Heterocycles

DOI: 10.1002/anie.200601298

Synthesis, Structure, and Properties of 4,7-Dimethoxybenzo[*c*]tellurophene: A Molecular Pyroelectric Material**

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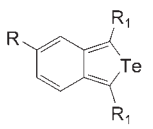
The formation of molecular crystals that possess a polar axis in the solid state is largely an unexplored area, and no generic understanding is available to this day. Materials with a polar axis (a permanent dipole moment in the solid state) potentially possess ferroelectric, piezoelectric, and pyroelectric properties.[1] Pyroelectric solids are used as the key material in a variety of components, which range from microphones and infrared detectors to frequency-doubling crystals in laser technology, just to mention a few.[2] Examples of the design and synthesis of organic materials with pyroelectric properties are scarce because of the difficulties in predicting the crystalline properties of matter.[3] An organic material must crystallize in one of the ten polar point groups to exhibit pyroelectric properties.[4] Although most organic molecules possess a permanent dipole moment, few crystallize in a polar space group. Generally, derivatives based on *meta*-disubstituted benzene have proven to be useful as they have a tendency to crystallize in one of these ten required polar point groups and, thus, exhibit a pyroelectric effect.[5] Apart from this rather vague design rule, little is known about the structural features that promote crystallization in a polar point group, and it is only on the odd and unexpected occasion that novel pyroelectric materials appear.[2a,b]

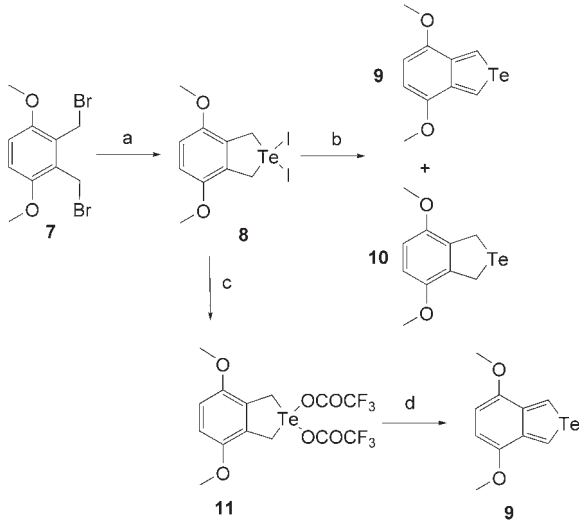
Herein, we describe the synthesis, structure, and properties of an unusually stable Te-containing heterocyclic compound that crystallizes in a polar space group and possesses pyroelectric properties: 4,7-dimethoxybenzo[*c*]tellurophene (**9**; Scheme 1).

The highly reactive *o*-quinoid heterocycles benzo[*c*]-furan,[6] benzo[*c*]thiophene,[7] and benzo[*c*]selenophene[8] have been the object of considerable interest both from a synthetic and a theoretical perspective.[9] A particularly interesting application of these types of compounds is their role as precursors for low-band-gap conducting polymers.[10] Cava and co-workers first reported benzo[*c*]tellurophenes (Scheme 1),[11–12] whose properties constitute a largely untouched area of tellurium-based heterocyclic chemistry[13–14] largely as a result of the lack of synthetic procedures and the inherent instability of the parent heterocycle.



1: R=H, R_1=H
2: R=OMe, R_1=H
3: R=NO_2, R_1=H
4: R=H, R_1=CO_2Et
5: R=H, R_1=CO_2Bn
6: R=H, R_1=*p*-Me$C_6H_4SO_2$

Scheme 1. Benzo[*c*]tellurophenes prepared by Cava and co-workers.



Scheme 2. Synthesis of 4,7-dimethoxybenzo[*c*]tellurophene (**9**). Reagents and conditions: a) NaI, Te, methoxyethanol (64%); b) Et_3N, benzene; c) CF_3COOAg, benzene (99%); d) Et_3N, benzene (72%).

