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SOFT–SOFT INTERACTIONS OF IODIDE AND TRIIODIDE IONS WITH TRIPHENYLTELLURONIUM CATIONS

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The crystal structures of triphenyltelluronium iodide and of triphenyltelluronium triiodide were solved by X-ray diffraction. Triphenyltelluronium iodide consists of ladder-like tetrameric units involving dicoordinated iodine atoms, bridging penta- and hexacoordinated tellurium atoms, and tri-coordinated central iodines that bridge one pentacoordinated and two hexacoordinated tellurium atoms. Triphenyltelluronium triiodide is made up of extended chains that are generated by pairwise interaction of $\text{Ph}_3\text{Te}-\text{I}_3$ units through weak $\text{Te} \cdots \text{I}$ contacts involving one terminal atom from each triiodide ion, and by connection of these four-membered units through both terminal atoms of the triiodide ions. This asymmetric contribution of the two terminal iodine atoms of the triiodide ion to the soft–soft network correlates with a significant difference of the two $\text{I}-\text{I}$ bond lengths (2.847 and 2.984 Å).

Keywords Secondary interactions; soft–soft interactions; telluronium salts; triiodide; X-ray crystallography

INTRODUCTION

Organic selenonium and telluronium iodides $\text{R}_3\text{E}^+ \text{I}^-$ ($\text{E} = \text{Se}, \text{Te}$) can be described as essentially ionic compounds, but their solid state structures reveal that directed electronic interactions of the type $n(\text{halide}) \rightarrow \sigma^*(\text{E}-\text{C})$ play a role in determining the contacts between pyramidal R_3E^+ cations and X^- anions.¹

Crystalline Me_3SeI involves pairs of pyramidal Me_3Se^+ cations and iodide anions. The $\text{Se} \cdots \text{I}$ distance (378 pm) is shorter than the sum of Se and I van der Waals radii (415 pm) and is also shorter than the $\text{S} \cdots \text{I}$ distance in the sulfur analogue (389 pm). The $\text{Se}-\text{I}$ contact and one of the $\text{Se}-\text{C}$ bonds are almost collinear, i.e., the coordination environment of Se can be regarded as ψ -trigonal-bipyramidal.² The phenyl derivative Ph_3SeI exhibits a slightly shorter $\text{Se} \cdots \text{I}$ contact (372.2 pm)³ than in Me_3SeI .

Telluronium cations R_3Te^+ tend to give higher aggregates with pentacoordinated monocapped-octahedral tellurium atoms (14–Te–6).^{1,4–7} In $[\text{Me}_3\text{Te}^+ \text{Cl}^- \cdot \text{H}_2\text{O}]$, the tellurium atom is involved in two $\text{Te} \cdots \text{Cl}$ contacts approximately trans to $\text{Te} \cdots \text{C}$, and one further long $\text{O} \cdots \text{Te}$ contact (308.9 pm); hydrogen bonding between H_2O and Cl leads to infinite chains. Solid $\text{Ph}_3\text{TeCl} \cdot \frac{1}{2}\text{CHCl}_3$ is a stair-like tetramer with two central (14–Te–6) and two peripheral (12–Te–5) Te atoms; two central Cl^- ions interact with three Te atoms,

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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and the two peripheral Cl^- ions interact with two Te atoms (the solvent is only weakly held in the lattice). The unsolvated compound is based on dimeric units.⁵ The solid fluorinated telluronium salt $(\text{C}_6\text{F}_5)_3\text{TeCl}$ is an unsymmetrically chloride-bridged chain polymer.⁷

Triphenyltelluronium iodide has been known since 1911,⁸ but in our hands, attempts to complete an X-ray crystallographic structure determination were unsuccessful for a long time; the structure, which seemed to be severely disordered, could not be satisfactorily refined with $Z' = 2$ in space group $P\bar{1}$ (see the Experimental section). Preliminary results⁹ suggested that solid Ph_3TeI adopts a tetrameric ladder-like structure, as do $[\text{Ph}_3\text{TeI}]_4$ and $[(\text{Ph}_3\text{TeI})_4(\text{MesTeI})_2]$.¹⁰ In the latter compound, two outer iodide anions from the $[(\text{Ph}_3\text{TeI})_4]$ unit coordinate to an MesTeI acceptor unit (Figure 1).¹⁰

