

Ordering in Channel Inclusion Compounds of TANO with Linear-Chain Compounds. I. High- and Low-Temperature Structures of TANO-*n*-Heptane

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Abstract

The nitroxide radical 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide or TANO ($C_9H_{16}NO_2$) forms channel inclusion compounds with numerous linear chain compounds. In the high-temperature phase, included chains are disordered in the channels (orientation and position). Structural results [$\lambda(Cu K\alpha) = 1.5418 \text{ \AA}$] are given for TANO-*n*-heptane. In the high-temperature phase, 233 K, formula $C_9H_{16}NO_2 \cdot xC_7H_{16}$ with $x \approx 0.08$, $M_r = 178.2$, space group $C2/c$, $a = 35.89 (2)$, $b = 5.886 (3)$, $c = 35.20 (2) \text{ \AA}$, $\beta = 120.0 (2)^\circ$, $V = 6439 (10) \text{ \AA}^3$, $Z = 24$, $D_x = 1.103 (2) \text{ Mg m}^{-3}$, $\mu = 0.62 \text{ mm}^{-1}$, $F(000) = 2343.4$, $R = 0.15$ (471 reflections), the heptane molecules are completely disordered along the channels but the TANO frame is disordered too: the TANO molecules show a chiral disorder. A lock-in transition occurs at 188 K, involving very large molecular shifts of TANO molecules parallel to the *b* axis. In the low-temperature phase, 173 K, formula $C_9H_{16}NO_2 \cdot \frac{1}{12}C_7H_{16}$, $M_r = 178.6$, space group Pc , $a = 17.59 (2)$, $b = 11.65 (1)$, $c = 34.55 (3) \text{ \AA}$, $\beta = 118.46 (7)^\circ$, $V = 6224 (20) \text{ \AA}^3$, $Z = 24$, $D_x = 1.143 (2) \text{ Mg m}^{-3}$, $F(000) = 2348$, $R = 0.15$ (2145 reflections), the heptane molecules are ordered. The TANO molecules are still disordered but to a lesser extent than in the high-temperature phase.

1. Introduction

TANO (Fig. 1) is a free nitroxide radical of great stability which forms inclusion compounds with a wide range of linear-chain molecules. Rozantsev (1970) first mentioned TANO compounds with *n*-alkanes. Continuous channels filled with linear chain

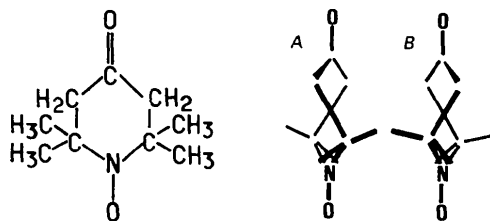


Fig. 1. Schematic TANO molecule, and the two enantiomeric forms A and B.

molecules (5% in weight) pass through a frame of TANO molecules (Le Bars-Combe & Lajzerowicz, 1984).

In recent years, the study of different types of inclusion compounds in various respects has increased greatly in interest. Some of these compounds are close to those formed by TANO: inclusion compounds of PHTP (perhydrotriphenylene), DCA (deoxycholic acid), thiourea and, above all, urea, with hydrocarbon chains. The latter, discovered in 1940, are still very much studied, especially urea-*n*-alkanes (Boysen, Forst & Jagodzinski, 1981; Forst, Jagodzinski, Boysen & Frey, 1984; Cho, Kobayashi & Tadokoro, 1986; Boysen & Forst, 1986). Many problems are not yet resolved. We found the same kind of problems in TANO inclusion compounds especially in TANO-*n*-alkanes, which we studied in more detail, *i.e.* disorder problems and therefore phase changes and movements of the included molecules.

These problems are connected to the current studies of chain compounds in which paraffins are a kind of model. In our case, paraffins are enclosed in channels which constitute a 1D surrounding. The studies are also related to those concerning iodine and platinum chains (Enders, Pouget & Comes, 1982).

It was convenient - if possible - to start by studying the structure of one of these TANO inclusion compounds. In paper I, after describing the common features of the series, we will present and discuss the structures and the disorder of the high-temperature (233 K) and low-temperature (173 K) forms of TANO-*n*-heptane. Then we will analyse in paper II the characteristics of the observed phase transitions.

2. Main features of TANO inclusion compounds

2.1. Preparation

As commercial TANO exists at only 95% purity, we preferred to prepare it (Briere, 1965) by catalytic oxidation of the corresponding amine and then recrystallization in petroleum spirit. The compound obtained, although well crystallized as orange needles, contained a small amount of solvent that we eliminated by heating for a few minutes at 326 K. Then we obtained a yellow powder, corresponding

to the orthorhombic form of pure TANO (melting temperature 309 K), the structure of which was refined by Bordeaux & Lajzerowicz (1974).

Without making a systematic study of the possibilities of inclusions, we included in TANO the following compounds:

- (i) *n*-alkanes C_nH_{2n+2} with $n \geq 7$ up to $n = 44$;
- (ii) mono and dihalogenated derivatives of alkanes;
- (iii) slightly branched derivatives of alkanes (methyl-*n*-alkanes).

