

An alkynyltelluronium iodide and its solid state structure: evidence for $p \rightarrow \sigma^*$ interactions

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Abstract

The synthesis of the first alkynyltelluronium salt is presented. X-ray investigations of this species reveal a two-dimensional polymeric structure, assembled through various secondary $\text{Te} \cdots \text{Te}$ and $\text{Te} \cdots \text{I}$ interactions. The structure itself can be rationalized in terms of $p \rightarrow \sigma^*$ interactions.

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1. Introduction

We have been interested for some time in aggregation phenomena favored by chalcogen–chalcogen interactions [1–6]. The examination of chalcogen-containing compounds in the Cambridge Crystallographic Database (CCD) reveals favored configurations of RXR' moieties ($X = \text{S}, \text{Se}$) which could be rationalized in terms of frontier orbital interactions [7–9]. An occupied p orbital on one RXR' unit interacts with an empty σ^* orbital of either the $\text{R}-\text{X}$ or $\text{R}'-\text{X}$ bonds of another RXR' unit. Our quantum chemical model calculations confirm this view [10]. It was found that the $p(\text{X}) \rightarrow \sigma^*$ interaction increases by increasing the acceptor capability of the $\text{X}-\text{C}$ bond. Recently, we used this concept to construct tubular structures in the solid state [1–6]. To get further insights how these weak interactions are responsible for the solid-state architecture we thought it would be of interest to increase the acceptor capability of a $\text{X}-\text{C}$ bond dramatically by a positive charge which is placed at the chalcogen centre. This concept is outlined in Fig. 1. On the left side we show the $p \rightarrow \sigma^*$ interaction between two R_2Te units. As a result, the $5p$ (donor) MO is stabilized and the σ^* (acceptor) MO is

destabilized. By using an alkyltelluronium salt as the acceptor part, the σ^* level is lowered in energy and thus, the $p \rightarrow \sigma^*$ interaction is increased when the donor part remains the same (Fig. 1, right).

In this paper, we report the preparation and structural characterization of the first alkynyltelluronium species. Several telluronium species R_3TeX have been characterized crystallographically [11–14], but to the best of our knowledge R has never been an alkyne moiety.

2. Results and discussion

Bis(methyltelluro)acetylene [15] was reacted with an excess of methyl iodide in acetone at room temperature to afford the corresponding telluronium iodide in 42% yield (Scheme 1). The air-stable salt precipitated as a colourless microcrystalline powder which was analyzed by usual spectroscopic techniques as well as elemental analysis. All these data showed that only one of the two tellurium atoms was methylated. Several attempts to achieve a methylation of both tellurium atoms next to the triple bond failed. Even heating as well as the use of stronger methylating reagents like Meerwein's salt were not successful.

In order to establish the structure of the alkynyltelluronium iodide a single crystal X-ray investigation was

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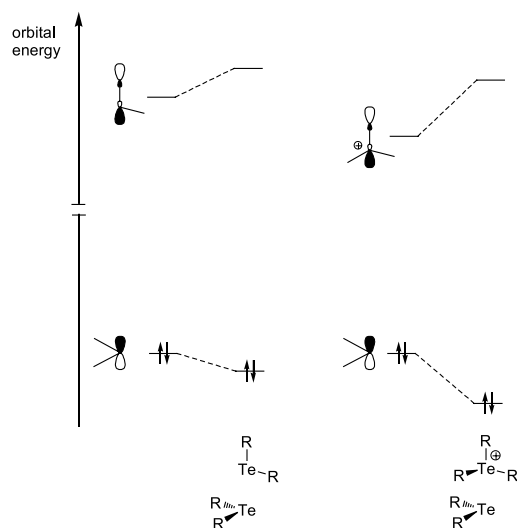
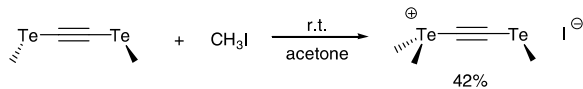


Fig. 1. Interaction between two R_2Te species (left) and one R_2Te and one R_3Te^+ species (right).



Scheme 1.

carried out. The molecular structure with separated ions is shown in Fig. 2. Relevant intramolecular distances, angles and torsional angles are given in Table 1.

The analysis of the solid state structure is even more interesting. The compound (space group $P2_1/c$) crystallizes in layers which show a zig-zag-like arrangement giving rise to a folded sheet structure (Figs. 3 and 4). Between the layers only weak hydrophobic interactions by methyl groups are observed. In contrast, in the layer itself there are relatively strong secondary interactions between tellurium and iodine. Each iodide is surrounded by four tellurium atoms. Two of them are neutral, two are cationic. An analysis of the distances reveals values of 3.45 and 3.70 Å (to cationic Te) and 3.58 and 3.76 Å (to neutral Te). Furthermore, it is interesting to note that the shorter of these distances point directly to the direction of a Te–C(sp) bond, whereas the longer ones point to the direction of a Te–C(sp³) bond, as anticipated by their different acceptor capability. As a con-

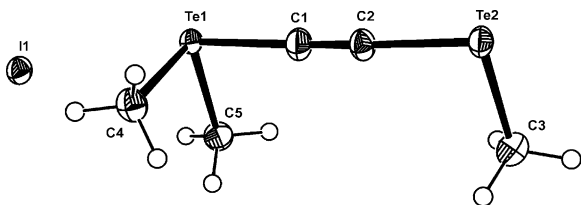


Fig. 2. Molecular structure of the alkynyltelluronium iodide **1** (at 50% probability level of the thermal ellipsoids).