The Te1-I2 distances are shorter than Te2-I2 and Te3-I2 , which might justify an alternative description of the compound as consisting of $[(\text{Ph}_3\text{Te})_4\text{I}_2]^{2+}$ cations that are in contact with two triiodide-like MesTeI_2^- anions, thereby sharing the atom I2. Much weaker cation-anion $\text{Te}\cdots\text{I}$ interactions than those with MesTeI_2^- anions are present in $[(\text{Ph}_3\text{Te})_2\text{TeI}_6]$, with two Ph_3Te^+ cations surrounding the central TeI_6^{2-} anion. Each cation exhibits three long contacts ($\text{Te1}\cdots\text{I}$ 3.8971(4) Å) to the regular octahedral TeI_6^{2-} anion (Te2-I 2.9456 Å) (Figure 2).¹⁰

Considering these aspects, we were keen to investigate the structural role that would be played by triiodide anions as weak, but potentially bridging soft anions in combination with triphenyltelluronium cations, and to determine the true structure of pure Ph_3TeI .

REACTIONS

Single crystals of Ph_3TeI (**1**) were obtained by evaporation of a methanol solution of the compound. Addition of the equivalent amount of molecular iodine to **1** dissolved

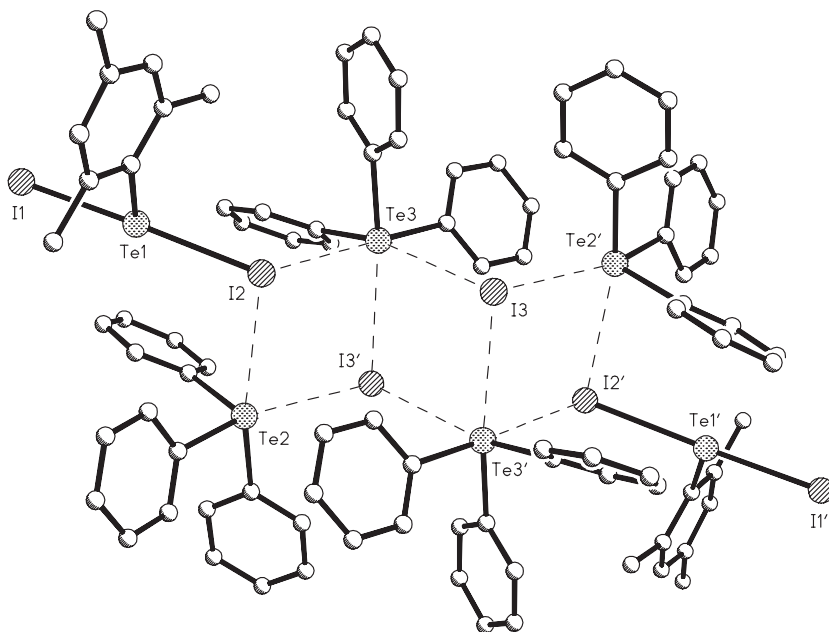


Figure 1 Inversion-symmetric structure of $[(\text{Ph}_3\text{TeI})_4(\text{MesTeI})_2]$ ¹⁰ in the crystal.