The treatment of **7**[15] with elemental Te and NaI in methoxyethanol yields the orange 4,7-dimethoxy-1,3-dihydrobenzo[*c*]tellurophene diiodide (**8**) in 64% yield (Scheme 2). Attempts to eliminate HI from **8** to yield **9** by using Et_3N in benzene gave a 2:1 mixture of the desired product **9** (major product) and 1,3-dihydro-4,7-dimethoxybenzo[*c*]tellurophene (**10**; minor product; isolated after removal of **9** by reaction with maleic anhydride), as seen by ^{1}H NMR spectroscopic analysis. As we were not able to separate the two products, **8** was converted into the bistrifluoroacetate **11** by treatment with CF_3CO_2Ag in anhydrous benzene.[16] Elimination from **11** to the desired product **9** was achieved by using Et_3N in benzene. Compound **9** was purified by column chromatography on silica gel in 72% yield. The benzo[*c*]tellurophene (**9**) was stable in the solid form at room temperature and ambient atmosphere for (at least) several months in the dark (no darkening of the product was observed). It was also stable in solution with benzene and

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[**] We thank Associate Professor Lars Henriksen and Theis Brock-Nannestad for useful discussions and Professor Klaus Bechgaard for conducting the cyclic voltammetry experiments.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

heptane, but it decomposed in $CHCl_3$ after a few hours to give a gray precipitate (probably elemental Te). Elemental analysis, cyclic voltammetry, and ^1H and ^{13}C NMR, UV/Vis, and IR spectroscopy (see the Supporting Information) were used to characterize **9**. Cyclic voltammetry of **9** showed that the heterocycle was oxidized irreversibly and had an oxidation potential of 0.65 eV in CH_2Cl_2 with nBu$_4$PF$_6$ as the electrolyte and Pt versus the standard calomel electrode as the reference. However, we did not observe any polymerization of the monomer during the oxidation process.

Final proof of the structure of **9** came from the single-crystal X-ray structure (Figure 1). Needle-shaped yellow crystals were grown by slow evaporation of a solution of **9** in benzene at room temperature in the dark.

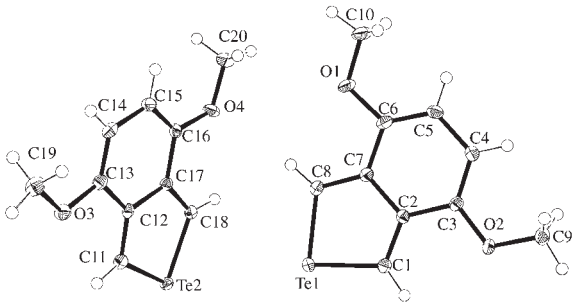

Figure 1. Asymmetric unit cell of the X-ray structure of **9** at 100 K.

The structure of **9** is as expected, planar, and shows similarity in bond lengths and angles with the tellurophene[17] and bitellurophene.[18] These data also agree well with microwave spectroscopic data recorded for tellurophene.[19] The crystal packing of **9** exhibits few similarities with the only reported structure of a benzo[*c*]selenophene.[20]

There are two molecules in the asymmetric unit (Figure 1). At a first glance, these seem to be located randomly in space. More information is evident in the crystal packing, in which a C_2 axis materializes and Te–Te interactions are the dominant force (Figures 2 and 3). In fact, the Te–Te distance is 4.06–4.10 Å, which is approximately 0.2 Å shorter than the van der Waal distance of Te (4.30 Å). The benzo[*c*]tellurophene cores are tilted with an angle of approximately 48° with respect to the C_2 axis and are arranged two by two. The vector of the molecular dipole has a significant component in the direction of the polar axis

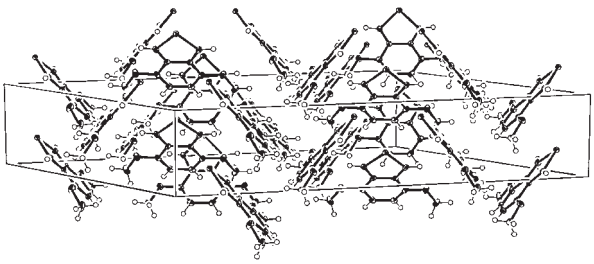

Figure 2. The crystal packing of **9** at 100 K. It can be seen how all the molecules are pointing in the same direction.

