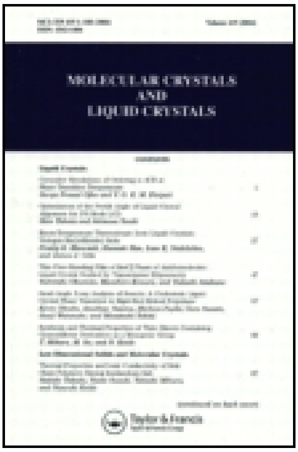

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Thermal Expansion of Tetrakis(alkylthio) tetrathiafulvalenes

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Thermal Expansion of Tetrakis(alkylthio) tetrathiafulvalenes

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The thermal expansion of tetrakis (alkylthio) tetrathiafulvalenes (abbreviated to TTC$_n$-TTFs. ($n = 1$–11)) having alkyl chains with n carbon atoms has been investigated from room temperature down to about 100 K by means of the four-circle X-ray diffraction technique. A linear thermal expansion parameter $\delta_l (= \Delta l/\Delta T)$ is suggested for correlating intermolecular interaction of TTC$_n$-TTF crystals. For the compounds with larger n, $n \geq 8$, the linear thermal expansion along the c-axis, δ_c, is smallest, while δ_b is larger and δ_a intermediate. This is consistent with the intermolecular interaction analyses for the crystal structure of TTC$_n$-TTF compounds. The molecular fastener effect is also found in the thermal expansion measurements. The contributions of the molecular fastener effect and the packing effect of the end C-atoms in the alkyl chains of TTC$_n$-TTF ($n = 8$–11) to the thermal expansion are discussed.

Keywords: Molecular fastener effect, thermal expansion, intermolecular interaction, molecular packing, TTF derivatives

INTRODUCTION

In recent years, the single component organic materials tetrakis (alkylthio) tetrathiafulvalenes (abbreviated to TTC$_n$-TTFs) and their homologues have been intensively investigated not only for their high electrical conduction itself but also for the carrier transport mechanism causing the high conductivity. TTC$_n$-TTFs are a series of TTF derivatives with four alkylthio substitutional groups as shown in Figure 1. We suggested a new phenomenon called the molecular fastener effect existing in the series of these compounds.[1] That is, the van der Waals attraction force between long side alkyl chain groups of successive molecules reduces the interplanar distance between adjacent TTF moieties so that the high conductivity is realized along the stacking direction of

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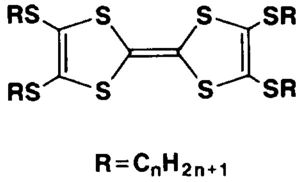


FIGURE 1 Molecular structure of TTC$_n$-TTF.

conjugated systems through the overlapping of the wave functions between adjacent molecules. For the TTC$_n$-TTFs with $n = 10, 11$, the conductivities reach $10^{-5}(\Omega\,\mathrm{cm})^{-1}$.[2]

Studies on the crystal structures,[3-6] electrical conductivities[2] and ionization energies[7] for these compounds have been carried out. In the previous paper[8], we reported the thermal properties of TTC$_n$-TTFs, where the essence of the molecular fastener effect was discussed from the thermodynamical point of view. In this paper we present the experimental results of the thermal expansion of TTC$_n$-TTFs crystals to discuss their correlation with intermolecular interaction using both usual linear thermal expansion coefficients α_l and absolute linear thermal expansion parameter δ_l ($= \alpha_l \times l$, l: lattice constant) suggested by us. We also discuss the molecular fastener effect existing in the thermal expansion properties of those compounds with longer alkyl chains, and its difference from packing effect.

EXPERIMENTAL

The syntheses and purifications of TTC$_n$-TTF ($n = 1$–11) were reported in the previous paper[9]. The single crystals were grown by recrystallization from a hexane-methanol solvent mixture. Two kinds of crystals were obtained for TTC$_8$-TTF and TTC$_9$-TTF, namely plates and needles, which have a small difference in the forms of alkyl chains between them.[3,4] We used plate polymorphs for the thermal expansion measurements. The temperature dependence of the lattice parameters for TTC$_n$-TTF ($n = 1$–11) was measured from room temperature down to about 100 K using the Rigaku Automated Four-Circle X-ray Diffractometer AFC-5 equipped with a liquid nitrogen flow system. All the lattice parameters measured were used directly for data analyses except for TTC$_1$-TTF, TTC$_2$-TTF and TTC$_7$-TTF which are monoclinic symmetry and were refined by URLAP program.[5]