We also obtained poorer quality crystals with:

- (i) mono- and diacids, monoalcohols derived from alkanes;
- (ii) alkenes, for example *trans*-3-heptane;
- (iii) and even polymers: polyethylene glycols of various lengths.

When the hydrocarbon was liquid, we obtained crystals by slow cooling of a solution of the hydrocarbon saturated with TANO. When it was solid, we needed an intermediary solvent: acetone, ethanol, methanol and above all *p*-xylene.

2.2. Main features

All these compounds have common features:

Stability: crystals are stable and can be kept several months. For the short chains the addition compound is destroyed by pulling under vacuum or light heating: the structure of the frame is modified and becomes orthorhombic, which is one of the stable forms of TANO alone. So the channel structure cannot exist without inclusion, *i.e.* with empty channels.

The melting temperature of the inclusion compounds, 10 to 30 K higher than pure TANO, increases with the length of the included chain, then stabilizes around 340 K for a length greater than 30 Å (Fig. 2).

Low ratio of inclusion: in TANO-*n*-alkanes, the inclusion represents less than 5% in weight, whereas it is much higher (about 27%) in the urea-*n*-alkanes. Owing to this low ratio, it will obviously be difficult to obtain data concerning the included chains alone.

Twin crystals: the crystals obtained, orange needles parallel to the *b* axis of the channels and of star-shaped section, are in fact constituted by the twinning of six crystals by their (100) and (001) faces. This is possible because the *a*, *c* angle is close to 120° and *a* and *c* are very similar.

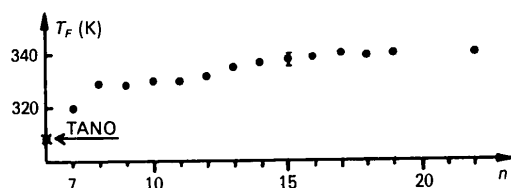


Fig. 2. Melting temperature of TANO- C_nH_{2n+2} versus *n*.

Table 1. Crystallographic parameters for three TANO-*n*-alkanes at room temperature

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)
TANO- <i>n</i> -heptane (C_7H_{16})	36.04 (8)	5.95 (2)	35.55 (8)	120.0 (4)
TANO- <i>n</i> -octane (C_8H_{18})	36.05 (8)	5.96 (2)	35.60 (8)	120.0 (4)
TANO- <i>n</i> -nonane (C_9H_{20})	36.08 (8)	5.95 (2)	35.85 (8)	120.7 (4)

Isomorphism: at room temperature, all the compounds are isomorphous: same space group ($C2/c$, $Z = 24$), similar crystallographic parameters (Table 1).

Chain disorder: X-ray rotation photographs around the *b* axis reveal the existence of homogeneous diffuse planes, perpendicular to the *b* parameter and therefore to the chain axis, whose spacing is directly related to the length of the chains. So there is incommensurability between the *b* parameter and the repetition length of the chains in the channels. The good periodicity of the chains is supported by the thickness of the different diffuse planes, which is roughly constant. The corresponding correlation length is greater than 100 Å. This shows that the chains are enclosed end to end in the channels and are disordered.

Phase transitions: we have mainly studied these on TANO-*n*-alkanes. According to the length of the included alkane, these compounds exhibit one or two phase transitions above 100 K. These transitions are accompanied on X-ray photographs by the vanishing of the diffuse planes which were related to the alkane disorder, and the appearance of Bragg peaks indicating a 3D ordering of the alkanes (*cf.* paper II). The study of these transitions by X-ray diffraction has shown that, among the TANO-*n*-alkanes, one was of particular interest, TANO-*n*-heptane (C_7H_{16}), because its phase change was less complicated from the point of view of the structure change: only one transition, accompanied by a doubling of the *b* parameter whereas *b* is multiplied by 5, 7 or 8 in other TANO-*n*-alkanes.

So, we will now describe successively the high- (HT) and low- (LT) temperature structures of TANO-*n*-heptane. In fact, we alternately improved the structure resolutions of the two phases.

3. TANO-*n*-heptane structures

3.1. Experimental

The crystals, enclosed in sealed Lindemann tubes, were cooled by a gaseous nitrogen jet. For the high temperature, we operated at 233 K rather than at room temperature in order to reduce the thermal motion of the molecules. Low-temperature-form measurements were done at a temperature of 173 K where frost problems are not yet too important, around 20 K under the transition temperature. Experimental details for the X-ray determination are in Table 2. Usual Lp corrections but no absorption or extinction corrections were done.

