21 (2002) 526; (g) N. Al-Salim, A.A. West, W.R. McWhinnie, T.A. Hamor, *J. Chem. Soc. Dalton Trans.* (1988) 2363.
- [2] (a) E. Schulz Lang, E.T. Silveira, U. Abram, E.M. Vázquez-López, R. Fernandez Jr., *Z. Anorg. Allg. Chem.* 625 (1999) 1401; (b) E. Schulz Lang, G. Manzoni de Oliveira, E.M. Vázquez-López, R.M. Fernandez Jr., *Inorg. Chem. Comm.* 6/7 (2003) 869.
- [3] E. Schulz Lang, G. Manzoni de Oliveira, E.T. Silveira, R.A. Burrow, E.M. Vázquez-López, *J. Organomet. Chem.* 664 (2002) 306.
- [4] E. Schulz Lang, C. Maichle-Mössmer, J. Strähle, *Z. Anorg. Allg. Chem.* 620 (1994) 1678.
- [5] G. Sheldrick, *SHELXS97* and *SHELXL97* – Programmes for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [6] S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarwar, *J. Chem. Soc. Dalton Trans.* (1997) 1031.
- [7] P.D. Boyle, W.I. Cross, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarwar, J.M. Sheffield, *Angew. Chem. Int. Ed.* 39 (2000) 1796.
- [8] L. Pauling, *The Nature of the Chemical Bond*, third ed., Cornell University Press, Ithaca, NY, 1960.
- [9] N.W. Alcock, W.D. Harrison, *J. Chem. Soc. Dalton Trans.* (1984) 869.
- [10] J.D. McCullough, C. Knobler, *Inorg. Chem.* 15 (1976) 2728.
- [11] J.D. McCullough, *Inorg. Chem.* 16 (1977) 2318.
- [12] P.H. Bird, V. Kumar, B.C. Pant, *Inorg. Chem.* 19 (1980) 2487.
- [13] J. Zukerman-Schpector, I. Haiduc, *Cryst. Eng. Comm.* 4 (2002) 178.