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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).

Investigations of the structure change by means of X-ray diffraction were done later (Chatani, Anraku & Taki, 1978): the phase transition can be regarded as an order-disorder transition with respect to the orientation of the guest molecules in the channel, with a cooperative deformation of the urea walls. But, recently, neutron and X-ray diffuse scattering have revealed that the phenomenon is more complicated (Forst, Jagodzinsky, Boysen & Frey, 1984; Boysen & Forst, 1986).

In this paper, we present the study of phase transitions in TANO-*n*-alkanes by means of calorimetry and X-ray diffraction.

## 2. Calorimetric analysis

We used a Perkin DCS II differential scanning calorimeter and investigated compounds TANO- $C_nH_{2n+2}$  with *n* from 7 (for *n* < 7, they do not exist) to 19. We used around 10 mg of dried crystals in a sealed aluminium cap. For *n* = 7 and 14, we confirmed the results with classic calorimetry measurements.

### 2.1. Characteristics of the phase transitions

According to the length of the hydrocarbon chains, one or two transitions are observed above 100 K (Fig. 1).

The first transition exhibits a strong hysteresis (50 to 80 K); its temperature decreases slightly with *n*. The corresponding DSC peak is spread out from 10 to 40 K when the temperature increases, but is narrower when it decreases (Fig. 2). These observations are consistent with the variation of cell parameters (Fig. 4). For *n* ≥ 17, this transition is not clearly observed when the temperature is lowered because it occurs at a temperature below 130 K where the base line of the apparatus is not good. For *n* = 11 and 12, the descent peak is split into two peaks 8–10 K apart.

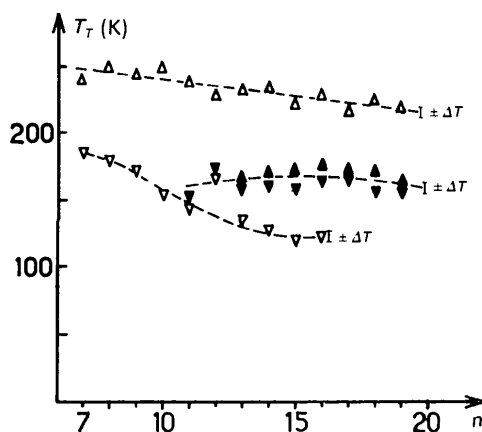


Fig. 1. Transition temperatures of TANO- $C_nH_{2n+2}$  versus *n*:  $\Delta$  temperature increasing and  $\nabla$  temperature decreasing for one transition;  $\blacktriangle$  temperature increasing and  $\blacktriangledown$  temperature decreasing for the other transition.

The second transition, observed if *n* ≥ 13, is weaker and without hysteresis. The correspondence between the transition temperatures has been clearly stated. If the sample is kept a long time at 100 K, the peak corresponding to the second transition seems to vanish. In particular, we did not observe it in the classic calorimetric records.

### 2.2. Melting and transition enthalpies (Table 1)

Melting enthalpies  $\Delta H_M$  slightly increase with the length of the guest. Transition enthalpies  $\Delta H_T$ , or the sum over the two when there are two, seem to decrease from *n* = 11. But they may have been underestimated because the transition which occurs at the lowest temperature (when the temperature decreases) is often incomplete. The sum  $\Delta H_T + \Delta H_M$  remains almost constant. We note that these transition enthalpies are large, for TANO-*n*-heptane  $\Delta H_T = 13\% \Delta H_M$ , so from this result alone, we can predict that the transition does not concern the heptane guest alone (5% in weight) but also the TANO hosts. Structural results support this affirmation (*cf.* paper I).

The entropy per alkane mole roughly estimated as  $\Delta H_T/T_T$ , is greater than  $83 \text{ J K}^{-1} \text{ mol}^{-1}$ . If we compare this with the theoretical value  $S_T = R \log p$  ( $R \log 2 = 5.8$ ) for an order-disorder transition concerning *p* positions of *q* molecules, we conclude that TANO molecules are also involved in the transition.

### 2.3. Comparison with urea-*n*-alkanes

Differences between TANO-*n*-alkanes and urea-*n*-alkanes are important from both qualitative and quantitative points of view.

