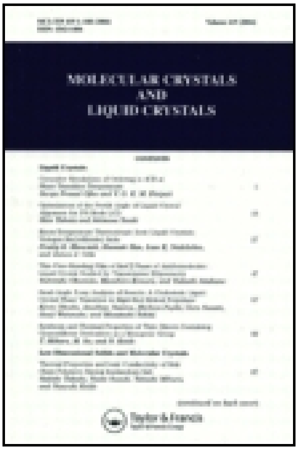

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J. K. Jeszka [b] , T. Enoki [c] , Z. Shi [a] , K. Imaeda [a] , H. Inokuchi [a] , N. Iwasawa [d] , H. Yamochi [e] & G. Saito [e]

[a] Institute for Molecular Science, Okazaki, 444, Japan

[b] Center of Molecular and Macromolecular Science of the Polish Academy of Sciences, ul. Boczna 5, 90-324, Lodz, Poland

[c] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, 152, Japan

[d] The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, 106, Japan

[e] Department of Chemisty, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-Ku, Kyoto, 606, Japan

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Thermal Properties of Tetrakis(Alkyltelluro)Tetrathiafulvalene (TTeC$_n$-TTF)

J. K. JESZKA,‡ T. ENOKI,§ Z. SHI,† K. IMAEDA,† H. INOKUCHI,† N. IWASAWA,‖
H. YAMOCHI¶ and G. SAITO¶

† *Institute for Molecular Science, Okazaki 444, Japan*
‡ *Permanent address: Center of Molecular and Macromolecular Science of the Polish Academy of Sciences, ul. Boczna 5, 90-324 Lodz, Poland*
§ *Present address: Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan*
‖ *The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan*
¶ *Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-Ku, Kyoto 606, Japan*

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Thermal properties of tetrakis(alkyltelluro)tetrathiafulvalenes (TTeC$_n$-TTF) are investigated using DSC technique. It is shown that combining tellurium substituted TTF skeleton with the alkyl chains of different length we got a variety of thermal properties due to a competition between the alkyl chains and the TTF moiety. This competition leads to a polymorphism and to an irregular dependence of the melting point as well as enthalpy and entropy of melting on the alkyl chain length between the carbon number $n = 4$ and 7. For the compounds with long alkyl chains ($n > 6$) the analysis of thermodynamic properties confirms the existence of the molecular fastener effect, i.e. fastening of the TTF skeletons and decreasing of the distances between them in the crystal structure by crystallization of the long alkyl chains.

Keywords: Organic semiconductor; TTF; thermal properties; molecular fastener

INTRODUCTION

Recently it has been shown that substituted tetrakis(alkylthio) and tetrakis(alkyltelluro)tetrathiafulvalenes (molecular structure presented in Figure 1), abbreviated as TTC$_n$-TTF and TTeC$_n$-TTF, respectively, exhibit many interesting properties.[1-4] Different characteristics of the sulphur substituted TTF skeleton and the attached alkyl groups make the properties of the crystals strongly dependent on the length of the alkyl chains.[1-5] The most interesting effect is the fastening of the TTF skeletons in the crystal due to Van der Waals interactions of the alkyl chains observed for n of the order of 10 and bigger. The distances between adjacent TTF skeletons with the π bond system in the crystal are reduced and electrical conductivity is increased through the overlap of the adjacent π systems by orders of magnitude.[3] This effect is called "molecular fastener effect".[2,4]

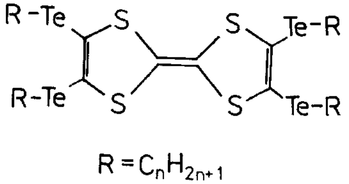

FIGURE 1 Molecular structure of TTeC$_n$-TTF.

Similar effect of the alkyl chains is expected when sulphur atoms are replaced by tellurium or selenium.[6] Because of the bigger atomic radius of tellurium atoms as compared with sulphur, the influence of the length of the alkyl chains on thermal and electric properties can be expected to be more pronounced.

In this paper we present thermal properties of the TTeC$_n$-TTF group investigated by differential scanning calorimetry (DSC). We show that the more pronounced competition between the tellurium substituted TTF moiety and the attached alkyl chains gives rise to a variety of thermal properties as the number of carbon atoms in the alkyl chains is changed from 1 to 18.