RESULTS AND DISCUSSION

Crystal structures and intermolecular interaction of TTC$_n$-TTFs

In the TTC$_n$-TTF ($n = 1$–11) series, TTC$_1$-TTF, TTC$_2$-TTF and TTC$_7$-TTF are monoclinic crystals with space group $P2_1/n$, $P2_1/c$, and $P2_1/a$ respectively, while the other compounds are triclinic. Furthermore, they have different molecular configurations. In the compounds with $n = 1$–3, TTC$_n$-TTF molecules are boat type, while those with $n = 4$–11 are chair type. Even in the same chair molecular configuration, the angles between the alkyl chain direction and the normal to the TTF plane are different,[5,6] which is shown schematically in the fouth column in Table I, where the thick line indicates the TTF plane and thin line the alkyl chain. Hence interpretation of the thermal expansion is complicated since it is a function of the molecular structure, the crystal structure and the intermolecular interaction. In this paper we mainly discuss the relationship between the thermal expansion and intermolecular interaction for TTC$_n$-TTF ($n = 8$–11) because they are isostructural as shown in Figures 2(a) and 2(b). The TTF planes of the molecules are parallel to each other along the c-axis and the alkyl chain stretches nearly along the b-axis. The variation of lattice parameters a, b, c is very regular in comparison with TTC$_n$-TTF ($n = 1$–7) as shown in Table I. The differences of lattice parameter b in the successive compounds $[b(n+1)–b(n)]$ are 2.423, 2.442, and 2.55 Å for $n = 8$, 9 and 10, respectively, which correspond to the addition of a C—C single bond onto each end carbon atom, while the lattice parameters c and a are nearly the same but c and a of TTC$_{11}$-TTF are slightly shorter than those of TTC$_9$-TTF. The separations of atoms between successive molecules along the c-axis are much less than those along the b-axis, which can be seen from the statistical result of the atom-atom distances between neighboring molecules along the a-, b-, c-axes (Table II) as well as the data in Table I. So, it is clear that the intermolecular interaction caused by van der Waals forces is the strongest in the c-axis direction while that of the b direction is the weakest.

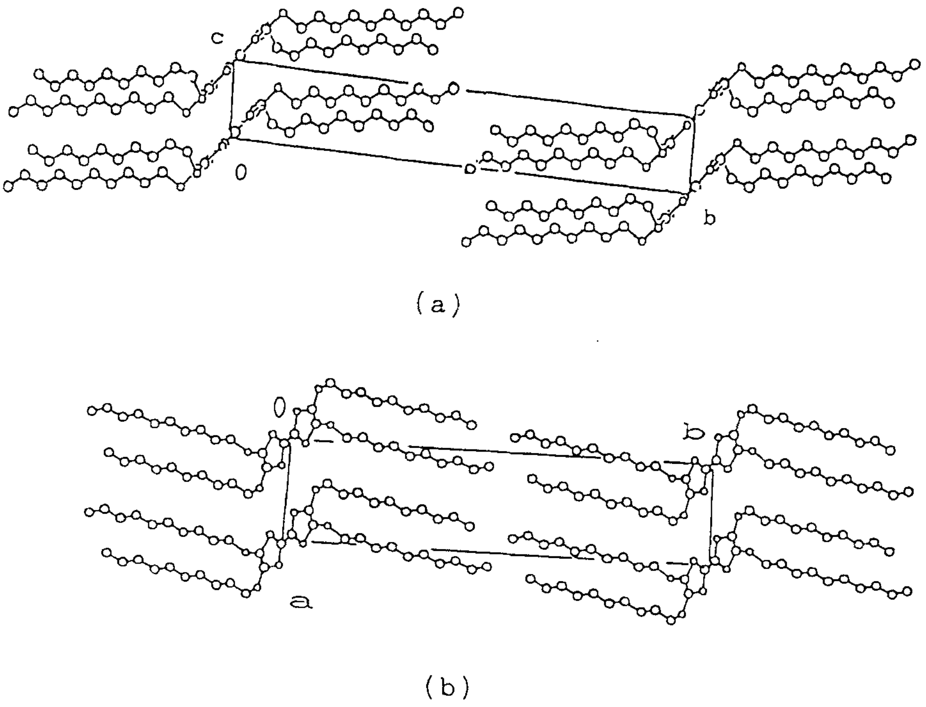
Linear thermal expansion coefficients α_l of TTC$_n$-TTFs