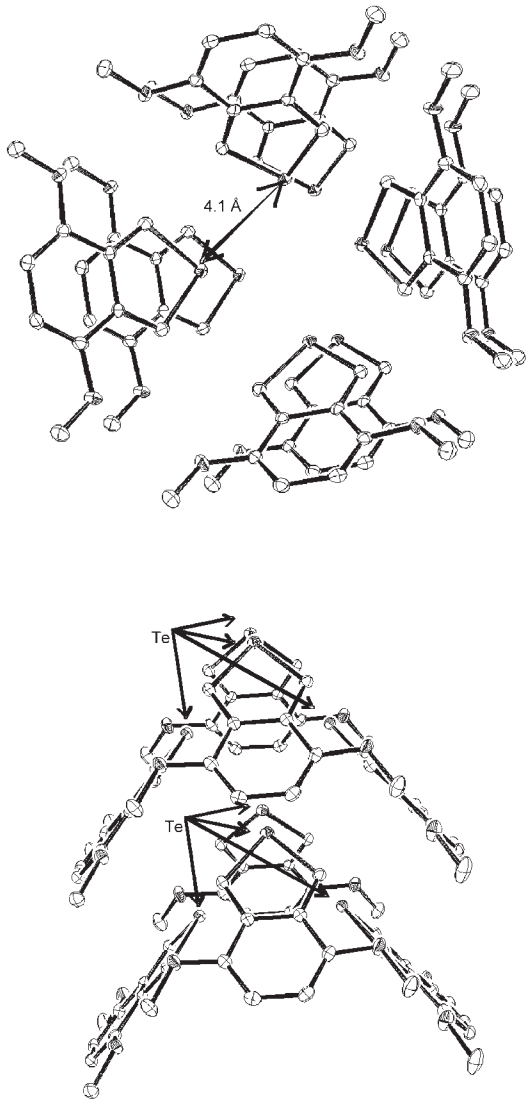

Figure 3. Two views of a section of the crystal structure of **9** at 100 K. Top: the Te–Te interactions looking down the C_2 axis. Bottom: the placement of the Te atoms in space (perpendicular to the C_2 axis). The hydrogen atoms have been removed for clarity.

(*b* axis). The vector sums of the molecular dipoles cancel in the *a*–*c* plane, whereas the vector sum gives a net dipole moment along the *b* axis, which results in a permanent polarization in the solid state. The distance between two Te atoms in benzo[*c*]tellurophene molecules that are stacked on top of each other is approximately 5.4 Å, which is too large to be accounted for by the van der Waal radius of Te. However, the distance that separates two layers of benzo[*c*]tellurophenes can be attributed to π–π interactions (ca. 3.5–3.6 Å) between the aromatic cores.[21] The unit cell is shown in Figure 2 and shows the molecular tilt with the *b* axis. Four molecules form a tilted square with twofold symmetry, with a distance between all Te atoms in the tilted square of 4.06–4.10 Å. This type of structure with a short Te–Te interaction and a polar space group has also been seen for the structure of 9-(9′-*H*-fluoren-9′-ylidene)-9*H*-telluroxanthene and could be a more general property of organotellurium compounds.[24]

The fact that all the benzo[*c*]tellurophene molecules point in the same direction in space introduces a permanent polarization into the crystal, thus prompting us to investigate the pyroelectric properties. The pyroelectric effect can be divided into three contributions: primary, secondary, and tertiary effects. The primary effect has origin in abrupt atomic or molecular movements within the crystals as a function of the temperature that leads to changes in the polarization in the material. This behavior is often observed in connection with phase transitions in which the spontaneous polarization either appears, cancels, or changes radically; for example, if the symmetry changes from polar to nonpolar. The secondary effect is due to the change in polarization as a function of the thermal expansion (change of the volume as a function of the temperature) of the unit cell. The tertiary effect is coupled to the piezoelectric properties that pyroelectric materials invariably have. By ensuring homogenous heating of the material and careful design of the detector geometry the tertiary effect can be eliminated from the experiment.