EXPERIMENTAL

The synthetic procedures of TTeC$_n$-TTF are described in Reference 4. Purification of the samples was performed by means of column chromatography with silica gel and recrystallization and checked by thin-layer chromatography. Thermal properties were investigated using Dupont 990 differential scanning calorimeter. The temperature was changed between −120°C and 15–20°C above the melting point.

Typical sample mass was 1.5 mg unless specified. Transition temperatures were determined by the intersection of the extrapolated linear parts of the maxima and baselines. The enthalpy and entropy changes at phase transitions were calibrated using mercury as a standard. Heating rate was 2°/min and cooling rate 1°/min (slow cooling) or 20°/min (fast cooling).

Microscopic observations were made using Boetius hot-stage polarizing microscope.

RESULTS AND DISCUSSION

Melting Behavior and Glass Transition

Figure 2 presents melting and freezing temperatures for TTeC$_n$-TTF series plotted vs. the number of carbon atoms(n) in the alkyl chains. Three regions of n can be distinguished, in which the change in n has different effect on the melting point. In the region I (n smaller than 3) the increase of n results in a rapid decrease of the melting temperature. In the region II (n between 4 and 7) there is no systematic relationship between the alkyl chain length and melting behavior. In the region III

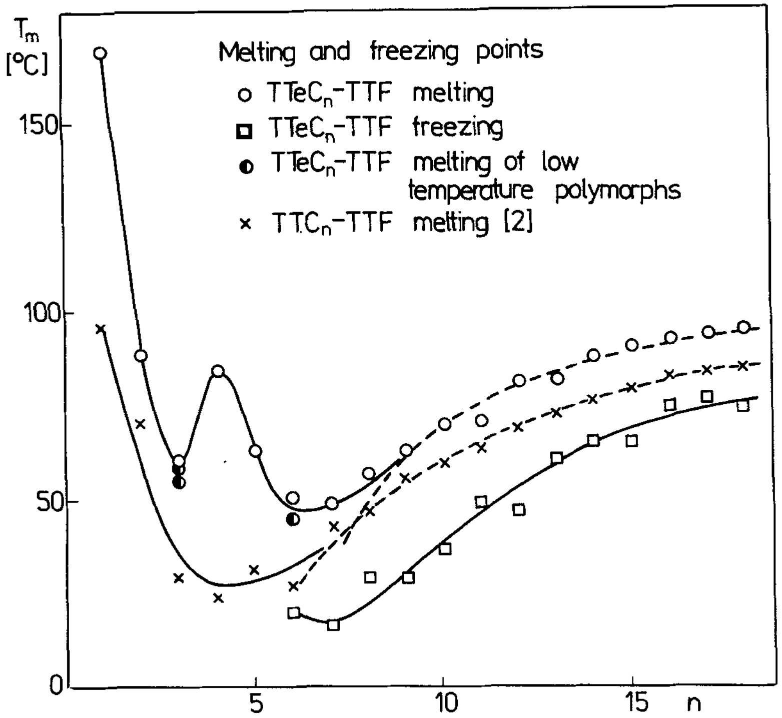

FIGURE 2 Melting and freezing points for TTeC$_n$-TTF series plotted as a function of n. Melting points for TTC$_n$-TTF are plotted for comparison. Broken lines for $n > 8$ for TTeC$_n$-TTF and $n > 6$ for TTC$_n$-TTF are fitted using the procedure described in the text. Solid lines for lower n and freezing points are guides for the eyes.

(n larger than 7) the melting temperature increases monotonically with increasing n.

The investigated compounds with the number of carbon atoms in the alkyl chain equal to 2,4,5,7,13,15 and 17 show single melting peaks irrespective of the proceeding thermal history. TTeC$_1$-TTF melts with decomposition since the melting point is too high. Other compounds show double peaks around the melting points except TTeC$_3$-TTF where complicated melting behavior is observed with at least three melting peaks.

As a typical example with two clearly resolved DSC maxima near the melting temperature, Figure 3 shows DSC traces for heating of TTeC$_6$-TTF. One can see a single melting maximum for the sample crystallized from solution and two well separated maxima of different relative intensity depending on the thermal treatment. Because the low temperature maximum can be considerably bigger than the high temperature one this behavior seems to be due to the polymorphism of the sample. Especially, after melting of the first polymorph, some subsequent recrystallization can be observed for heating runs after slow cooling as shown in Figure 3. This conclusion was confirmed by microscopic observations using a hot-stage polarizing microscope. In the TTeC$_6$-TTF samples crystallized from the melt two kinds of crystallites can be observed: needles and platelets. The bigger, quickly