Figure 3 shows a typical pattern of linear thermal expansions along the a-, b-, and c-axes with temperature for TTC$_8$-TTF, where the ordinate, Δl, is defined as the difference of lattice parameters $l(= a, b \text{ or } c)$, $\Delta l(T) = l(T) - l(287.8\,\text{K})$. The lattice parameters have nearly linear temperature dependence with a change of slope about 220 K for all TTC$_n$-TTFs. This suggests a change in thermodynamical properties around 220 K for all the compounds investigated in the present experiments. Although

TABLE I

Crystal structure data at room temperature for TTC$_n$-TTFs ($n = 1$–11)

n	Space group	Z	Molecular configuration	a(Å)	b(Å)	c(Å)	V(Å^3)
1	$P2_1/n$	4		15.668(1)	7.804(1)	14.010(2)	1645
2	$P2_1/c$	4	boat	10.220(2)	8.759(2)	22.950(4)	2040
3	$P\bar{1}$	2		12.136(1)	13.156(1)	7.9415(9)	1222
4	$P\bar{1}$	1		9.023(7)	14.658(9)	5.397(4)	704
5	$P\bar{1}$	1	chair	9.031(3)	17.604(3)	5.367(4)	819
6	$P\bar{1}$	2		18.47(1)	18.516(8)	5.498(4)	1856
7	$P2_1/a$	2		8.797(2)	46.90(1)	5.141(1)	2059
8	$P\bar{1}$	1		7.8443(6)	28.095(3)	5.115(1)	1101
9	$P\bar{1}$	1	chair	7.8568(7)	30.518(2)	5.1192(8)	1199
10	$P\bar{1}$	1		7.850(3)	32.960(9)	5.115(4)	1291
11	$P\bar{1}$	1		7.840(3)	35.51(2)	5.097(8)	1387



(a)

(b)

FIGURE 2 Crystal strucutres of TTC$_{10}$-TTF projected on the *bc* plane (a) and *ab* plane (b). TTC$_n$-TTF ($n = 8, 9, 11$) have similar structures belonging to the same space group.

TABLE II

Comparison of the number of atom pairs whose separations are less than the reference values between two successive molecules along *a*, *b*, *c*-axis directions for TTC$_{10}$-TTF

Direction	S-S < 4.0 Å[‡]	S-C < 4.0 Å[‡]	C-C < 4.5 Å[‡]
a-axis	5	5	11
b-axis	0	0	2
c-axis	10	16	33

[‡] Reference values from the active radius of van der Waals forces

the origin of the change remains unsolved and has to be investigated using additional detailed information obtained from other kinds of experiments, we will discuss the thermal expansion properties hereafter based on the two temperature subregions. The linear thermal expansion coefficients α_l defined in Equation (1) are summarized in Table III;

$$\alpha_l = \frac{\Delta l}{l \times \Delta T}. \tag{1}$$

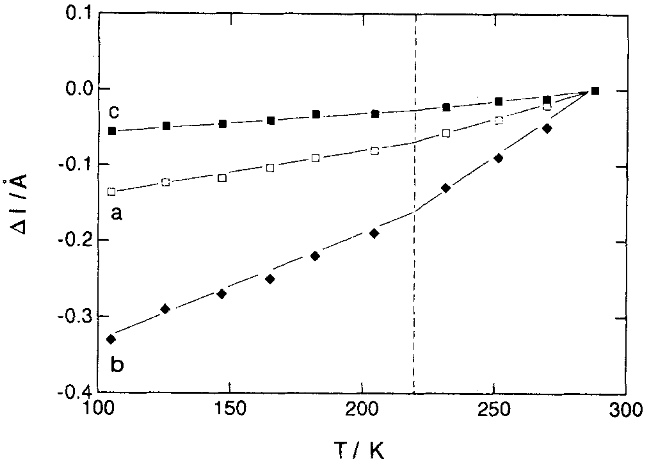


FIGURE 3 Temperature dependences of the differences of lattice parameters $l(=a, b, c)$, $\Delta l = l(T) - l(287.8\ \mathrm{K})$ for TTC$_8$-TTF. □:Δa, ◆:Δb, ■:Δc. The vertical dashed line denotes the temperature where the slopes of the Δl-T plots are changed.

From Table III it can be seen that all linear thermal expansion coefficients α_a, α_b, α_c in the high temperature region are larger than those in the low temperature region except TTC$_2$-TTF, TTC$_5$-TTF and TTC$_7$-TTF. For the latter two compounds this is presumably due to phase transitions.

