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Sander Van Smaalen [a] , Jan L. De Boer [a] , Cor Haas [a] & Jan Kommandeur [a]
[a] Laboratories of Inorganic and Physical Chemistry, Material Science Centre, University of Croningen, Nijenborgh 16, 9747 AC, Groningen
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ANISOTROPIC THERMAL EXPANSION IN TCNQ SALTS.

SANDER VAN SMAALEN, JAN L. DE BOER, COR HAAS and JAN KOMMANDEUR
Laboratories of Inorganic and Physical Chemistry, Material Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen

Abstract Crystals containing stacks of TCNQ-ions have roughly thermal expansion coefficients along the stack, which are three times the values at right angles to it. It is shown that a simple degree of freedom argument, taking into account the librational modes can explain this phenomenon.

1. INTRODUCTION

Morpholinium TCNQ salts belong to the class of organic segregated stack compounds. These salts are known for their anisotropy in many of their physical properties. One of these properties, considered in this paper, is the thermal expansion.

A considerable anisotropy in the thermal expansion was noted by Blessing and Coppens[1] for TTF(TCNQ) and by Guy et al.[2] for TMTSF ReO_4. We report here a similar anisotropy for a set of morpholinium TCNQ salts. We also give a full analysis of this effect.

Lonsdale[3] was the first to point out that librations may lead to anisotropic thermal expansion. In this paper we show that for stacked plate-like molecules, like TCNQ, the librations lead to an anisotropy in the thermal expansion of about a factor of three. Also, several arguments are given which show that the quasi-one-dimensional electron band does not play any role in the thermal expansion.

2. MEASUREMENTS AND RESULTS

The thermal expansion is determined by determination of the lattice parameters of morpholinium TCNQ single crystals as a function

of temperature. From the lattice parameters at two different temperatures, T_1 and T_2, one obtains a mean-value for the thermal expansion tensor for that range of temperatures by,

$$\alpha_{ij} = \tfrac{1}{2}\{G_{ij}(T_2) - G_{ij}(T_1)\}\,(T_2 - T_1)^{-1} \qquad (2\text{-}1)$$

where $G_{ij}(T)$ is the metric tensor belonging to the lattice parameters at temperature T. It has the components $G_{ij}(T) = \bar{a}_i \cdot \bar{a}_j$, where the $\bar{a}_i$ (1,2,3) are the unit-cell vectors. In order to analyse these results the principal components and principal axes of α are determined[4,5].

Most morpholinium TCNQ salts crystallize in space group $P\bar{1}$. This means that there are no restrictions on the components of the thermal expansion tensor. For higher symmetries it is required that the principal axes lie in certain crystallographically unique directions.

In the crystals, the TCNQ molecules are arranged in stacks, with the planes of the molecules more or less perpendicular to the stack direction. The stacks are arranged parallel to each other. Only one of the compounds we considered, $HEM(TCNQ)_2$, has stacks in two different, but crystallographically equivalent, directions.

These structural features give rise to the idea that tensorial physical properties, such as thermal expansion, have a unique behaviour in the stack direction, in contrast to their behaviour in the plane perpendicular to the stack. Therefore, in the analysis of the experiment results we will focus our attention on the relation between the principal axes and components of the thermal expansion tensor and the stack direction in the crystals.

Lattice parameters were determined on a NONIUS CAD-4 diffractometer by least-square analysis of twenty to twenty-five accurately measured high order reflections. For each temperature and each of the compounds these values are listed in table I. From the lattice parameters the mean thermal expansion tensor was calculated according to equation (2-1). Subsequently the principal