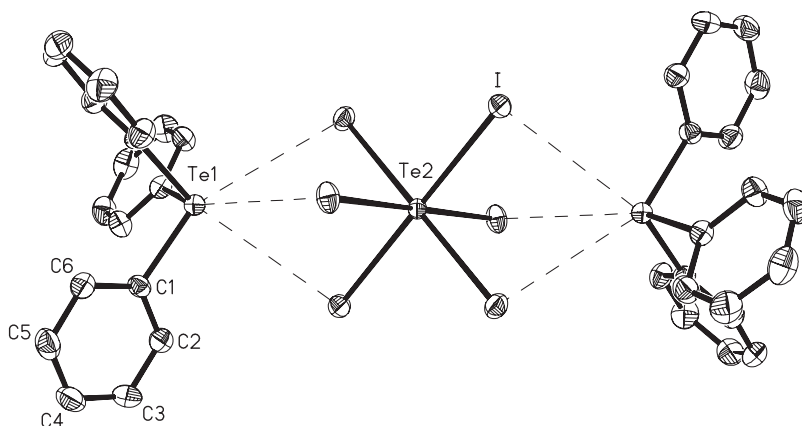


Figure 2 Structure of $[(\text{Ph}_3\text{Te})_2\text{TeI}_6]^{10}$ in the crystal.

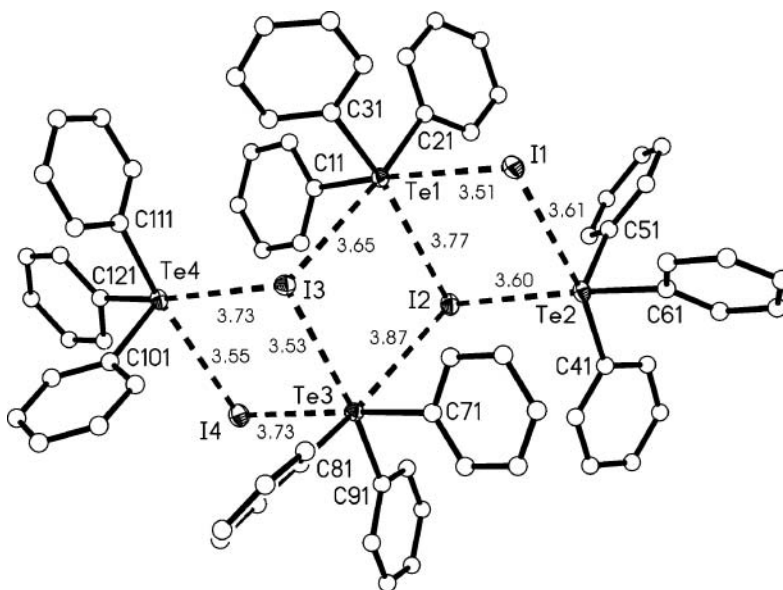


Figure 3 The structure of compound **1** in the crystal. Ellipsoids represent 50% probability levels; carbon atoms were refined isotropically. Hydrogen atoms are omitted. Te–I distances in the figure are rounded for clarity; exact values may be taken from the following list of selected bond lengths (Å) and angles (°): I1–Te1 3.5081(12), I1–Te2 3.6077(15), I2–Te2 3.5697(13), I2–Te1 3.7727(15), I2–Te3 3.8730(14), I3–Te3 3.5350(14), I3–Te1 3.6531(13), I3–Te4 3.7334(13), I4–Te3 3.5189(13), I4–Te4 3.5545(14), Te1–C21 2.135(7), Te1–C11 2.137(7), Te1–C31 2.154(6), Te2–C41 2.117(7), Te2–C51 2.122(6), Te2–C61 2.149(7), Te3–C71 2.149(7), Te3–C81 2.149(7), Te3–C91 2.135(7), Te4–C101 2.112(7), Te4–C111 2.128(7), Te4–C121 2.140(7); Te1–I1–Te2 94.70(3), Te2–I2–Te1 90.89(3), Te2–I2–Te3 102.35(2), Te1–I2–Te3 88.23(3), Te3–I3–Te1 95.54(3), Te3–I3–Te4 91.36(3), Te1–I3–Te4 103.41(2), Te3–I4–Te4 94.68(3), C21–Te1–C11 93.7(2), C21–Te1–C31 94.5(2), C11–Te1–C31 95.3(2), C11–Te1–I1 171.17(17), C21–Te1–I3 174.16(17), C31–Te1–I2 169.06(17), C61–Te2–I2 176.19(18), C41–Te2–I1 170.39(17), C71–Te3–I4 177.52(17), C91–Te3–I3 171.19(17), C81–Te3–I2 167.25(16), C111–Te4–I4 171.77(18), C121–Te4–I3 171.22(18).

in dichloromethane leads to a dark brown solution. When this is carefully overlaid with *n*-hexane, needles of Ph_3TeI_3 (**2**) are formed. These exhibit a metallic-blue luster, but appear dark red in transmitted light.