Table 1
Selected bond lengths (Å), bond angles and torsional angles (°) for **1**

Bond lengths	
Te1–C1	2.069(4)
Te1–C4	2.132(3)
Te1–C5	2.136(3)
Te2–C2	2.067(4)
Te2–C3	2.149(4)
C1–C2	1.177(6)
Bond angles	
C1–Te1–C4	92.07(15)
C1–Te1–C5	92.61(15)
C4–Te1–C5	97.09(16)
C2–Te2–C3	92.39(15)
C2–C1–Te1	178.6(4)
C1–C2–Te2	178.1(3)
Torsional angles	
C3–Te2–Te1–C4	94.1(4)
C3–Te2–Te1–C5	–3.2(4)

sequence of the substitution pattern, each tellurium atom is surrounded by two iodides and a cationic tellurium centre, and by the same token, each telluronium centre is associated with two iodides and a neutral tellurium. Finally, each neutral Te experiences five connectivities including the two covalently bonded carbon atoms in a distorted square pyramidal geometry, whereas each cationic tellurium experiences six connectivities in a slightly distorted octahedral geometry (Figs. 3 and 4). Relatively short secondary Te···Te contacts were observed (3.77 Å). This distance is significantly shorter than the sum of the corresponding van der Waals radii (4.40 Å) [16].

In conclusion, we show in this short note that the solid-state structure of the compound is in two dimensions strongly determined by orbital–orbital interactions. Due to the orthogonality of the p orbitals which interact directly with low-lying σ^* orbitals a zig-zag-like folded sheet structure within the layer arises. In the third dimension, between the layers, there are only weak hydrophobic interactions between the methyl groups.

In summary, we report the first synthesis, the molecular and the solid-state structure of an alkynyltelluronium salt. The arrangement of the ions in the solid state can easily be understood in terms of frontier orbital $p \rightarrow \sigma^*$ interactions.

3. Experimental

3.1. General remarks

The NMR spectra were measured with Bruker Avance 500 and 300 using the solvent as internal standard (δ). The IR spectrum was recorded with a Bruker Vector 22, UV light absorption spectrum using a Hewlett Packard

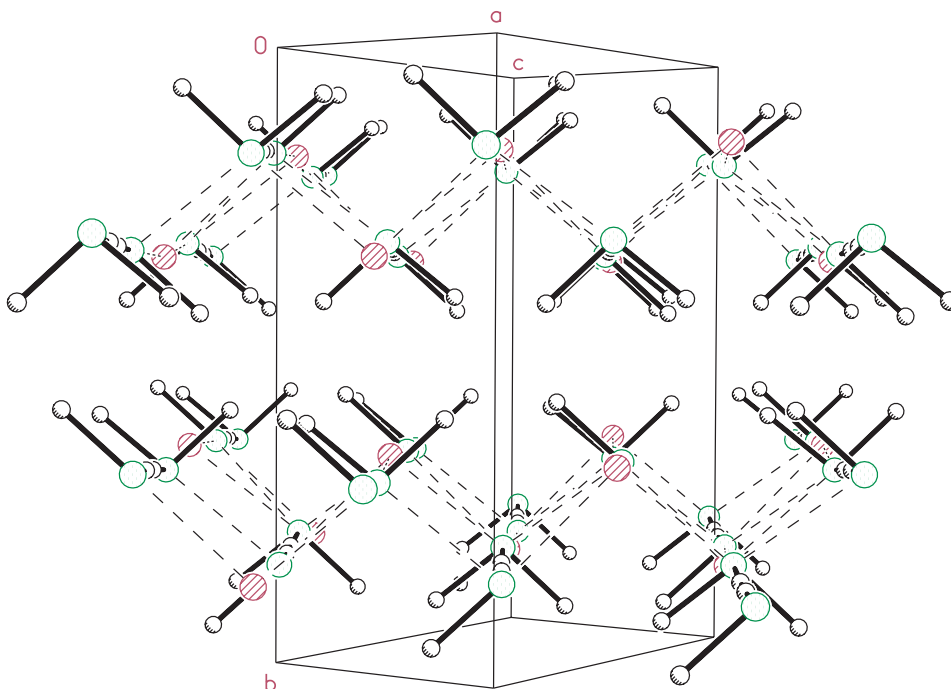


Fig. 3. Side view of two layers of **1** showing the zig-zag arrangements. The iodide anions are brushed. Short secondary interactions between heavy atoms as well as the unit cell are indicated. Hydrogen atoms are omitted for the sake of clarity.