Table 1 Lattice parameters at various temperatures of some TCNQ salts and some structural properties

compound[1]	space group	stack[2] axis	φ(°)[3]	temp. (K)	lattice parameters a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
METM(TCNQ)$_2$[p]	$P\bar{1}$	c	.9	96	15.425(3)	14.905(4)	6.371(3)	91.08(3)	101.47(3)	107.43(2)
				196	15.459(2)	14.950(4)	6.437(1)	90.96(2)	101.67(1)	107.47(1)
				297	15.513(3)	15.022(2)	6.516(1)	90.72(1)	101.91(1)	107.47(1)
MPM(TCNQ)$_2$[p]	$P\bar{1}$	c	4.5	96	7.823(4)	28.380(6)	6.400(4)	90.50(3)	75.58(5)	91.46(3)
				297	7.864(1)	28.529(4)	6.563(1)	90.33(1)	75.72(1)	91.42(1)
MEM(TCNQ)$_2$[q]	$P\bar{1}$	c	10.6	96	13.920(4)	7.518(1)	13.114(9)	91.08(2)	80.66(4)	105.30(2)
				173	14.005(2)	7.532(1)	13.208(4)	91.56(2)	80.91(2)	105.47(1)
				229	14.074(2)	7.537(1)	13.297(4)	91.94(2)	80.95(2)	105.57(1)
				290	14.139(4)	7.543(1)	13.423(4)	92.22(2)	80.74(3)	105.69(2)
MEM(TCNQ)[p]	$P\bar{1}$	c	11.1	99	19.598(6)	13.426(4)	6.719(3)	90.25(3)	96.36(3)	82.90(2)
				297	19.744	13.458	6.870	90.90	96.86	83.22
EBM(TCNQ)$_2$[p]	$P2_1/c$	101	8.14	96	7.876(4)	28.503(11)	15.525(6)	90	123.81(4)	90
				253	7.947(2)	28.518(5)	15.805(5)	90	123.86(3)	90
				290	7.967(2)	28.528(5)	15.886(3)	90	123.86(2)	90
HMM(TCNQ)$_2$[p]	P4	a and b	19.3	103	6.902(4)	6.902(4)	52.724(36)	90	90	90
				297	7.032(3)	7.032(3)	52.915(17)	90	90	90
TTF(TCNQ)[r]	$P2_1/c$	b	34	40	12.210(5)	3.729(1)	18.343(6)	90	104.38(2)	90
				100	12.228(6)	3.756(1)	18.378(10)	90	104.42(4)	90
				295	12.302(6)	3.817(1)	18.449(9)	90	104.49(5)	90

1. The abbreviations of the compound names stand for:
   METM is methyl ethyl thio morpholinium;
   MPM is methyl propyl morpholinium;
   MEM is ethyl morpholinium;
   MEM is methyl ethyl morpholinium;
   EBM is ethyl n-butyl morpholinium;
   HMM is methyl morpholinium;
   TTF is tetra thiofulvalene;
   TCNQ is tetra cyano quino dimethane.
2. Crystallographic direction of the stack axis
3. φ is the angle between the normal on the plane of the molecule and the stack axis. There are two independant TCNQ molecules in the unit cell. The reported value is the mean for those two TCNQ molecules.

Structures of these compounds are reported elsewhere:

p. R.J.J. Visser, to be published

q. B. van Bodegom, J.L. de Boer, Acta Cryst. B37, 119 (1981)

r. reference 1.

Table II Principal components of the mean thermal expansion tensor of TCNQ salts between two temperatures, calculated from X-ray data

compound	T_1(K)	T_2(K)	principal components $\alpha_1\ 10^5$	$\alpha_2\ 10^5$	$\alpha_3\ 10^5$	α_3/α_2	$\phi(°)$ [1]
METM(TCNQ)$_2$	96	196	1.22	2.93	10.5	3.6	9.4
	96	297	1.42	5.20	11.8	2.3	12.1
MPM(TCNQ)$_2$	96	297	2.48	2.68	13.2	4.9	11.4
HEM(TCNQ)$_2$	96	173	-2.21	7.86	14.3	1.8	37.2
	96	229	-2.12	8.35	14.6	1.7	32.3
	96	290	-1.29	8.22	14.6	1.8	23.0
MEM(TCNQ)	99	297	-0.50	4.47	12.4	2.8	15.4
EBM(TCNQ)$_2$	96	253	0.34	5.02	12.0	2.4	15.9
	96	290	0.46	5.22	12.6	2.4	15.3
HMM(TCNQ)$_2$ [2]	103	297	1.87	9.80	9.80		$\bar{e}_1$//c
TTF(TCNQ) [3]	40	100	1.98	3.45	11.2	3.2	0
	40	295	1.99	3.05	9.4	3.1	0
	100	295	1.77	3.13	8.7	2.8	0

