Solid State and Solution Conformation of Di-2-thienyl Telluride: X-Ray Structure and Dipole Moment Studies

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Di-2-thienyl Telluride, X-Ray, Crystal Structure

The crystal and molecular structure of di-2-thienyl telluride was determined by X-ray analysis. Crystal (monoclinic) data were: a = 9.526(4), b = 6.252(4), c = 16.302(5) Å; β = 97.29(3)°, Z = 4, space group P2₁/c. Hydrogen bonds are absent and only van der Waals forces are determining crystal packing. The C₁₁—Te—C₁₅ bond distances suggest little conjugation of Te atom with the rings. Comparisons with published structures for C₅₋ₓ—X—C₅ (X = chalcogen) type molecules revealed that the C(1)—Te—C(5) angle takes the lowest value (95.6°) in the molecule under study. The remaining bond lengths and angles are close to standard values. The molecular conformation found in the crystal is “butterfly-like”, with thienyl ring planes nearly perpendicular to the C(1)—Te—C(5) plane and the S atoms distal to each other.

Dipole moment was measured via classical vector addition method in terms of rotation angles about C(1)—Te and C(5)—Te bonds, showed that the molecular conformation found in the crystalline state is retained in solution.

Introduction

Knowledge of molecular structures and conformations of chalcogen bridged compounds of the type Ar—X—Ar (Ar = heteroring; X = S, Se, Te) is of interest in view of their increasing application in coordination and environmental chemistry as well as in both synthetic and mechanistic studies. Although there is previous information regarding conformations of molecules Ar—X—Ar (Ar = pyridine, phenyl; X = S) [1—4], there still remains a dearth of data regarding conformational properties of molecules containing penta-heterocyclic moieties, such as thiophene, and a heavy chalcogen (X = Te). Our continuing interest in these systems was therefore focused on the di-2-thienyl telluride molecule, whose solid state structure and solution conformation were determined by using X-ray analysis of the crystal, and dipole moment measurement and analysis.

An additional aim of this work is to obtain quantitative comparison of fluid and solid state conformation of this molecule. There is no doubt, from the methodological point of view, that combined methods are of increasing utility for the study of conformational problems and, in particular, for investigating the influence of the various factors which determine the molecular conformation in the aggregation states.

Experimental

Di-2-thienyl telluride

Crystalline sample of the compound was prepared according to previously described procedure [5]; m.p. 49–50°C.

Crystal structure determination

A crystal of dimensions 0.10×0.10×0.15 mm was used for data collection* on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The radiation Mo—Kα (λ = 0.71073 Å) was used (μ = 34.5 cm⁻¹).

Crystal data: C₆H₅S₂Te, F. W. 293.86, monoclinic, a = 9.526(4), b = 6.252(4), c = 16.302(5) Å, β = 97.29(3)°.

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97.29(3)°, V = 963.0 Å³, Z = 4, D = 2.03 g cm⁻³, F(000) = 552, space group P2₁/c.

The intensities of 984 unique reflections for which I > 3σ(I) (total number of collected reflections = 1698) were measured (up to 2θ = 50°), at a temperature of −107 ± 1°, using the ω-θ scan method. The scan rate varied from 1 to 20° min⁻¹; scan width was calculated from θ = 0.7 + 0.35 tan θ. No significant variation in the intensities of three representative reflections, which were monitored every 41 min, was observed and then no decay correction was applied. Corrections for Lorenz and polarization effects were applied to the data. An empirical absorption correction based on a series of ψ-scans was applied to the intensity data. Relative transmission coefficients ranged from 0.824 to 0.996. An extinction correction was not necessary.

The structure was solved using a centrosymmetric direct method program and refined by least-squares methods to the final R value 0.041 (R = 2(|F₀| − |Fcalc|)/Σ|F₀|; function minimized: Σw(|F₀| − |Fcalc|)², weighting scheme: w = 1; no. variables: 100]. Final difference Fourier maps were featureless and did not reveal positions of hydrogen atoms. No residuals larger than 0.8 e Å⁻³ were present at the conclusion of the refinement.

Computations were carried out on a CDC 7600 system using the SHELX-76 program [6]. Final positional parameters for the molecular structure shown in Fig. 1 are reported in Table I. Bond distances and angles are given in Table II. Anisotropic thermal parameters and structure factors are given as Supplementary Material*.

### Table I. Atomic fractional co-ordinates for di-2-thienyl telluride.

<table>
<thead>
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<th>Atom</th>
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<th>y/b</th>
<th>z/c</th>
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<td>.6805(0)</td>
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<td>.1237(23)</td>
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<td>.4011(34)</td>
<td>.8205(11)</td>
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<td>C(8)</td>
<td>.4526(14)</td>
<td>.2181(41)</td>
<td>.8629(8)</td>
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</table>

Estimated standard deviations are given in parentheses.