CRYSTALLOGRAPHIC STUDIES

Using the original data, we were able to show that compound **1** in fact crystallizes in the triclinic space group $P1$ with $Z = 4$ (see the Experimental section), and consists of isolated tetrameric units with a step-like central arrangement of the Te_4I_4 core (Figure 3); all core angles (at tellurium and iodine) are approximately 90° or 180° . The coordination at Te1 and Te3 is $[3 + 3]$ distorted octahedral, whereas Te2 and Te4 are $[3 + 2]$ square pyramidal (apices C51 and C101, respectively). Iodines I1 and I4 bridge two tellurium centers, I2 and I3 three. There is no clear pattern to the $\text{Te} \cdots \text{I}$ distances, which range from 3.51 to 3.87 Å.

The crystal packing involves five $\text{C}-\text{H} \cdots \text{I}$ contacts with $\text{H} \cdots \text{I} < 3.3$ Å and angles around 140° , which might be interpreted as weak hydrogen bonds. Within the tetramer, there are a further 11 such contacts, although six of these have narrow angles $< 133^\circ$. Details of these are given in the deposited CIF files. There are also five intermolecular $\text{C}-\text{H} \cdots (\text{ring centroid})$ contacts with $\text{H} \cdots \text{Centroid} < 2.85$ Å, but no stacking interactions.

The triiodide **2** (Figure 4) crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The asymmetric unit contains one cation and one anion, and these are connected by two $\text{Te} \cdots \text{I}$ contacts (to I1 and I2).

The packing involves double chains of alternating anions and cations parallel to the x axis (Figure 5). The coordination at tellurium is completed by two further $\text{Te} \cdots \text{I}$ contacts to I1 of a second and I3 of a third anion; all contact distances lie in the range 3.77–4.01

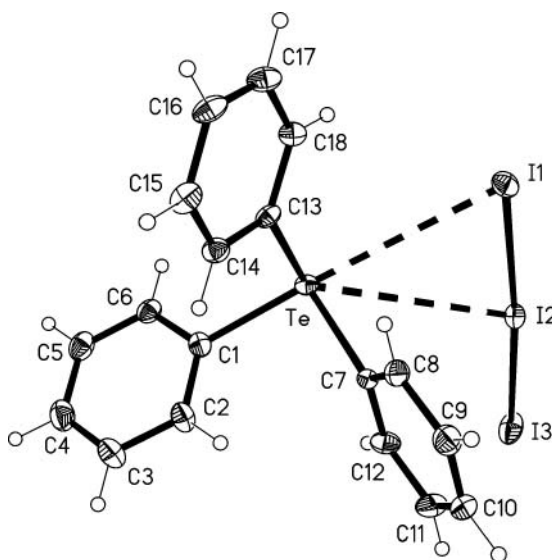


Figure 4 The structure of compound **2** in the crystal (asymmetric unit only). Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles ($^\circ$): I1–I2 2.9837(8), I2–I3 2.8472(7), I1–Te 3.7670(6), I2–Te 4.0079(6), Te–C7 2.116(4), Te–C13 2.117(4), Te–C1 2.126(4); C7–Te–C13 $98.21(16)$, C7–Te–C1 $96.30(16)$, C13–Te–C1 $95.43(17)$.