TABLE III

Thermal expansion coefficients α_l and α_v of TTC$_n$-TTF single crystals (n = 1–11)

Compound	Temperature region/K	α_a /10^{-5}K^{-1}	α_b /10^{-5}K^{-1}	α_c /10^{-5}K^{-1}	α_v /10^{-4}K^{-1}
TTC$_1$-TTF	100–200	3.0	6.4	5.3	1.6
	200–290	6.1	9.6	8.7	2.7
TTC$_2$-TTF	100–200	6.1	4.7	3.9	1.5
	200–290	5.8	10.0	7.2	2.3
TTC$_3$-TTF	100–220	3.0	4.4	7.3	1.7
	220–290	5.6	7.8	11.1	3.0
TTC$_4$-TTF	100–220	4.7	9.0	4.7	1.9
	200–290	6.3	16.8	14.5	3.8
TTC$_5$-TTF	155–174	20.3	9.1	10.7	2.3
	220–290	7.8	15.6	5.2	3.0
TTC$_6$-TTF	230–290	5.4	7.7	13.4	2.7
TTC$_7$-TTF	100–220	15.9	2.6	2.6	2.0
	220–290	21.8	1.2	9.2	2.9
TTC$_8$-TTF	100–220	7.2	5.0	4.9	1.7
	220–290	12.9	8.2	7.5	2.9
TTC$_9$-TTF	100–220	4.9	4.0	6.4	1.7
	220–290	11.4	4.4	9.4	2.8
TTC$_{10}$-TTF	100–220	8.9	7.1	3.2	2.0
	220–290	12.1	9.0	6.2	2.9
TTC$_{11}$-TTF	100–220	5.9	4.4	6.3	1.9
	220–290	10.7	6.7	7.7	2.6

Hereafter we mainly discuss the thermal expansion behaviour of TTC_n-TTFs ($n = 8$–11) which have similar crystal structures and regular variation in lattice parameters. Their linear thermal expansion coefficients α_l are shown in Figure 4, which shows that $\alpha_a > \alpha_b > \alpha_c$ for TTC_8-TTF and TTC_{10}-TTF, and $\alpha_a > \alpha_c > \alpha_b$ for TTC_9-TTF and TTC_{11}-TTF. We cannot find any reasonable explanation for these results on the basis of their crystal structure and intermolecular interaction. We doubt whether thermal expansion coefficients α_l are appropriate parameters to relate the intermolecular interaction for these compounds. As α_l is a relative value as shown in Equation (1), even if the lattice constant b varies greatly with temperature (i.e. Δb is the largest) owing to the weaker intermolecular interaction, the ratio of $\Delta b/b$ would become quite small since b is much longer than c and a. In contrast, $\Delta c/c$ becomes relatively larger because the lattice constant c is much smaller. In fact the relative change represents the average value of two effects, namely the variation of intermolecular separation and the variation of molecular dimensions with temperature in the specified direction. These effects may well have different temperature dependences, and therefore attempts to relate thermal expansion coefficients to intermolecular interaction could be misleading.

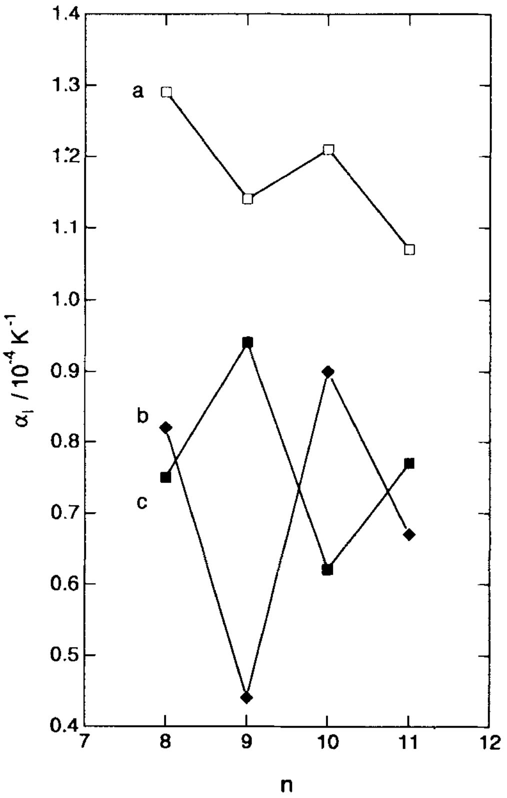


FIGURE 4 Linear thermal expansion coefficients α_a(□)α_b(◆) and α_c(■) for TTC_n-TTFs ($n = 8$–11) in the temperature region 220–290 K. The solid lines are guides for the eye.