### Dipole moment

The electric dipole moment of di-2-thienyl telluride was determined in benzene solution at 30 ± 0.1 °C, using apparatus and techniques described earlier [7]. The total solute polarization (P₂*) was obtained by extrapolation to infinite dilution using the Halverstadt-Kumler method [8]. The value of the experimental molar refraction (Rₑ) for the NaD line was used as the electronic and atomic polarization (Pₑ+Pₐ) in calculating μ. The determined polarization data were: α = 0.81; β = −0.620; Rₑ/cm³ = 63.74; P₂*/cm³ = 91.5. The μ value (in Debye) obtained was μ = 1.18 D (estimated error: ±0.01 D).

### Results and Discussion

#### X-ray analysis

The Te–C(1) and Te–C(5) bond distances [2.08(1) and 2.10(1) Å, respectively] are slightly less...
than the sum of the covalent radii (1.37 + 0.77 Å) [9]. This could be interpreted in terms of little conjugation occurring between tellurium atom and thienyl rings. Moreover, the mean value of 2.09 Å is somewhat smaller than the mean value (2.13 Å) found for the Te–C₉ bond in three diaryl ditellurides [10–12].

The C(1)–Te–C(5) bond angle of 95.6(4)° is less than the value of 101° reported for di-p-tolyl telluride [13], the only monotelluride structure solved up to now, but from two-dimensional X-ray data. It should be considered, on the other hand, that in ten well-solved structures of diaryl sulphides [13–23] the CSC angle ranges from 102 to 105° and the averaged value is 103.3(6)°. This angle at the chalcogen atom in di-2-thienyl telluride is therefore considerably smaller (ca. 8°). Recently a comparable value (96.3°) was reported for diphenacylselenide [24].

The torsional angles in the thienyl rings show the planarity of both the rings to be within ±2°, while the bond lengths and angles are all consistent with the accepted values from earlier investigations [25–27]. In particular, it should be stressed that in both rings the two C–C bonds adjacent to the C–S bonds exhibit more double-bond character than the remaining one. The dihedral angle between the least-squares planes of the rings is 96.8° (Fig. 2) and the Te···S(1) and Te···S(2) contacts are 3.34 and 3.33 Å, respectively.

Fig. 2. Molecular conformation and relative orientations of the rings.

There is no intermolecular distance less than 3.5 Å between non-bonded atoms, so that only van der Waals forces are effective between molecules in the crystal (Fig. 3).

Dipole moment analysis

The theoretical dipole moment (µcalc) of di-2-thienyl telluride was calculated as a function of the twisting angles θ, ϕ by a three-dimensional vector addition method of group moments, using the group moment of thiophene (µth = 0.54 D [28]), the bond moment µC–Te = 0.89 D (deduced from the observed moment of diphenyl telluride, 1.14 D [29]) and the geometry specified above by X-ray analysis. The direction of action of the component moments is shown in Fig. 4 where also the cis-planar conformation, which was assumed to have θ = ϕ = 0°, is out-
Fig. 4. Cis-planar conformation assumed as \( \Theta = \Phi = 0^\circ \). Direction of action of the component moments and assumed rotation (clockwise) of the rings are outlined.

The rotations about C–Te bonds were assumed clockwise from \( \Theta = \Phi = 0^\circ \).

Rotations in the whole range from 0 to 180° cause significant changes in the \( \mu_{\text{calc}} \) values (range from 0.47 D for \( \Theta = \Phi = 0^\circ \) to 2.07 D for \( \Theta = \Phi = 180^\circ \)), the difference thus being suitable to provide conformational information by the comparison of \( \mu_{\text{calc}} \) as a function of \( \Theta, \Phi \) with measured dipole moment (\( \mu_{\text{exp}} \)).

The condition \( \mu_{\text{exp}} = \mu_{\text{calc}} \) was verified for the single fixed conformation in which \( \Theta = \Phi = 90^\circ \). Alternate possibility of essentially free rotations was excluded on the basis of the difference found between \( \mu_{\text{exp}} \) and the calculated averaged value (\( \bar{\mu}_{\text{calc}} = 1.50 \) D). The \( \bar{\mu}_{\text{calc}} \) value of 1.45 D which was calculated assuming equal populations of propeller conformers twisted by 30° (30,30; 30,150; 30,210; 150,210) also made unlikely such possibility.

It is therefore possible to interpret the \( \mu_{\text{exp}} \) value unequivocally in terms of a single rigid conformation, namely the classical “butterfly” one (90,90), in which the rings are perpendicular to the C(1)–Te–C(5) plane and the S ring atoms are distal to each other.

The above findings suggest that the unique equilibrium conformation in both solid and solution state is determined essentially by steric and electrostatic repulsive effects between the thienyl rings (this being made possible by the unusually small C(1)–Te–C(5) angle found, which makes less orthogonal arrangements energetically unfavoured). In addition, it should be considered that only van der Waals forces were found effective as intermolecular forces determining the crystal packing.

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