Table 2. *Experimental conditions and refinement*

	HT structure (233 K)	LT structure (173 K)
Number of heptane molecules per cell	~2	2
Number of independent molecules	3 TANO	12 TANO 1 heptane
Diffractometer	Philips	
Radiation	Cu K α (graphite-monochromated)	
Scan type	$\omega/2\theta$	
Crystal size (mm)	0.3 \times 0.3 \times 0.4	0.3 \times 0.3 \times 0.3
Number of reflections for lattice parameters	12	
2 θ range of reflections ($^\circ$)	34–52	
Max. 2 θ for data collection	2 θ < 108 $^\circ$ ($\sin \theta$)/ λ < 0.52 \AA^{-1}	2 θ < 91.4 $^\circ$ ($\sin \theta$)/ λ < 0.465 \AA^{-1}
<i>h, k, l</i> range	–34 \rightarrow 28, 0 \rightarrow 5, 0 \rightarrow 30	–13 \rightarrow 12, 0 \rightarrow 9, 0 \rightarrow 26
Number of symmetry-independent reflections measured	4208	5144
Number of reflections observed	2229 [$I > 2\sigma(I)$]	2868 [$I > 3\sigma(I)$]
Number of reflections used	471 ($\sin \theta$)/ λ < 0.3 \AA^{-1} 0.15 (without <i>h0l</i> reflections)	2145 ($\sin \theta$)/ λ < 0.4 \AA^{-1} 0.14
<i>wR</i> ($w = 1$)	0.15	0.15
Conventional <i>R</i>	0.15	0.15
Number of parameters	43	102
ρ max. ($e \text{\AA}^{-3}$)	0.96 (1.5 in the channel)	0.8
Scattering factors	<i>International Tables for X-ray Crystallography</i> (1974); for H atoms, Stewart, Davidson & Simpson (1965)	

3.2. High-temperature phase (HT)

(a) *Structure refinement.* Using *MULTAN* (Germain, Main & Woolfson, 1971) based upon multiresolution direct methods, we obviously did not localize the heptane molecule which is disordered both in position along the channel and in orientation.

With regard to the three independent TANO molecules which constitute the *a priori* ordered frame, *MULTAN* gave poor results: distorted TANO molecules which were not improved by refinement of the structure, poor agreement between observed and calculated structure factors, especially for the *h0l* reflections. Examination of the Fourier map led to the conclusion that the TANO frame is disordered too: on each molecular site, we find two different enantiomers of TANO molecules with unequal occupation. As in the other known forms of TANO alone (Bordeaux & Lajzerowicz, 1974; Le Bars-Combe, 1982), the molecule is chiral with a twisted ring, C₂>N–O is planar, and C=O and N–O bonds are almost lined up, constituting a quasi 2 axis for the molecule (Fig. 1). So the TANO molecule has two enantiomeric forms that we call *A* and *B*, symmetrical about the mean plane of the piperidine ring. One enantiomer changes into the other by an interconversion of the ring. It is known (Briere, 1965) that the twisted ring of TANO inverts continuously in sol-

Table 3. *Coordinates (\AA) of TANO enantiomer A in the local reference system as defined in Fig. 3*

C, N, O atom coordinates from the orthorhombic form of TANO (Bordeaux & Lajzerowicz, 1974). Coordinates of the optical antipode *B* are obtained by changing *z* into $-z$. E.s.d.'s are 0.002 \AA .

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	0.0	0.0	0.0
O(2)	1.276	0.0	0.0
C(4)	–0.709	1.309	0.0
C(1)	–2.896	–0.009	–0.094
C(2)	–2.082	1.130	–0.643
C(3)	–2.118	–1.133	0.537
C(5)	–0.815	1.786	1.445
C(6)	0.096	2.288	–0.821
C(7)	–0.695	–1.304	–0.001
C(8)	0.072	–2.262	0.909
C(9)	–0.705	–1.848	–1.429
O(1)	–4.099	–0.024	–0.168

ution. The same may be true in the solid TANO–*n*-heptane compound but X-rays, which cannot distinguish the static or dynamic aspect of the disorder, do not permit a conclusion to be reached. Nevertheless, we will see later that the disorder of TANO molecules changes when the temperature is lowered. The dynamic character of the disorder is supported by this observation.

To describe and refine this structure which presents a conformational local disorder of TANO molecules, we had to use a program of molecular block refinement, *ORION* (Andre, Fourme & Renaud, 1971). For each molecular group, the variable parameters are: six parameters of position, one isotropic *B* factor, one occupancy rate (the sum of the occupancy rates of the two enantiomers is constrained to be 1). The coordinates of the molecular model are given in Table 3, the reference system is defined in Fig. 3. Heptane molecules, fully disordered, could not be taken into account in the refinement; we assume that their contribution to the diffraction is rather isotropic except for the *F(h0l)* because heptane molecules are in located channels perpendicular to the *ac* plane. So the *F(h0l)* were excluded from the refinement. Nevertheless, the results of the refinement are not good (Tables 2 and 4).^{*} It was not possible to describe thermal molecular motion by TLS tensors, this description being usable only if the refinement is of good quality. So we retained an isotropic thermal motion for the six TANO molecules, variable only for the three molecules of higher occupancy rates, and fixed to 4 \AA^2 for the others.