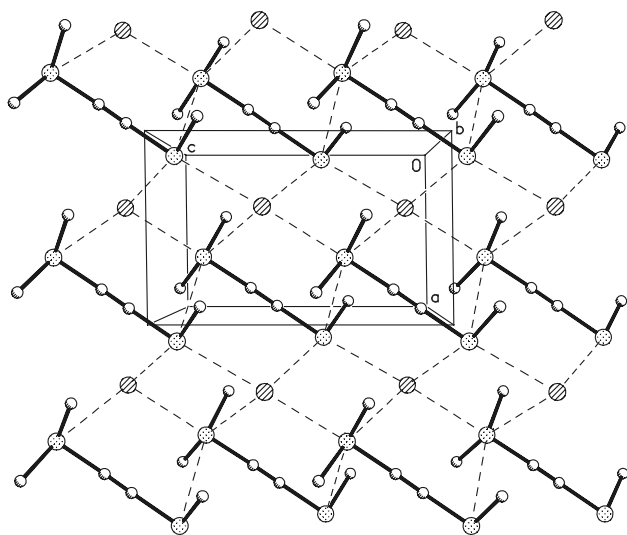


Fig. 4. Top view of a layer of **1**. The iodide anions are brushed. Short secondary interactions between the heavy atoms as well as the unit cell are indicated. Hydrogen atoms are omitted for the sake of clarity.

8452A spectrometer. The reaction was carried out in dried glassware under argon atmosphere using dried solvent.

3.2. Synthesis of alkynyltelluronium iodide **1**

Bis(methyltelluro)acetylene (107 mg, 0.35 mmol) was dissolved in acetone (20 ml). Neat methyl iodide (1.5 g,

10.6 mmol) was added dropwise over a period of 5 min. The mixture was stirred for 2 h at room temperature. In vacuo, the mixture was reduced to a quarter of its volume. The resulting solution was cooled for 24 h to $-20\text{ }^{\circ}\text{C}$. A colourless powder precipitated which was filtered and washed with diethyl ether. Yield: 65 mg (42%). Colourless solid. M.p. $125\text{ }^{\circ}\text{C}$ (dec.). ^1H NMR (300 MHz, d_6 -DMSO): δ 2.11 (s, 3H, TeCH_3), 2.32 (s, 6H, $\text{Te}(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, d_6 -DMSO): δ -11.8 (TeCH_3), 14.4 ($\text{Te}(\text{CH}_3)_2$), 75.2 (C), 83.7 (C). IR (KBr): 2925, 2063, 1628, 1405, 1228, 1212, 863, 635. UV–Vis (CH_2Cl_2 , 0.036 mg ml^{-1}) λ (nm) ($\log \epsilon$): 256 (3.09). Elemental Anal. Calc.: C, 13.31; H, 2.01. Found: C, 13.56; H, 2.19%.

3.3. X-ray crystallography and structure solution

The crystallographic data were recorded with a Bruker Smart CCD diffractometer at $200(2)\text{ K}$ at a wavelength λ of 0.71073 \AA . Relevant crystal and data collection parameters are given in Table 2. Structure solution and refinement was carried out using SHELXTL [17]. An empirical absorption correction was carried out using SADABS [17] based on the Laue symmetry of the reciprocal space. Hydrogen atoms were included at calculated positions. The ORTEP drawing was obtained by using ORTEP-3 for Windows program by Farrugia [18]. Suitable crystals were obtained by infusion of neat methyl iodide into an acetone solution of bis(methyltelluro)acetylene [15].

Table 2
Crystal data and structure refinement for **1**

Chemical formula	C ₅ H ₉ Te ₂ I
Formula weight (g/mol)	451.23
Crystal size (mm)	0.32 × 0.26 × 0.06
Crystal shape	Polyhedron
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.536(1)
<i>b</i> (Å)	15.049(1)
<i>c</i> (Å)	10.336(1)
β (°)	90.755(1)
<i>V</i> (Å ³)	1016.51(5)
<i>D</i> _{calc.} (g cm ⁻³)	2.95
<i>Z</i>	4
<i>F</i> (000)	784
$\theta_{\min}/\theta_{\max}$ (°)	2.39/27.46
<i>h</i> _{min} / <i>h</i> _{max}	–8/8
<i>k</i> _{min} / <i>k</i> _{max}	–19/19
<i>l</i> _{min} / <i>l</i> _{max}	–13/13
Absorption coefficient μ (mm ⁻¹)	8.70
Max./min. transmission	1.00/0.58
Reflections collected	10109
Independent reflections	2315
Observed reflections	2218
Parameters	77
<i>R</i> (<i>F</i>)	0.021
<i>R</i> _w (<i>F</i> ²)	0.054
<i>S</i> (goodness of fit) on <i>F</i> ²	1.17
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} (e Å ⁻³)	0.96, –0.84

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 218069 for compound **1**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (int code) +44(1223)336-033 or e-mail: data_request@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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