1. ϕ is the angle between the third principle axis and the stack axis.
2. The exact collinearity of the first principle axis and the c-axis is determined by symmetry.
3. Symmetry requires one of the principle axes to be along the stack axis. This happens to be the third principle axis.

axes and principal components were determined[4,5]. The principal components of the thermal expansion tensor are presented in table 2. In the last but one column of table 2 we give the ratio of the third and the second principal components, a quantity we take as a measure for the anisotropy. The last column of table 2 contains the value for the angle between the third principal axis (that with the highest eigenvalue) and the stack axis. From the results presented in table 2 it appears that for all compounds investigated the third principal axis of the thermal expansion tensor has a direction close to the stack axis, i.e., the thermal expansion in the direction of the stack axis is large in all cases. In this respect, it should be noted that for EBM(TCNQ)$_2$, HMM(TCNQ)$_2$ and TTF(TCNQ) symmetry requires some of the principal axes to have a specific direction.

3. THEORY OF THE ANISOTROPY OF THE THERMAL EXPANSION

An estimate of the anisotropy of the thermal expansion of a crystal is obtained immediately by the following argument.

It is well-known that thermal expansion finds its origin in the cubic term in the intermolecular potential. A dimensional analysis leads then directly to the following equation for the linear thermal expansion coëfficient:

$$\alpha = \frac{1}{r}\frac{\Delta r}{\Delta T} (:) \frac{1}{r}\frac{d}{f^2} k_B \qquad (3\text{-}1)$$

where f and d are respectively d second order and a third order derivative of the lattice energy with respect to some structural parameter.

In a stacked crystal, normal to the plane of the molecules there are two librational and one translational degree of freedom contributing to the thermal expansion. In the plane of the molecule only the translational mode will contribute. One can argue that for each degree of freedom a term of equal magnitude of the form (3-1) contributes to the thermal expansion coëfficient. From this analysis it is expected that

$$\alpha_{//} : \alpha_{\perp 1} : \alpha_{\perp 2} = 3 : 1 : 1 \qquad (3\text{-}2)$$

A similar argument gives for rigid cylindrically shaped molecules with a small diameter:

$$\alpha_{//} : \alpha_{\perp 1} : \alpha_{\perp 2} = 1 : 2 : 2 \qquad (3\text{-}3)$$

where // means parallel to the cylindrical axis.

A more accurate analysis of the anisotropy is obtained by considering the lattice energy explicitly.

An approximate expression for the potential energy of the stack is

$$E_{pot} = \sum_i \left\{ \frac{1}{2} f u_i^2 + \frac{1}{2} g \Psi_i^2 + \frac{1}{6} d u_i^3 + \frac{1}{2} h u_i \Psi_i^2 \right\} \qquad (3\text{-}4)$$

where u_i is the deviation of the distance between molecules i and i-1 from its value by $T \equiv 0$. Ψ_i is the difference of the rotation angles of molecule i and i-1 (See figure 1). The parameters f, g, d and h are second- and third order derivatives of the energy, evaluated at $\Psi = 0$ and $u = 0$.

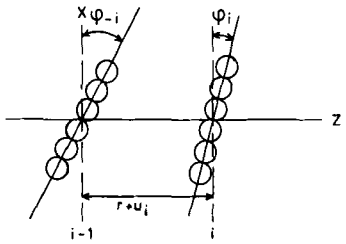

Fig. 1. Projection along y of two molecules of a stack of flat molecules, with their plane perpendicular to the stack (z-axis is stack axis)

The linear thermal expansion is determined by the mean elongation of the intermolecular distance, <u>. An expression for this quantity is obtained by putting the derivative of the energy (3-4) with respect to u_i equal to zero and then to replace each term in the resulting equation by its average value. One obtains:

$$\langle u \rangle = -\frac{1}{2} \frac{d}{f} \langle u^2 \rangle - \frac{1}{2} \frac{h}{f} \langle \Psi^2 \rangle \qquad (3\text{-}5)$$

The first term in (3-5) gives the contribution arising from the translational motion to the thermal expansion. The second term gives the contribution from the libration.