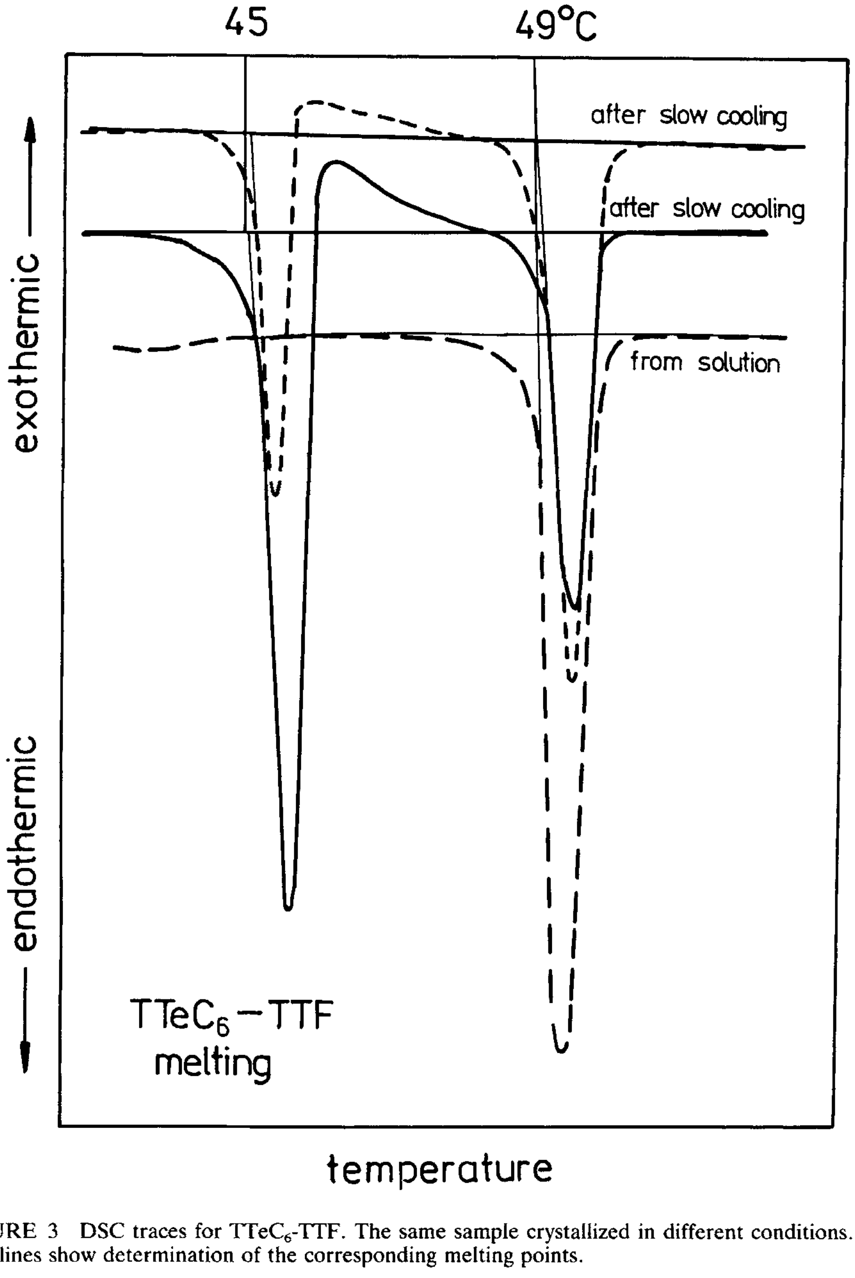

FIGURE 3 DSC traces for TTeC$_6$-TTF. The same sample crystallized in different conditions. Thin solid lines show determination of the corresponding melting points.

growing platelets melt first at a temperature corresponding to the low-temperature maximum. In spite of the different relative intensity of the two maxima the total entropy change calculated for the two transitions (taking into account the recrystallization) is within the experimental error the same in all cases.

The unusual phenomenon of melting of a low-temperature polymorph and subsequent recrystallization instead of thermodynamically plausible solid-to-solid transition seems to be due to the complicated molecular structure of these compounds[4,6,7] and their high molecular weight. Rearrangement of such molecules in the solid state necessary to form a different crystal structure is probably much too slow to take place during constant heating and the system undergoes transition to the high-temperature lowest-energy phase via liquid state.