Absolute linear thermal expansion parameter δ_l and intermolecular interaction

Thermal expansion depends on the sum of two contributions, each of which is proportional to the specific heat contribution corresponding to the phonon modes for intermolecular vibrations or intramolecular vibrations.[10] The typical magnitudes of intramolecular vibrational energies are $\sim 10^3\,\mathrm{cm}^{-1}$, so that the thermal expansion associated with these vibrations is not effective in the temperature range below room temperature. Intermolecular vibrational energies are smaller ranging ~ 10–$10^2\,\mathrm{cm}^{-1}$. This suggests that the main contribution to thermal expansion may be ascribed to intermolecular vibrations in the temperature region investigated in this work. (The accordion vibrations of alkyl chains whose energy ranges 200–300 cm^{-1} have to be taken into account for the thermal expansion although they are classified into the intramolecular vibrations.)

Taking into account the above consideration, we introduce the absolute linear thermal expansion parameter δ_l to separate intermolecular and intramolecular contributions from the observed thermal expansion of lattice parameters;

$$\delta_l = \alpha_l \times l = \Delta l/\Delta T. \qquad (2)$$

In this temperature range, we can neglect the contribution from intramolecular vibrations. The absolute thermal expansion parameter δ_l in Equation (2) means the change in intermolecular separation between adjacent molecules along the l-direction per degree rise in temperature. Generally speaking, δ_l would be larger for weaker intermolecular interaction. Figure 5 shows the absolute linear thermal expansion parameter δ_l of TTC$_n$-TTF ($n = 8$–11). It is clear that δ_c values are the smallest, δ_b are the largest, and δ_a intermediate for all these compounds with $n = 8$–11. These results are in good agreement with the analyses of the intermolecular interaction along these directions as shown in Table II. Hence it is the absolute linear thermal expansion parameter δ_l, rather than of α_l, that should be related to the intermolecular interactions for organic molecular crystals.

Molecular fastener effect and packing effect

The molecular fastener effect has been found in TTC$_n$-TTF and related compounds.[1,2] In the thermal expansion measurements, the molecular fastener effect is also apparent. Figure 5 shows the dependence of the linear thermal expansion parameter δ_l on the number of carbon atoms n in each alkyl chain, in the temperature region of 220–290 K. For the compounds with $n = 8$–11, δ_a and δ_c zigzag with the limits of $(8.4$–$10.1) \times 10^{-4}\,\text{Å}\mathrm{K}^{-1}$ and $(3.1$–$4.7) \times 10^{-4}\,\text{Å}\mathrm{K}^{-1}$ respectively. The fact that linear thermal expansion parameters δ_c and δ_a are smaller for TTC$_{10}$-TTF and TTC$_{11}$-TTF than those for TTC$_8$-TTF and TTC$_9$-TTF, respectively, further confirms the existence of molecular fastener effect, i.e. the longer alkyl side chains of TTC$_n$-TTF ($n = 10, 11$), which have only two more carbon atoms in each alkyl side chain than TTC$_n$-TTF ($n = 8, 9$) enhance the intermolecular interaction leading to the reduction in the absolute linear thermal expansion parameter along the c and a direction.

In addition, there exists a packing effect (even-odd effect) in the thermal expansion behavior for TTC$_n$-TTF ($n = 8$–11). Figure 5 shows that the zigzag phenomena of δ_l