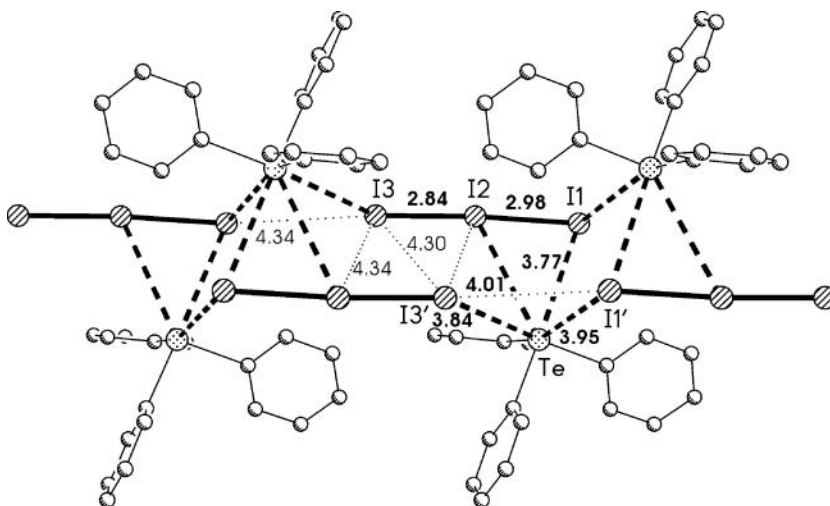


Figure 5 Packing diagram of compound **2**; part of the infinite chain parallel to the x axis. $\text{Te} \cdots \text{I}$ contacts are indicated by dashed and $\text{I} \cdots \text{I}$ contacts by dotted lines. Distances ($\text{I}-\text{I}$ and $\text{Te} \cdots \text{I}$ in boldface, $\text{I} \cdots \text{I}$ dotted) are rounded for clarity; exact distances (\AA) are as follows: $\text{Te} \cdots \text{I1}'$ ($-x, -y, 1-z$) 3.9504(6), $\text{Te} \cdots \text{I3}'$ ($1-x, -y, 1-z$) 3.8384(7), $\text{I3} \cdots \text{I1}$ ($1+x, y, z$) 4.3362(10), $\text{I3}' \cdots \text{I2}$ 4.3445(7), $\text{I3} \cdots \text{I3}'$ 4.2960(8). Selected bond angles ($^\circ$): $\text{C1}-\text{Te} \cdots \text{I1}$ 177.40(12), $\text{C7}-\text{Te} \cdots \text{I1}'$ 162.76(11), $\text{C13}-\text{Te} \cdots \text{I3}'$ 152.36(11), $\text{I1}-\text{I2}-\text{I3}$ 175.366(14), $\text{I2}-\text{I1}-\text{Te}$ 71.778(11), $\text{I2}-\text{I1}-\text{Te}'$ ($-x, -y, 1-z$) 106.686(15), $\text{Te}-\text{I1}-\text{Te}$ 97.022(12), $\text{I2}-\text{I3}-\text{Te}''$ ($1-x, -y, 1-z$) 142.033(17). Te' and Te'' are not labelled explicitly but lie top right and top left, respectively, in the figure.

\AA . If the contact $\text{Te} \cdots \text{I2}$ is neglected, the geometry at tellurium is the well-known $[3 + 3]$ pattern with approximately octahedral geometry.

The $\text{I}-\text{I}$ distances within the anion [$\text{I1}-\text{I2}$ 2.9837(8), $\text{I2}-\text{I3}$ 2.8472(7) \AA] reflect the fact that I1 is involved in two $\text{Te} \cdots \text{I}$ contacts but I3 only in one. The latter atom additionally forms three very long (ca. 4.3 \AA) $\text{I} \cdots \text{I}$ contacts of the type that we have described as “tertiary,”¹¹ which may however only represent chance features of the packing without any great energetic significance.

Whereas we attribute great importance to the soft-soft contacts in compound **2**, other types of contact should not be ignored. However, there are no stacking interactions (shortest intercentroid distance 4.8 \AA), the shortest $\text{H} \cdots \text{I}$ distances (possibly representing weak hydrogen bonds of the type $\text{C}-\text{H} \cdots \text{I}$) are 3.23 \AA and there is only one short $\text{H} \cdots \text{Centroid}$ distance [$\text{H10} \cdots \text{Cent}(\text{C13}-\text{I8})$ 2.72 \AA].