We investigated the X-ray structure as a function of the temperature to determine whether the observed pyroelectric effect is a primary or secondary effect. Therefore, the X-ray diffraction data of **9** were recorded at 100, 150, 200, 250, 300, 323, 343, and 373 K. An exothermic phase transition was observed at about 353 K, as shown by differential scanning calorimetry (DSC; see the Supporting Information). The X-ray data could be collected at 343 K, but the crystal blackened and its edges became rounded upon heating to 373 K. No diffraction could be observed when the temperature was lowered back down to 343 K. This behavior indicates that the observed crystal structure may not be an equilibrium structure. We, however, rule out the possibility of polymorphism as all diffraction disappears after the heating step to 373 K. We observed a decrease in the diffraction intensity as a function of time when collecting data at 343 K, and no diffraction was observed after 2 h. It, therefore, seems plausible that **9** loses tellurium at high temperature.

The structural refinement of **9** was unproblematic at all temperatures, except at 323 K, for which we employed constraints on the molecular geometry by forcing the benzene ring to approach a hexagonal geometry.

If the pyroelectric effect is a primary effect, a structural change as a function of the temperature, which affects the polarization, has to be observed. A change in the polarization can only happen if the angle between the C_2 axis and the plane of the molecule changes. We have plotted the angle between the least-squares-fitted plane and the C_2 axis as a function of the temperature for one of the molecules in the asymmetric unit cell (the same results were obtained for the other molecule in the asymmetric unit; see the Supporting Information). No significant changes were observed which means that a primary pyroelectric effect can be excluded.

In Figure 4, the polar axes of the unit cell and the cell volume is plotted as a function of the temperature, thus clearly indicating a secondary pyroelectric effect.

The secondary pyroelectric effect is solely due to the thermal expansion of the material with temperature. Compound **9** expands when heated, and as the dipoles in the unit cell stay constant the polarization decreases, thus giving the secondary pyroelectric effect as [Eq. (1)]:[2b]:

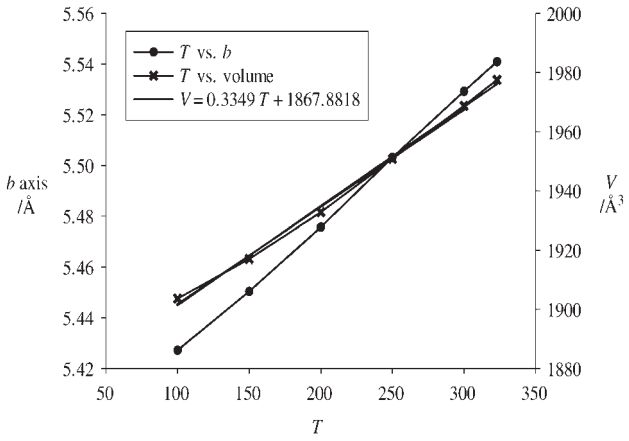

Figure 4. Length of the *b* axis and the volume of the unit cell as a function of temperature.

$$\frac{dP(T)}{dT} = p_2(T) = -\frac{Z}{a\,T^2 + 2\,b\,T + \frac{b^2}{a}}\mu\cos(\theta) \qquad (1)$$

where P, $aT^2+2bT+b^2/a$, T, Z, μ, and θ are the polarization, the derivatives of the linear thermal expansion with respect to the temperature, the temperature, the molecular entities per unit cell, the molecular dipole moment, and the angle between the molecular plane and the C_2 axis, respectively. The dipole moment of the molecules can be enhanced in the solid state, as reported previously,[2c] but this amounts to only minor changes in the overall magnitude of the pyroelectric effect.

The dipole moments of the single molecules and the unit cells were calculated at the B3LYP/3-21G level of theory using the Gaussian 98 suite of programs.[22] The molecular coordinates from the X-ray crystal structures were used as input, and the results are summarized in Table 1. We observe that the dipole moment stays relatively constant with temperature, except for when the temperature was raised to near the phase transition.