What are the reasons for this apparently mediocre result? A poor molecular model is irrelevant even if

* Lists of calculated H-atom coordinates of the TANO molecular model, crystallographic coordinates, occupancy rate and structure factors for the HT and LT structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43800 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Different parameters at the end of the high-temperature refinement of TANO-*n*-heptane at 233 K

Principal molecules have group numbers (grp) 1 to 3, secondary molecules have group numbers 4 to 6. The type of enantiomer is indicated by A or B. u_1, u_2, u_3 are the crystallographic coordinates of the origin of the molecular groups [N(1) atoms], M their occupancy rate. θ angles are defined as follows: if xyz is the reference system linked to the molecule, and $a, b, a \wedge b$ the orthogonal system linked to the crystallographic axes, if the two systems first coincide, $\theta_1, \theta_2, \theta_3$ are the angles around successively a, b and $a \wedge b$ in turn which bring the xyz system into its final position.

Average e.s.d.'s: grp 1 to 3: 0.6° (angles); 0.02 Å (u), 0.6 Å² (B), 0.02 (M); grp 4 to 6: 0.9° (angles), 0.04 Å (u).

		$\theta_1(^{\circ})$	$\theta_2(^{\circ})$	$\theta_3(^{\circ})$	u_1	u_2	u_3	M	$B_{iso}(\text{Å}^2)$
B	grp1	-160.5	-47.7	80.1	0.30	0.34	0.18	0.63	bg1 3.9
B	grp2	122.1	25.4	50.3	0.62	0.04	0.44	0.68	bg2 5.2
A	grp3	-99.3	9.6	133.0	0.56	0.75	0.12	0.61	bg3 6.0
A	grp4	23.0	-35.3	85.3	0.30	0.36	0.17	0.37	bg4 4.0
A	grp5	131.7	24.8	50.9	0.62	0.07	0.44	0.32	bg5 4.0
B	grp6	73.2	14.3	137.1	0.56	0.76	0.12	0.39	bg6 4.0

the piperidine rings have some flexibility. Indeed, the attempts with other models did not improve the results, and this model has given satisfactory results for the LT form (*cf.* below). On the other hand, our description of the local disorder in TANO molecules is certainly too simple to match reality: for example, we are not sure that there are only two positions on each site. Because of this insufficiency, we could not refine with high values of θ angles. Nevertheless, the results represent a good approximation: an electron-density difference synthesis with all $F_{obs} - F_{calc}$ exhibits a maximum density of 0.96 e \AA^{-3} outside the channels, where, of course, density is higher (1.5 e \AA^{-3}) because of the contribution of the disordered heptane. This density, slightly higher than the one usually encountered for H atoms, does not show special contrast which might cast doubts on the consistency of the disorder description.

(b) *Description of disorder in the HT phase.* The parameter values at the end of the refinements are given in Table 4.

Local disorder: on each independent site, we find two TANO molecules, one is said to be 'principal' with an occupancy rate of about 64%, the other is said to be 'secondary' with a rate constrained to be complementary to 1. These two enantiomeric molecules are slightly shifted with respect to each other, especially with regard to the $\text{C}=\text{N}-\text{O}$ part. Of the three 'principal' molecules, two of them correspond to one enantiomer and the third to the other.

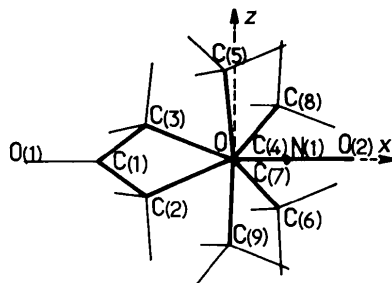
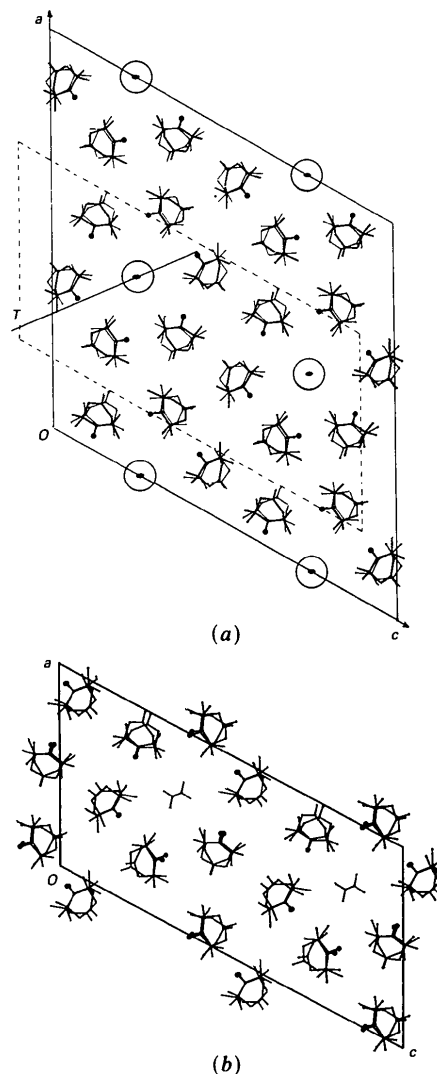
Fig. 3. TANO molecule with the local xyz reference system.