When molten samples were cooled quickly enough the glassy state could be obtained and during subsequent heating glass transition and crystallization from the solid amorphous state was observed as in the case of TTC$_n$-TTF.[2] Formation of the glassy state during fast cooling depends on several factors, the most important being the presence of nucleation centers and nucleation rate and the enthalpy and entropy change on crystallization. Due to the first factor for $n < 10$ the small samples used in most of the experiments were relatively easily supercooled to form the glassy state even when the cooling rate was smaller than 20°/min. For $n > 7$ supercooling becomes more and more difficult due to the last factor.

Regardless of n the samples quenched in liquid nitrogen show glassy state below about −50°C and the crystallization from the solid glassy state between −40 − +30°C.

Enthalpy and Entropy Changes on Melting

Figures 4 and 5 present enthalpy and entropy changes on melting (denoted by ΔH and ΔS respectively) plotted vs. the alkyl chain length n. One can see that in the regions I and II, i.e. for short alkyl chains both ΔH and ΔS are small and show no systematic dependence on n while an approximately linear dependence on n is

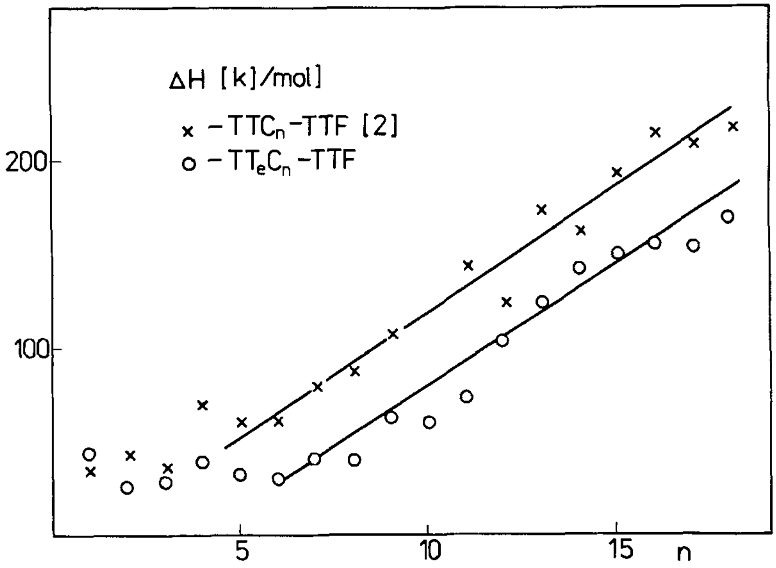

FIGURE 4 Enthalpy changes on melting for TTeC$_n$-TTF plotted vs. number of carbon atoms in the alkyl chains. Parameters of the solid line in region III ($n > 7$) are determined by the fitting procedure described in the text. Data for TTC$_n$-TTF with the fitted straight line are plotted for comparison.

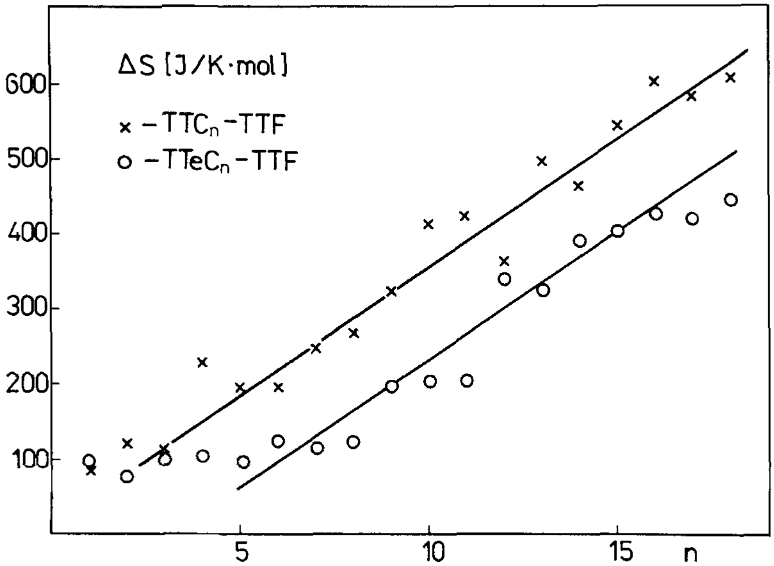

FIGURE 5 Enthropy changes on melting for TTeC$_n$-TTF plotted vs. number of carbon atoms in the alkyl chains n. The straight line is obtained by the fitting procedure described in the text. Data for TTC$_n$-TTF[2] and the corresponding fit are shown for comparison.