Table 1: Calculated dipole moments.[a]

T [K]	μ [D][b]	μ [D][c]
100	2.17	15.96
150	2.16	14.10
200	2.19	12.92
250	2.16	13.47
300	2.18	12.89
323	2.59	15.96

[a] B3LYP/3-21G. [b] Single molecule. [c] Component along the *b* axis in a single unit cell, the value is equal to the total dipole moment of one unit cell.

On the basis of the equation for the thermal expansion (Figure 4) and the calculated dipole moment (Table 1), it becomes possible to calculate the pyroelectric effect as a function of the temperature (Figure 5).

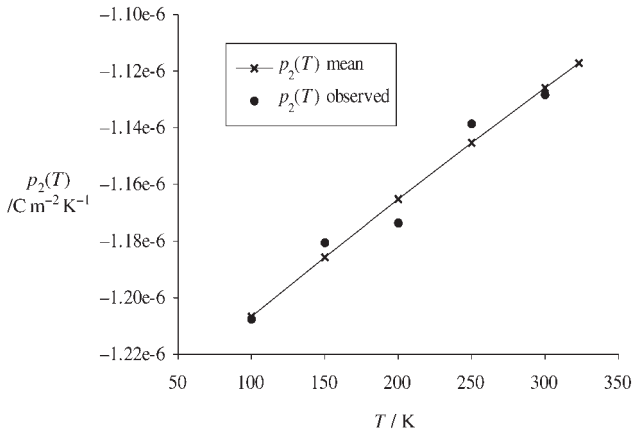

Figure 5. The calculated secondary pyroelectric coefficient as a function of the temperature. The $p_2(T)$ calculated is the secondary pyroelectric coefficient calculated by use of Equation (1), the calculated dipole moments from Table 1, the thermal expansion from Figure 4, and the angle between the molecular plane and the C_2 axis. The $p_2(T)$ mean is the secondary pyroelectric coefficient calculated by use of equation above, the mean value of the calculated dipole moments from Table 1, the thermal expansion from Figure 4, and the mean angle between the molecular plane and the C_2 axis.

From the point of view of application, primary pyroelectric materials have the advantage that large effects are seen near the phase transition, and therefore very sensitive detector systems can be designed. Their disadvantage is that the operation of the detector system is limited to temperatures near the phase transition. The application of the secondary pyroelectric effect in a detector system has the advantage that it can work over a large temperature range, and organic systems generally have high merit factors.[2b]

We are puzzled by the stability of **9** relative to the other known 1,3-unsubstituted benzo[*c*]tellurophenes, which decompose upon isolation.[11–12] We speculate that the stability of **9** is due to the steric effect that the methoxy groups in the 4- and 7-positions impose on the 1- and 3-positions of the heterocycle. This steric effect prevents these reactive positions from polymerizing, and we consider this to be a *peri* effect.[23]

To summarize, we have presented the synthesis and characterization of a stable benzo[*c*]tellurophene derivative, including the first crystal structure of this type of heterocycle. In addition, we observe an unusual stabilizing effect of the electron-donating methoxy substituents in the 4- and 7-positions. The pyroelectric properties of **9** have been investigated, and a secondary effect was found. This discovery suggests that tellurium-containing heterocycles could be attractive in materials science.

Experimental Section

All synthetic procedures and characterization data are given in the Supporting Information. Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. CCDC 299607–299612 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 3, 2006
Published online: ■■ ■■, ■■■■

Keywords: density functional calculations · heterocycles · molecular pyroelectrics · X-ray diffraction

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Communications

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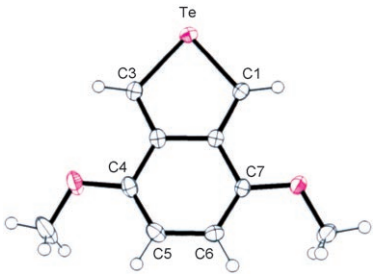

More than just curiosities: The synthesis and characterization of a stable benzo[*c*]-tellurophene are presented. Te—Te interactions are shown to be one of the main driving forces for the crystal-packing properties of this electron-rich benzo[*c*]-tellurophene; furthermore, investigation of its pyroelectric properties reveals a secondary pyroelectric effect.