Fig. 4. (a) Projection of the HT structure of TANO-*n*-heptane on the ac plane. Thick lines: principal molecules, thin lines: secondary molecules. \bullet , O atom linked to the N atom of a principal molecule. Circles show the locations of the channels parallel to the b axis. T is the trace of the plane where the heptane will be located in the LT form. (The dashed-line cell is for the LT form). (b) Projection of the LT structure (173 K) of TANO-*n*-heptane on the ac plane. Only principal molecules are represented. \bullet , O atoms linked to N atoms.

Packing: on the projection of the structure parallel to the b axis (Fig. 4a), the position of the channels is indicated by hollow circles. Channel axes, twofold axes of the structure, are 18 Å apart and their diameter, taking into account van der Waals radii of atoms, is rather small, between 4.2 and 5 Å. Six disordered TANO molecules deduced two by two by the twofold axis define the channel, picking up one or two methyls inside the channel. The N–O groups are tangential to the channel. Each set of three principal molecules almost forms a 3_1 helix with the angles between $\begin{matrix} C \\ \curvearrowright \\ C \end{matrix}$ N–O planes and the b axis quasi equal (44, 46, 48°). We note that this is true except that one molecule of this helix has a chirality opposite to the two others.

To sum up, we can describe the packing of the HT phase as follows: two pseudo helices, linked by a twofold axis constituted by three TANO molecules, define a channel lined with methyls. The heptane molecule is not localized in this channel. The structure as a whole is close to a hexagonal arrangement. Can a more symmetric hexagonal phase exist at a higher temperature, as has been found in paraffins? With the β angle equal to 120°, this would mean that the a and c parameters would become equal. On the plots of lattice parameters of TANO- n -alkanes as a function of temperature (see paper II, Fig. 4), we can see that a and c slightly converge, but their equality would be realized much above melting. So melting occurs before a possible transition towards a hexagonal phase.

Intermolecular contact: there are no short contacts between 'principal' molecules ($C \cdots O > 3.32$ and $C \cdots C > 3.6$ Å). This means that the network of 'principal' molecules is loose. Between 'principal' and 'secondary' molecules, $C \cdots O > 3.0$ Å; there is one short contact $C \cdots C = 3.13$ Å, the other contacts $C \cdots C > 3.32$ Å. The only very short contacts occur between C and O atoms of 'secondary' molecules ($C \cdots O = 2.52$, $C \cdots C > 3.43$ Å) but the interconversion of TANO rings probably leads to local order, avoiding these short contacts.

Thermal motion: B factors (Table 4) of 'principal' molecules are large. B factors of 'secondary' molecules were fixed at 4 Å².

3.3. Low-temperature phase (LT)

(a) *The search for a starting structure.* The change from space group $C2/c$ (high-temperature phase) to space group Pc (LT phase), with a doubling of the b parameter but halving of the a parameter, supposes astonishingly large shifts of TANO molecules parallel to b , which had nevertheless to be proved. Indeed, if two molecules were related by the $\frac{1}{2} \frac{1}{2} 0$ translation in the high-temperature phase, they are now related by the $\frac{1}{2} 0 0$ translation (or 100 if expressed in the low-

temperature cell). The low-temperature-structure resolution was difficult: large cell, 13 independent molecules (12 TANO molecules, one heptane molecule), weak superstructure F_{obs} . We had to use the Karle recycling procedure four times, which exists in a *MULTAN* program. It consists of identifying fragments of molecules in the Fourier transform of the normalized structure factors and then using these known atomic positions in a modified tangent formula in order to improve the process of phase determination. We have been helped in locating these fragments by the following assumption: the LT projection on the ac plane looks like the HT projection. First, Wilson tests show that this projection is centered as in the HT form while the whole LT structure is not centered. Next, the set $F(h0l)$ which represents the Fourier transform of the projection parallel to the b axis of the whole structure is less modified at the phase transition. At the end of the fourth Karle cycle, we had located the 12 independent TANO molecules but not the heptane molecule.

(b) *LT structure refinement and results.* Refinement was first carried out with molecular blocks, and then with independent atoms. As the conformations of molecules seemed to be greatly distorted, we performed an electron-density synthesis which revealed a residual local disorder of TANO molecules. At the same time we were able to locate the heptane molecule. Finally, refinement was carried out with molecular blocks: 24 TANO molecules, *i.e.* 12 free to move 'principal' molecules with a variable occupancy rate and an isotropic variable B factor, and 12 fixed 'secondary' molecules, optical antipodes of the former, with an occupancy rate complementary to the former and a fixed B of 2.5 Å². The heptane molecule was introduced as a model, in the planar classical configuration ($C-C=1.535$ Å, $C-C-C$ angle = 112°) with variable group coordinates and isotropic B factor.