CONCLUSION

Solid Ph_3TeI (**1**) is a molecular tetramer, and Ph_3TeI_3 (**2**) exhibits an extended, ribbon-like, supramolecular structure. Cation-anion soft-soft interactions in the triiodide salt **2** are weaker, and $\text{Te}-\text{C}$ distances are slightly shorter than in the tetrameric iodide **1**. As in $[(\text{Ph}_3\text{TeI})_4(\text{MesTeI})_2]$, compared with $[(\text{Ph}_3\text{Te})_2\text{TeI}_6]$,¹⁰ distortions of the Ph_3Te^+ cations (by $\text{Te}-\text{C}$ bond expansion) in **1** and **2** correlate well with secondary $n(\text{I}^-) \rightarrow \sigma^*(\text{Te}-\text{C})$ interactions within the iodide- and triiodide-bridged structures.^{1,10}

EXPERIMENTAL

X-Ray Structure Determinations

Data were recorded using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Stoe STADI-4 diffractometer. Absorption corrections were based on ψ -scans. Structures were refined using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-711843 (1) and CCDC-711844 (2), and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Special Features

The iodide **1** could not be satisfactorily refined with $Z' = 2$ in space group $P\bar{1}$; despite apparently sensible heavy atom positions, the phenyl rings were badly resolved and appeared to be disordered. Refinement in space group $P1$ with $Z = Z' = 4$ was therefore attempted; a complete system of ordered rings was slowly built up and refined satisfactorily, although there are necessarily some negative features associated with the pronounced pseudosymmetry: (i) the Flack parameter of 0.42(2) indicates racemic twinning; (ii) carbon atoms could only be refined isotropically; (iii) a system of restraints to local ring symmetry was necessary to improve stability of refinement. Dimensions involving light atoms should be interpreted with caution.

Crystal Data for 1

$\text{C}_{18}\text{H}_{15}\text{ITe}$, $M_r = 485.80$, triclinic, space group $P1$, $a = 12.023(4)$, $b = 12.309(4)$, $c = 12.896(4) \text{ \AA}$, $\alpha = 66.67(2)$, $\beta = 71.14(2)$, $\gamma = 79.11(2)^\circ$, $V = 1654.3(9) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.951 \text{ Mg/m}^3$, $\mu(\text{Mo-K}\alpha) = 3.7 \text{ mm}^{-1}$, $F(000) = 912$, $T = 133 \text{ K}$; orange prism $0.5 \times 0.4 \times 0.3 \text{ mm}^3$. Of 8533 reflections collected to $2\theta 55^\circ$, 8349 were independent ($R_{\text{int}} = 0.020$). Final $R1 = 0.0278$ ($I > 2\sigma(I)$), $wR2 = 0.0682$ (all data) for 363 parameters and 171 restraints; $S = 1.05$, max. $\Delta\rho 1.17 \text{ e \AA}^{-3}$.

Crystal Data for 2

$\text{C}_{18}\text{H}_{15}\text{I}_3\text{Te}$, $M_r = 739.60$, monoclinic, space group $P2_1/n$, $a = 10.021(2)$, $b = 14.911(2)$, $c = 13.826(2) \text{ \AA}$, $\beta = 95.509(10)^\circ$, $V = 2056.4(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 2.389 \text{ Mg/m}^3$, $\mu(\text{Mo-K}\alpha) = 5.9 \text{ mm}^{-1}$, $F(000) = 1336$, $T = 133 \text{ K}$; red prism $0.8 \times 0.28 \times 0.24 \text{ mm}^3$. Of 3865 reflections collected to $2\theta 50^\circ$, 3607 were independent ($R_{\text{int}} = 0.020$). Final $R1 = 0.0243$ ($I > 2\sigma(I)$), $wR2 = 0.0559$ (all data) for 200 parameters; $S = 1.13$, max. $\Delta\rho 0.67 \text{ e \AA}^{-3}$.

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