observed only for $n > 6$ in contrast to TTC$_n$-TTF.[2] It means that for small n packing of the molecules in the crystal lattice and consequently the lattice energy differs considerably as the alkyl chain length is changed. The crystal structure data available for $n = 1$ and 2[8,9] indeed show that not only alkyl chain but also TTF backbone packing is considerably different for these two compounds. The increased intermolecular Te-Te distance in TTeC$_2$-TTF as compared with TTeC$_1$-TTF is probably responsible for a reduction of the enthalpy change on melting as the alkyl group contribution is negligible in this case. Generally for $n = 1, 2$ and perhaps 3 packing of the TTF skeleton seems to dominate the properties of the crystal and its melting as due to its size and π-bond system its interactions with neighbor molecules must be stronger than interactions of the aliphatic chains (note that the length of an alkyl chain reaches the length of the central tellurium-substituted TTF skeleton at about $n = 7$).

In the region II ΔH and ΔS are small and practically constant (no systematic dependence on n is observed). Complex DSC traces and irregular melting point dependence on n suggest that there is a competition between packing of the tellurium, substituted TTF moiety and the alkyl groups. Low enthalpy of fusion and small differences of the lattice energy for different packing of the same molecules favor the existence of polymorphs in this region. In other words in the region of medium n there is some sort of equilibrium between the lowering of the free energy of the system due to optimum packing of the TTF skeleton and the increase of the free energy due to the fact that the packing manner of the TTF skeleton is not necessarily adjusted with the packing of the alkyl chains, as shown in the cases of

TTC$_n$-TTF[2,4,7] and TSeCn-TTF[6] where crystal structure analyses and thermal properties demonstrate the equilibrium.

Comparing with TTC$_n$-TTF[2] we note that an analogous behavior is observed for n between 3 and 6 but in this case melting point is almost n independent and enthalpy of fusion shows an irregular dependence on n. This difference between sulphur substituted and tellurium substituted compounds is caused by larger atomic radius of tellurium as compared with sulphur. In the case of sulphur the competition between packing of the TTF skeleton and the attached alkyl chains is not so strong.

In the region III (n higher than 6) a systematic increase of ΔH and ΔS is observed. It is indicative of the dominant influence of the packing of long alkyl chains. Packing of TTF moieties seems to be more or less fixed and gives a constant contribution to the thermodynamic parameters while the contribution of the alkyl groups increases with n. Hence in this region thermodynamic properties can be analyzed according to the formulae:

$$\Delta H = H_0 + nH \tag{1}$$

$$\Delta S = S_0 + nS \tag{2}$$

$$T_m = \frac{\Delta H}{\Delta S} = \frac{H_0 + nH}{S_0 + nS} \tag{3}$$

as it has been done for TTC$_n$-TTF group in Reference 2. However, because both in the case of TTC$_n$-TTF and TTeC$_n$-TTF an independent fitting of ΔH and ΔS plots resulted in a poor fit of melting points, we use here a different procedure which gives self-consistent data for H, H_0, S, S_0 and T_m.

Because the precision of T_m measurements is much better than that of ΔH or ΔS we start with fitting the T_m data. This can be done using the recast Equation (3):

$$\frac{T_{m,\infty}}{T_m - T_{m,\infty}} = an + b \tag{4}$$

where $T_{m,\infty} = \lim_{n\to\infty} T_m = H/S$, $a = (H_0/H - S_0/S)^{-1}$ and $b = S_0/Sa$.

If the Equation (3) holds, the left-hand side of Equation (4) should be linear in n. Thus, adjusting only one parameter $T_{m,\infty}$ to have a linear dependence on n in a required range of n ($n > 8$ in this case), we get from the least square fit of the experimental T_m (strictly speaking $T_{m,\infty}/(T_m - T_{m,\infty})$) a and b. In the second step we adjust the second parameter (H or S) to have good fit to experimental ΔH and ΔS data. This second adjustable parameter is enough because once its value is fixed we calculate immediately the third (S or H respectively using $T_{m,\infty}$) and H_0 and S_0 using a and b values. If the fit of experimental ΔH and ΔS data obtained using "the best H" is not satisfactory the $T_{m,\infty}$ value is corrected and the procedure is repeated.