The values of the different parameters at the end of the refinement procedure are given in Table 5.*

(c) *Description of the LT structure.* At 173 K, the disorder of the TANO molecules remains very unequal (*cf.* Table 4): almost in the same ratio as in the high-temperature form for two groups (Nos. 23 and 24), rather significant for group No. 15 and weak for the nine other groups: 6 to 19%.

Heptane molecules are located in planes perpendicular to the ac plane, making an angle of 114° with the a axis. If the projection of the structure on the ac plane (Fig. 4b) is similar to the HT one (Fig. 4a), this is not the case for the other projections. For example, the projections on the heptane plane (Fig. 5) show that the structure is radically modified by very important relative shifts of the TANO molecules parallel to the b axis: about 3 Å for a distance of

* See deposition footnote.

Table 5. *Parameter values at the end of the refinement of LT TANO-*n*-heptane (173 K)*

Definitions are given in the caption of Table 4. Average e.s.d.'s: principal molecules numbered grp 1 to 12: 0.5° (angles), 0.02 to 0.03 Å (*u* coordinates), 0.03 (*M*), 0.5 Å² (*B*). Corresponding secondary molecules (13 to 24) were fixed. Heptane (grp 25): average e.s.d.'s are 2° (θ_1), 0.5° (θ_2, θ_3), 0.04 Å (*u*), 0.6 Å² (*B*).

		θ_1 (°)	θ_2 (°)	θ_3 (°)	u_1	u_2	u_3	<i>M</i>	<i>B</i> _{iso} (Å ²)
<i>B</i>	grp1	-153.9	-49.6	70.6	0.96	0.44	0.08	0.91	bg1 3.8
<i>A</i>	grp2	17.8	-39.2	82.8	0.95	0.03	0.08	0.80	bg2 3.8
<i>A</i>	grp3	157.5	46.8	110.5	0.72	0.30	0.71	0.71	bg3 1.2
<i>A</i>	grp4	-161.0	34.6	95.1	0.73	0.20	0.22	0.93	bg4 1.6
<i>B</i>	grp5	-127.0	-21.4	-125.7	0.09	0.28	0.45	0.87	bg5 2.6
<i>A</i>	grp6	-118.3	-31.1	-125.8	0.09	-0.21	0.45	0.89	bg6 3.9
<i>B</i>	grp7	121.7	31.3	59.7	0.59	0.45	0.34	0.83	bg7 0.7
<i>B</i>	grp8	52.6	21.1	-57.1	0.58	0.04	0.84	0.88	bg8 2.0
<i>A</i>	grp9	-100.0	13.6	133.2	0.47	0.46	0.02	0.84	bg9 3.5
<i>A</i>	grp10	109.3	10.2	-131.4	0.47	0.03	0.53	0.92	bg10 1.9
<i>B</i>	grp11	97.2	-8.2	-43.4	0.21	0.29	0.77	0.62	bg11 3.3
<i>B</i>	grp12	-105.2	-13.7	44.6	0.21	0.20	0.27	0.67	bg12 2.7
<i>A</i>	grp13	-152.1	-50.0	70.4	0.96	0.45	0.08	0.08	bg13 2.5
<i>B</i>	grp14	18.3	-43.8	80.2	0.95	-0.03	0.08	0.19	bg14 2.5
<i>B</i>	grp15	159.5	43.8	-106.2	0.72	0.30	0.71	0.28	bg15 2.5
<i>B</i>	grp16	-159.5	35.4	96.6	0.73	0.20	0.22	0.06	bg16 2.5
<i>A</i>	grp17	-125.6	-22.1	-126.2	0.09	0.28	0.45	0.12	bg17 2.5
<i>B</i>	grp18	-119.4	-30.3	-128.0	0.09	-0.21	0.45	0.10	bg18 2.5
<i>A</i>	grp19	120.0	30.9	59.8	0.59	0.45	0.34	0.16	bg19 2.5
<i>A</i>	grp20	51.8	22.1	-58.6	0.58	0.04	0.84	0.11	bg20 2.5
<i>B</i>	grp21	-102.8	12.9	134.2	0.47	0.46	0.02	0.15	bg21 2.5
<i>B</i>	grp22	107.1	11.3	-132.7	0.47	0.03	0.53	0.07	bg22 2.5
<i>A</i>	grp23	99.2	-10.7	-39.3	0.21	0.28	0.77	0.37	bg23 2.5
<i>A</i>	grp24	-99.7	-8.2	41.6	0.20	0.20	0.27	0.32	bg24 2.5
	grp25	114.8	-2.6	89.2	0.32	-0.43	0.14	1.00	bg25 8.0

18 Å. If we consider the arrangement around the channel, except for the chirality the pseudo HT helix 3₁ has become a LT pseudo 3 axis and TANO molecules are now 3 by 3 at the same level. So the