The mean square amplitudes are calculated approximately as a function of temperature by using only the harmonic part of the potential (3-4), together with the expression for the kinetic energy of the chain. The resulting set of coupled harmonic oscillator equations of motion can be solved exactly. The high temperature limit of this solution gives,

$$\langle u^2 \rangle = \frac{k_B T}{f} \qquad (3\text{-}6a)$$

and,

$$\langle \psi^2 \rangle = \frac{k_B T}{g} \qquad (3\text{-}6b)$$

It is noted that for the values of f,g, the mass of the molecule and the moment of inertia of the molecule there is only a small difference between the exact solution and the result obtained from equation (3-6), above a temperature of 100 K. Since we are interested in thermal expansion above this temperature only, the high temperature form (3-6) will be used for all calculations. To be able to calculate the anisotropy of the thermal expansion we also calculate the expansion in the directions x and y, perpendicular to the stack. Now U is defined as the increase of the intermolecular distance along the x and y axis, for an arrangement of the molecules as shown in figure 2. The calculation proceeds exactly as the derivation of formulas for the expansion along the stack (z-axis). The result is:

$$\langle u_\alpha \rangle = -\frac{1}{2} \frac{d_\alpha}{f_\alpha} \langle u_\alpha^2 \rangle \qquad (3\text{-}7)$$

and ($\alpha = x, y$)

$$\langle u_\alpha^2 \rangle = \frac{k_B T}{f_\alpha} \qquad (3\text{-}8)$$

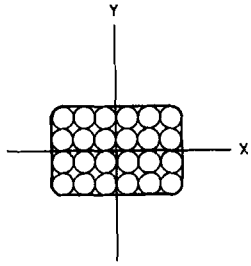

Fig. 2. Projection along z of one molecules of a stack of flat molecules.

The effect of librations on the expansion along x and y is considered elsewhere[5].

First, a stylized model for the molecules is considered, which enables us to calculate the anisotropy of the thermal expansion analytically. As shown in the figures 1 and 2, the molecules are considered to be a rectangular array of mxn atoms. The interaction of two adjacent molecules along the stack is described by considering only the interaction between atoms with the same x- and y coordinate. For a rotation around the y-axis this interaction for a pair of such atoms is (fig. 1):

$$V_{i-1,i} = \frac{1}{2}a(u_i + x\Psi_i)^2 + \frac{1}{6}b(u_i + x\Psi_i)^3 \qquad (3\text{-}9)$$

where a and be represent the harmonic and anharmonic interactions between the atoms. The potential energy of the stack is now obtained by summing $V_{i-1,i}$ over the mxn atoms and over the molecules in the stack:

$$E_{pot} = nm \sum_i \left\{ \frac{1}{2}a\, u_i^2 + \frac{1}{6}a\, l^2\, \Psi_i^2 + \frac{1}{6}b\, u_i^3 + \frac{1}{6}bl^2\, \Psi_i^2\, u_i \right\} \qquad (3\text{-}10)$$

where l is one half of the length of the molecule along x.
(The result (3-10) is an approximation for the sum over n and m for large n and m.)

Combining equations 3-10 and 3-4 expressions are obtained for the derivatives f, d, g and h in terms of a, b, n, m and the dimensions of the molecule, l. Substituting these expressions in the equations (3-5) and (3-6) (bearing in mind that there are two

librational modes contributing along the stack), one obtains for the mean elongation along z:

$$\langle u_z \rangle = \frac{-3b}{2\,nma^2}\, k_B\, T \qquad (3\text{-}11)$$

Analogous calculations for the expansion along x and y give,

$$\langle u_x \rangle = \frac{-b}{2na^2}\, k_B\, T \qquad (3\text{-}12a)$$

$$\langle u_y \rangle = \frac{-b}{2ma^2}\, k_B\, T \qquad (3\text{-}12b)$$

To obtain the thermal expansion coëfficient in a particular direction the mean elongation in this direction must be divided by the appropriate length per molecule. Neglecting the differences in Van der Waals radii and atomic radii, the ratio of the lengths along x, y and z is, m : n : 1. Substituting this in (3-1) shows that $\alpha_x = \alpha_y$ ($\alpha_\perp$) and for the anisotropy, one then obtains:

$$a_{//} = 3\alpha_\perp \qquad (3\text{-}13)$$

To obtain a more accurate description of the thermal expansion a more realistic model for the molecules and the intermolecular interaction potential is required. As a molecule we use TCNQ with the configuration taken from the crystal structure of HBTM $(TCNQ)_2$ [6]. The interaction of two of such molecules is described by the method of atom-atom potentials[7]. The parameters in this potential are those derived by Hermans et al.[8]

Using this potential the derivatives f, g, h and d were calculated numerically (finite difference method). With these values for the derivatives the linear thermal expansion coëfficients could be calculated with equations (3-1), (3-5) and (3-6). The results are given in table 3.

Table III Calculated linear thermal expansion coefficient.

Quantity	value
α_z(trans)	3.26×10^{-5} K^{-1}
α_z(libr,x)	3.56×10^{-5} K^{-1}
α_z(libr,y)	5.22×10^{-5} K^{-1}
α_z	12.05×10^{-5} K^{-1}
α_x	5.79×10^{-5} K^{-1}
α_z/α_x	2.1

α_z(trans) is the contribution to the linear expansion coefficient from the translational mode along the z (stack) axis

α_z(libr,x) and α_z(libr,y) are contributions to the linear expansion coefficient along z from librations around x and y respectively.

α_z is the resultant linear expansion coefficient along z.

α_x is the linear expansion coefficient along x; only the contribution from translation is taken into account.

4. DISCUSSION

In section 3 a model is presented with which the anisotropy in the thermal expansion of crystals with stacked plate-like molecules is obtained. A number of degrees of freedom argument and a crude calculation lead to an anisotropy in the thermal expansion of exactly three. The expansion along the stack is three times as large as the expansion perpendicular to the stack. A slightly more realistic calculation gives an anisotropy of two point one. From table 2 we infer that the experimental value for the anisotropy is in the range of 1.5 to 4.5. Therefore, it can be concluded that the model accounts for the anisotropy found. There are a number of effects which are not included in the model, but which do play a

role in determining the thermal expansion. A number of these effects will be mentioned below.

The first discrepancy between the model and real crystals is that the latter also contain ions different from TCNQ. In the morpholinium TCNQ salts these ions mimic more the shape of a sphere than of a plate. It can therefore be argued that their contribution to the anisotropy in the thermal expansion will be small, although a rigorous estimate cannot be made.

A second effect is the so-called Poisson contraction. The librations around y and x have the effect to diminish the expansion along x and y. This effect can apparently become so large that the expansion in one direction becomes negative (table 2).

The last effect we mention is that in the model we assume the molecules to be perpendicular to the stack, whereas in real crystals the molecules are tilted (table 1). The effect of this tilt will be to diminish the anisotropy and to increase the angle between the third principal axis and the stack direction[5].

Since much attention paid to the properties of these compounds is focussed on the effects of the one dimensional electron band, the question arises whether this band contributes to the thermal expansion. The answer to this question is no. It is noted that the thermal expansion of other plate-like organic molecules, however without a band structure, is of similar magnitude as that of TCNQ salts[9]. An attempt to calculate the thermal expansion by minimising the free energy, showed that the contribution of band electrons is orders of magnitude lower than the phonon contribution[10]. Moreover it is noted that in normal metals the band electrons contribute to the thermal expansion only at very low temperatures (less than about 10 K)[11].

5. CONCLUSIONS

For a number of N-substituted morpholinium TCNQ salts a highly anisotropic thermal expansion is found. These results could be

explained by using a simple model, in which the separate contributions from librational phonon modes and translational phonon modes to the thermal expansion is calculated. The electrons of the one-dimensional band do not give an appreciable contribution to the thermal expansion.

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