This procedure performed using a suitable computer program gives in the case of TTeC$_n$-TTF for $n > 8$ the parameters:

$$H = 13.0 \text{ kJ/mol}, \qquad H_0 = -52 \text{ kJ/mol},$$

$$S = 33.3 \text{ J/Kmol}, \qquad S_0 = -105 \text{ J/Kmol and } T_{m,\infty} = 117°\text{C}$$

An important point in this analysis is that H_0 is negative which suggests that the Te substituted TTF skeleton may be packed more tightly at the expense of the free energy of the attached alkyl chains (the molecular fastener effect). It is surprising that this effect was not found in the case of the first molecular fasteners TTC$_n$-TTFs[2] (H_0 is reported to be positive). However reinterpretation of the results reported in Reference 2 using the procedure described above gives for TTC$_n$-TTF values of these parameters ($n > 6$)

$$H = 13.5 \text{ kJ/mol}, \qquad H_0 = -16 \text{ kJ/mol},$$

$$S = 34.6 \text{ J/K mol and } S_0 = -14 \text{ J/K mol}$$

to be compared with

$$H = 11.8 \text{ kJ/mol}, \qquad H_0 = 6.0 \text{ kJ/mol},$$

$$S = 32.2 \text{ J/K mol and } S_0 = 43.1 \text{ J/K mol}$$

reported in Reference 2.

It can be seen that after the recalculation the molecular fastener effect is also observed in TTC$_n$-TTF and that the data for sulphur and tellurium substituted compounds are consistant. It means that H and S values which describe the properties of the alkyl chains are in good agreement while H_0 and S_0 values which are related to the sulphur or tellurium substituted TTF skeleton are bigger (less negative) for TTC$_n$-TTF as can be expected taking into account the smaller atomic radius of sulphur atoms. However because of the simplified assumptions in Equations (1) and (2) interpretation of the parameters of these equations must be qualitative rather than quantitative.

It is interesting to compare these parameters with the data for long chain paraffins.[10] It seems appropriate to make a comparison with the enthalpy of alkyl chains calculated using the data for the paraffins with the number of carbon atoms equal to $2n$ multiplied by two (in order to have the number of chain ends equal to 4). The hexagonal α_H phase which involves rotational motion of the molecule about its long axis can not exist in TTeC$_n$-TTF since the motion is hindered if one end is fixed to the TTF moiety. Therefore we take the enthalpy change on β_T (triclinic) to liquid and β_m (monoclinic) to liquid transitions including α_H phase) for odd and even paraffins respectively.

Enthalpy changes on melting of aliphatic chains calculated in such a way give the slope which is similar ($H = 16$ kJ/mol) but the values of ΔH are 50–80 kJ/mol higher than these obtained for tellurium compounds and 10–40 kJ/mol higher than reported in Reference 2 for TTC$_n$-TTF. It also suggests that packing of the TTF skeleton decreases the energy of the sublattice of alkyl chains, i.e. the enthalpy changes of TTeC$_n$-TTF are smaller than these of the alkyl chains alone.

It should be noted that negative H_0 and the decrease of the enthalpy change as compared with the value for *n*-alkane indicate that packing of alkyl chains is not the best or that there is a strain in this sublattice. However such strains are not necessarily related to the molecular fastener effect which can be unambiguously confirmed by X-ray measurements only. Contribution of one CH_2 group to entropy (8.65 J/K mol) is also in the case of TTeC$_n$-TTF smaller than calculated in Reference 2 on the basis of possible conformations of the alkyl chains (9.13 J/K mol) and smaller than determined for paraffins (10.8 J/K mol) which is not surprising as not all conformations of the alkyl chains are allowed because of the steric hinderance of the TTF moiety and other chains.

CONCLUSIONS

The discussion of thermal properties of the TTeC$_n$-TTF group presented above shows that combining tellurium substituted TTF skeleton with the alkyl chains of different length we get a variety of thermal properties due to a competition between the alkyl chains and the TTF moiety, especially because of a larger size of tellurium atoms as compared with carbon.

This competition leads to a polymorphism of the crystalline samples of the compounds with alkyl chain length between 4 and 7. As neither TTF moiety nor alkyl chains are packed tightly, in an optimum way, in this case enthalpy and entropy changes on melting are small and does not depend on the chain length in a systematic way.

For the compounds with long alkyl chains ($n > 6$) the analysis of thermodynamic properties confirms the existence of the molecular fastener effect (i.e. fastening of the TTF skeletons and decreasing of the distances between them in the crystal structure by crystallization of the long alkyl chains).

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