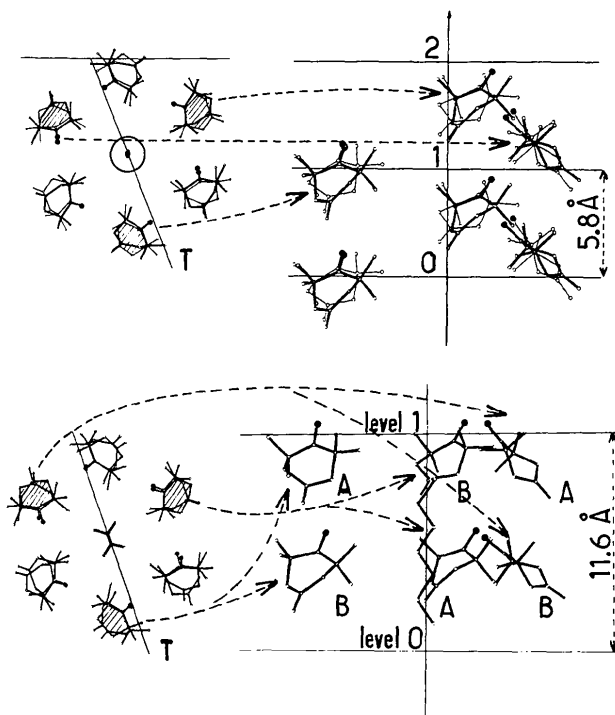


Fig. 5. Arrangement of molecules around a channel. Left: in projection on the *ac* plane; right: on the plane of trace *T* (only for hatched molecules). Top: HT TANO-*n*-heptane; bottom: LT phase.

relative displacements are about $b/3 = 2$ Å. When they shift, molecules are slightly rocked, less than 7° on average from their HT position.

Intermolecular contacts: between 'principal' TANO molecules, there is only one short contact $C \cdots C = 3.28$ Å, the others are greater than 3.3 Å, $C \cdots O > 3.15$ Å. Between 'principal' and 'secondary' molecules, six $C \cdots C$ contacts lie between 3.02 and 3.3 Å, and six $C \cdots O$ lie between 2.92 and 3.1 Å. As the occupancy rates of the 'secondary' molecules concerned are low, this is not worrying. Contacts between 'secondary' molecules are sometimes very short ($C \cdots O = 2.64$ Å), but they have no significance. Between TANO and heptane molecules, the shorter contacts occur with methyls of TANO: 3.39 Å with a 'principal' TANO molecule, 3.31 Å with a 'secondary' one. From consideration of the e.s.d., there is no particular remark to make on intermolecular contacts which remain of a van der Waals type.

Thermal motion: the *B* factors of the TANO molecules are correct for a structure refined at 173 K as regards the possible correlations between *B* and the occupancy rates. On the other hand, heptane has a large thermal motion. Perhaps there remains a disorder for the heptane molecule that we have not found. But, on the final electron-density difference map, nothing can be interpreted in that way, the maximum density being $0.8 e \text{ \AA}^{-3}$.

4. Discussion

Let us compare the organization of the molecules around a channel in the two phases and let us try to

understand the modifications of structure corresponding to the phase change.

In the HT phase, heptane is not located in position along the channel axis and in rotation around this axis. TANO molecules exhibit a local disorder which statistically corresponds to the presence of two optical antipodes on each molecular site. Without prejudging the character, static or dynamic, of this disorder, we can observe that the change from one enantiomer to the other by interconversion of the piperidine ring modifies significantly the channel walls. If, for example, one TANO molecule points one of its four methyls strongly towards the channel axis, in the other conformation this methyl is replaced by two methyls set back from the channel axis.

If we consider the change of the accessible space in the channels, which is related to the different van der Waals envelope of TANO molecules when there are interconversions of TANO rings, we can see that possible reorientation of heptane molecules is con-

nected to the existence of disorder in TANO molecules.

At low temperature, a residual disorder remains very unequal for TANO molecules. In Fig. 6 we notice that van der Waals spheres of groups 11 and 12 do not interfere at all with heptane. They actually correspond to the molecules that keep an important disorder ratio (32 and 38%) at low temperature. Effectively, they can locally take the shape of one or other enantiomer even with a fixed heptane. Then we see that the van der Waals sphere of one methyl overlaps more the projection of the heptane envelope (hatched part in Fig. 6). The corresponding methyl penetrates deeply into the channel and fits in the gap between two successive heptanes. This is shown explicitly in Fig. 7. We can say that this methyl, called C(8), has locked the heptane in its translation parallel to the axis of the channel, while the other methyls, except those of groups 12 and 13, have locked the heptane in its rotation around this axis.

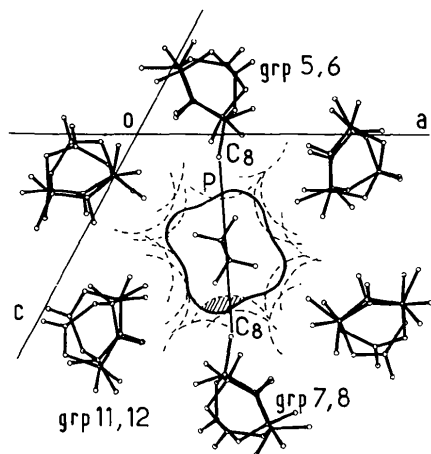


Fig. 6. LT TANO-*n*-heptane: van der Waals envelopes of the projection of the channel and of the heptane molecule on the *ac* plane. Only principal molecules are shown.