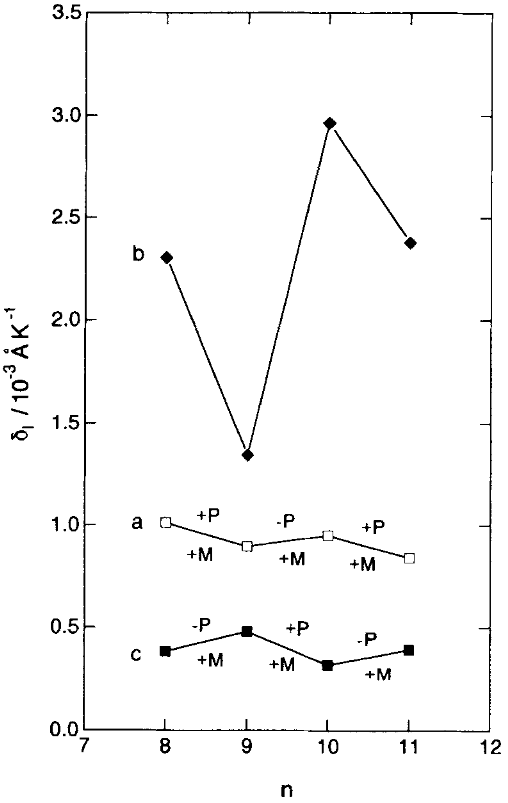


FIGURE 5 Absolute linear thermal expansion parameters δ_a(□), δ_b(◆) and δ_c(■) for TTC_n-TTFs ($n = 8$–11) in the temperature region 220–290 K. *M* and *P* mean the contributions of the end C-atoms to δ_l owing to the molecular fastener effect and packing effect, respectively (see Text). The solid lines are guides for the eye.

with *n* are even more typical than those in the melting behavior of these compounds[8] and 1- or 2-*n*-alkylnaphthalenes.[11] Studies on crystal structure show that packing directions of the end carbon atom in alkyl chain of TTC_8-TTF and TTC_9-TTF are different from each other but they are the same as those of TTC_{10}-TTF and TTC_{11}-TTF, respectively, which may be the reason for the even-odd difference in thermal expansion properties. As shown in Figure 5 the even-odd difference in the *b*-axis direction is much larger than those along the *a*- or *c*- axis direction. There are two possible reasons; one is that the original intermolecular interaction along the *b*-axis is much weaker than the *c* and *a* directions. This would make the *b*-axis more sensitive to chain length than the *a* and *c* directions. Another reason is that unlike in the *a* and *c* directions, the end methyl group in each alkyl chain is the only group located at the boundary of the neighboring molecule in the *b* direction. So, much more obvious even-odd difference along the *b*-axis may also further confirm that one of the most important factors determining intermolecular interaction is the position of those groups located in the boundary of molecules, not those far from the boundary. We can imagine that all the states of boundary atoms are changed for the *b* direction when a methylene group is added to the alkyl chain, while all the states of boundary atoms are not changed except the end methyl group itself for the *a* and *c* directions. This is why the zigzag phenomena in the *b*-axis are so much more marked than in the *a*- and *c*-axes. Nevertheless, the zigzag phenomena of the *c* and *a* directions caused by the end methyl group in thermal expansion behavior are also very obvious. Figure 5 shows that the zigzag behavior of δ_c is in the opposite direction to that of δ_b and δ_a presumably due to the packing direction of the end methyl group in the space, i.e. the direction favorable to the *a*- and *b*-axes is unfavorable to the *c*-axis for intermolecular interaction. On the other hand, the direction unfavorable to the *a*- and *b*-axes is favorable to the *c*-axis.

Next, we compare the influence of the packing effect and molecular fastener effect of end methyl group on linear thermal expansion parameters, δ_c and δ_a. As a methylene group is added to each alkyl chain of TTC$_n$-TTF, we suggest that there are two forces which are changed. One is the molecular fastener force which always increases the intermolecular interaction along *c*- and *a*-axes indicated in Figure 5 by $+M$. Another is the force caused by the packing effect of end methyl group which may increase or decrease the interaction, depending on the packing direction of end methyl groups in space, which is indicated in Figure 5 by $+P$ (enhanced intermolecular interaction) or $-P$ (decreased intermolecular interaction). First, we discuss the influence of these two factors on linear thermal expansion along the *c*-axis direction, which is the direction of the strongest intermolecular interaction among these axis directions. As shown in Figure 5, $\delta_{c,9}$ (i.e. δ_c for TTC$_9$-TTF) and $\delta_{c,11}$ are larger than $\delta_{c,8}$ and $\delta_{c,10}$ respectively in the temperature region 220–290 K and their differences are all 0.9×10^{-4} ÅK^{-1}. This means that the packing direction of the end methyl groups of the compounds with an odd number or carbon atoms in each alkyl chain (i.e. TTC$_9$-TTF and TTC$_{11}$-TTF) is unfavorable to the intermolecular interaction along the *c*-axis direction. So, in Figure 5 it is "$-P$" from TTC$_8$-TTF to TTC$_9$-TTF, and TTC$_{10}$-TTF to TTC$_{11}$-TTF. The packing effect of the end methyl group reduces the intermolecular interaction force even though one more carbon atom in each alkyl chain would increase that by the intermolecular fastener force. As the number of C-atom is even, say TTC$_{10}$-TTF, its $\delta_{c,10}$ is much smaller than $\delta_{c,9}$. This means both molecular fastener effect and packing of end C-atom would all be favorable to increase intermolecular interaction of *c*-axis direction as shown in Figure 5 ($+M$ and $+P$). The difference of $\delta_{c,10}$ and $\delta_{c,9}$ is 1.6×10^{-4} ÅK^{-1}. Based on these considerations we have the following simultaneous equations:

$$\begin{cases} M_c + P_c = -1.6 \times 10^{-4}\,\text{Å}\,\text{K}^{-1} \\ M_c - P_c = 0.9 \times 10^{-4}\,\text{Å}\text{K}^{-1}, \end{cases} \tag{3}$$

where M_c, P_c mean the total contribution of four end methyl groups in four alkyl chains of each molecule to the absolute linear thermal expansion parameter along the *c*-axis direction, δ_c, owing to the molecular fastener effect and packing effect, respectively, From Equation (3) we can obtain;

$$M_c = -0.4 \times 10^{-4}\,\text{Å}\,\text{K}^{-1}$$

$$P_c = -1.3 \times 10^{-4}\,\text{Å}\text{K}^{-1}.$$

So, it is clear that the packing effect of end methyl is much stronger than the molecular fastener effect of the end methyl for the thermal expansions of these compounds in the c direction. In fact, we can also get the M_c value as follows: $\delta_{c,10}$ and $\delta_{c,11}$ are all $0.7 \times 10^{-4}\,\text{Å}\text{K}^{-1}$ less than $\delta_{c,8}$ and $\delta_{c,9}$ respectively. Taking into account that the packing directions of end C-atom of TTC$_8$-TTF and TTC$_9$-TTF are the same as those of TTC$_{10}$-TTF and TTC$_{11}$-TTF respectively, we can suppose that the difference $0.7 \times 10^{-4}\,\text{Å}\text{K}^{-1}$ is only caused by the molecular fastener effect of the last eight carbon atoms in four alkyl chains of each molecule. So, for four end C-atoms it is $-0.4 \times 10^{-4}\,\text{Å}\text{K}^{-1}$.

For the thermal expansion of a-axis, the molecular fastener effect has also been observed in the result that $\delta_{a,10}$ and $\delta_{a,11}$ are 0.6 or $0.5 \times 10^{-4}\,\text{Å}\text{K}^{-1}$ less than $\delta_{a,8}$ and $\delta_{a,9}$ respectively. This means that TTC$_{10}$-TTF and TTC$_{11}$-TTF do not expand so readily as TTC$_8$-TTF and TTC$_9$-TTF because of the increase of intermolecular interaction forces caused by the molecular fastener effect. We assume P_a is the contribution of packing effect of the end C-atoms to δ_a, and M_a is that of the molecular fastener effect of the end C-atoms just like P_c and M_c above. We would also have the following simultaneous equations according to the measured data:

$$\begin{cases} M_a + P_a = -1.2 \times 10^{-4}\,\text{Å}\,\text{K}^{-1} \\ M_a - P_a = 0.6 \times 10^{-4}\,\text{Å}\text{K}^{-1}. \end{cases} \tag{4}$$

Thus, we have solutions as follows:

$$M_a = -0.3 \times 10^{-4}\,\text{Å}\,\text{K}^{-1}$$
$$P_a = -0.9 \times 10^{-4}\,\text{Å}\text{K}^{-1}.$$

The absolute values of P_a and M_a are a little less than those of P_c and M_c, which is reasonable because the lattice parameters a of TTC$_n$-TTF ($n = 8$–11) are about 2.7 Å longer than c and the intermolecular interaction force caused by end C-atoms along a-axis direction should be weaker than that along c-axis.

Bearing in mind that as the chain length is increased the molecular fastner effect is accumulative whereas the packing effect is determined by the terminal methyl, it is to be expected that the zigzag phenomena would gradually reduce with increasing n. Thus had measurements of thermal expansion been made for $n > 11$, the oscillation in δ_c and δ_a would steadily reduce.

Volume thermal expansion coefficient α_v

Next we discuss the n dependence of the volume thermal expansion coefficient α_v;

$$\alpha_v = \frac{\Delta V}{V \times \Delta T}. \tag{5}$$

The volume thermal expansion coefficients α_v in the high temperature region are without exception larger than those in the low temperature region (Table III). Figure 6 shows that there is peak at $n = 4$ in the α_v vs. n curve. Comparing the behavior of the volume thermal expansion with that of the melting point for TTC$_n$-TTF with $n = 1$–11, shown in the inset in Figure 6, we notice that the peak in α_v at $n = 4$ coincides with the

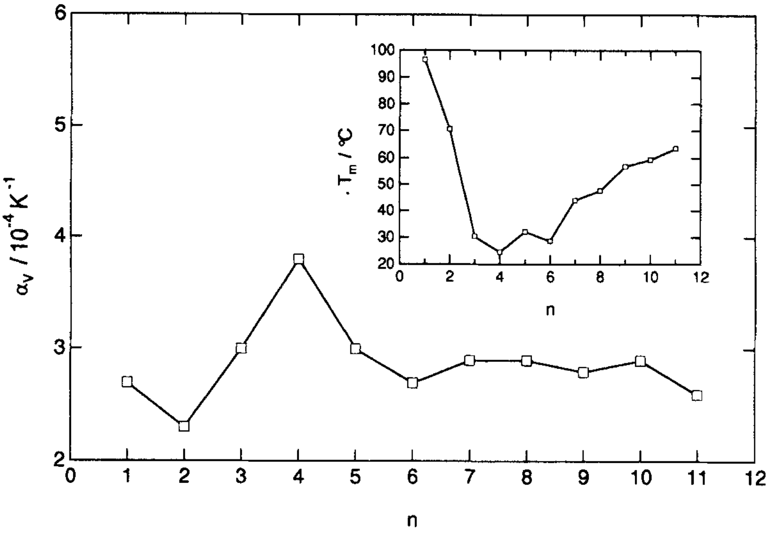


FIGURE 6 C-atom number *n* dependence of volume thermal expansion coefficient α_v for TTC$_n$-TTFs ($n = 8$–11) in the temperature region 220–290 K. The *n* dependence of the melting point is shown in the inset for comparison.

minimum in the melting point curve. Namely, the compounds with $n = 3, 4, 5$ having lower melting points are just those compounds which have larger volume thermal expansion coefficients (α_v). For the compounds with longer alkyl chains both curves in Figure 6 tend to change smoothly. This means the alkyl chains have already dominated intermolecular interactions in the crystal structure. The reverse correlation of these two properties is not unexpected because both melting behavior and volume thermal expansion coefficient reflect the intermolecular interaction. In general, strong intermolecular interaction enhances the melting point and reduces thermal expansion.

However, unlike the absolute linear thermal expansion parameters δ_l, it is not necessary to consider the direction of the intermolecular interaction force for the volume thermal expansion α_v. So the zigzag behavior of α_v would become very small or even completely cancelled out because the zigzag behavior of the *c*-axis thermal expansion is in the opposite sense to that of the *a*- and *b*-axis, as mentioned above. For the same reason, the zigzag behavior in melting points would also be smaller than that in linear thermal expansion δ_c, δ_a, δ_b for the compounds with $n = 8$–11.

CONCLUSION

The experimental results on the thermal expansion properties of TTC$_n$-TTFs suggest that intermolecular interaction in organic molecular crystals should be correlated with the absolute linear thermal expansion parameter δ_l instead of the linear thermal expansion coefficient α_l. For the compounds with long alkyl chains ($n = 8$–11), the linear thermal expansion parameter δ_c is the smallest in the close packing direction of

C_6S_8 moieties, while in the direction of the extended alkyl chain δ_b is the largest and δ_a^4 is medium, which is consistent with the intermolecular interaction along these axis directions.

After adding alkylthio groups onto the TTF moities, the original stronger intermolecular interaction in TTF crystal is disturbed and the decrease of intermolecular interaction force makes the volume thermal expansion coefficient α_v increase, and the melting point decreases rapidly until TTC_n-TTF. With further increase of n, the role of alkyl chain in intermolecular interaction is gradually enhanced from $n = 5$ to 7 and makes α_v decrease markedly. When $n > 8$, the alkyl chains finally dominate the intermolecular interaction owing to the molecular fastener effect of long alkyl chains and α_v tends to change more smoothly just like their melting point behavior.

Studies on the thermal expansion properties confirm the existence of the molecular fastener effect both in the *c*- and *a*-axis direction for the compounds with long alkyl chains ($n = 8$–11). Furthermore, analysis of the effect of adding an extra methylene in each alkyl chain on thermal expansion parameter δ_t shows that the packing effect is stronger than the molecular fastener effect for both in *c* and *a* direction, and these two effects along the *c*-axis are obviously stronger than those in the *a*-axis direction respectively, which is also in good agreement with crystal structure analyses for these compounds.

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