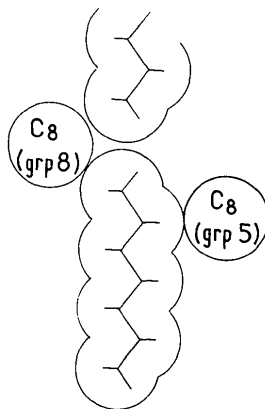


Fig. 7. LT TANO-*n*-heptane: section of van der Waals envelopes of heptane and of two C₈ methyls in the plane of trace *P* (Fig. 6).

5. Concluding remarks

In the analysis of the disorder of the HT phase of TANO-*n*-heptane, we find that the included chains present a double disorder (position along the channel axis and reorientation around this axis). The molecules of the TANO frame are disordered too, two molecules of opposite chiralities being unequally present on each molecular site.

From a structural point of view, the transition of TANO-*n*-heptane is entirely an order-disorder one for heptane molecules, which are locked in one position at low temperature. It is partially an order-disorder transition for TANO molecules which keep a residual local disorder at 173 K.

This work also exhibits the reconstructive character of the transition for there is a change from *C2/c* to *Pc* space group with a loss of the translation symmetry *C* and large relative shifts of TANO molecules, a mean shift of 3 Å for a distance of 18 Å.

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Ordering in Channel Inclusion Compounds of TANO with Linear-Chain Compounds. II. Phase Transitions of TANO-*n*-Alkanes

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Abstract

Numerous phase transitions of channel inclusion compounds of the nitroxide radical 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide or TANO ($C_9H_{16}NO_2$) with *n*-alkanes (C_nH_{2n+2}) were investigated by differential scanning calorimetry (DSC) and X-ray diffraction (one transition if $7 \leq n \leq 11$, two transitions if $12 \leq n \leq 19$). Temperatures and enthalpies of transition and fusion are given. In the high-temperature phase (HT), complete disorder of the included alkanes is found in the channels parallel to the *b* axis: homogeneous diffuse layers perpendicular to *b* are seen on X-ray photographs, whose spacing is strictly related to the alkane length *l* (incommensurate with the *b* parameter). For all the compounds studied, lock-in transitions exist. In the low-temperature phase (LT), diffuse layers disappear and new Bragg reflections appear. The new lattice is $a(LT) = a(HT)/2$, $b(LT) = mb(HT) = nl$ (*m* and *n* integers). The observations suggest helical arrangements of TANO molecules. In the case of TANO-*n*-heptane ($m = 2$, $n = 1$), of which HT and LT structures were described in paper I [Le Bars-Combe & Lajzerowicz (1987). *Acta Cryst.* **B43**, 386–393], the evolution of the cell parameters and the intensities of reflections are presented as a function of temperature. For $n \geq 12$, intermediary complex phases exist.

1. Introduction

Channel inclusion compounds which are formed by the free nitroxide radical called TANO with a wide range of linear-chain or slightly branched molecules (around 5% of inclusion in weight) all present disorder phenomena of the included chains in the channels of the structure. The evolution of this disorder as a

function of temperature is accompanied by one or two phase transitions above 100 K (Le Bars-Combe & Lajzerowicz, 1984).

In paper I (Le Bars-Combe & Lajzerowicz, 1987), we presented the main features of these compounds and gave the structural results for high- (233 K) and low- (173 K) temperature phases of TANO-*n*-heptane.

We made the following findings: in the high-temperature (HT) phase, channels parallel to the *b* axis, 4.5 to 5 Å in diameter, 18 Å apart, are filled with heptane molecules lying end to end with a double disorder: reorientation around their axis and disorder of position along the channels. So they have a repetition length incommensurate with the periodicity of the TANO frame. It was proved that the TANO molecules are also disordered: on each molecular site, there is interconversion of the TANO ring, so TANO molecules change from one enantiomer into the other. Either one TANO molecule or its optical antipode is present with unequal occupancy. When the temperature is lowered, a lock-in transition occurs at 188 K which implies very important shifts of TANO molecules parallel to the channel axis. In the low-temperature (LT) phase, heptane molecules are ordered and located in one position, while partial disorder remains for TANO molecules but to a lesser extent than in the HT phase.

Thus, structural analysis of the TANO-*n*-heptane transition has proved that it is an order-disorder one (entirely for heptane molecules, partly for TANO molecules) and that it has a strongly reconstructive character.

A good deal of information has been accumulated in calorimetry for channel inclusion compounds with linear-chain molecules especially for urea-*n*-alkane compounds (Parsonage & Pemberton, 1967).