For urea-*n*-alkanes (*n* = 10 to 20) only one transition is observed, except for *n* = 16 where there are two. Transition temperatures, enthalpies and entropies increase with the length of the guest, regularly for the *n*-even alkanes and irregularly for the *n*-odd alkanes (Pemberton & Parsonage, 1965; Cope & Parsonage, 1969). On the contrary, for TANO-*n*-

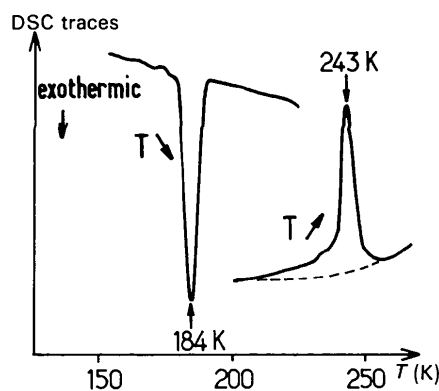


Fig. 2. Transition of TANO-*n*-heptane, DSC diagram (sensitivity  $21 \text{ mJ s}^{-1}$ ,  $10 \text{ K min}^{-1}$ ). Hysteresis is about 59 K.

Table 1. Transition temperatures and melting enthalpies of TANO-*n*-alkanes

Comparison with alkanes and urea-*n*-alkanes. For compounds 1 to 6, the average between descent and ascent peaks is given. For compounds 7 to 10, we have done the sum over the two ascent transition peaks. To calculate  $\Delta H_T$  per included alkane mole, we needed the ratio of alkane in the compound. As we knew this for five compounds,  $n = 7, 8, 9, 14, 16$ , from the superstructure LT phase (ratios 4·7, 4·6, 4·8, 5·2, 5·5% respectively) we have interpolated for the other compounds.

		TANO- <i>n</i> -alkanes					Alkanes	
	$T_F$ (K)	$\Delta H_M$ (J g <sup>-1</sup> )	$T_T$ (K)		$\Delta H_T$ (J g <sup>-1</sup> )	$\Delta H_T$ [kJ (mol alkane) <sup>-1</sup> ]	$\Delta H_M$ (kJ mol <sup>-1</sup> )	
			Descent	Ascent				
1	TANO- <i>n</i> -heptane (C <sub>7</sub> H <sub>16</sub> )	320	84 (a)	186	240	10·9 (a)	23·9 (a)	14·03 (c)
2	TANO- <i>n</i> -octane (C <sub>8</sub> H <sub>18</sub> )	329	96 (b)	180	250	8·4 (b)	20·5 (b)	20·77 (c)
3	TANO-D- <i>n</i> -octane (C <sub>8</sub> D <sub>18</sub> )	333	87 (b)			10·5 (b)		
4	TANO- <i>n</i> -nonane (C <sub>9</sub> H <sub>20</sub> )	329	79 (b)	172	245	12·1 (b)	32·2 (b)	15·49 (c)
5	TANO- <i>n</i> -decane (C <sub>10</sub> H <sub>22</sub> )	330	87 (b)	154	250	10·9 (b)	31·4 (b)	28·72 (c)
6	TANO- <i>n</i> -undecane (C <sub>11</sub> H <sub>24</sub> )	330	92 (b)	143-153	238	5·9 (b)	18·8 (b)	22·19 (c)
7	TANO- <i>n</i> -dodecane (C <sub>12</sub> H <sub>26</sub> )	331	100 (b)	165-175	228	8·0 (b)	27·2 (b)	36·84 (c)
8	TANO- <i>n</i> -tridecane (C <sub>13</sub> H <sub>28</sub> )	335	100 (b)	159-135	163-232	4·2 (b)	15·5 (b)	28·51 (c)
9	TANO- <i>n</i> -tetradecane (C <sub>14</sub> H <sub>30</sub> )	337	92 (a)	161-128	170-234	4·6 (a)	16·7 (a)	45·09 (c)
10	TANO- <i>n</i> -hexadecane (C <sub>16</sub> H <sub>34</sub> )	339	100 (b)	164-122	174-228	4·6 (b)	17·6 (b)	53·38 (c)
	Urea- <i>n</i> -decane			111			0·84 (d)	
	Urea- <i>n</i> -undecane			122			1·38 (e)	
	Urea- <i>n</i> -dodecane			123			1·09 (d)	
	Urea- <i>n</i> -hexadecane			135-152			1·76 (d)	

Notes: (a) DSC measurements within 1 to 2%. (b) DSC measurements within 5 to 10%. (c) From Finke, Gross, Waddington & Huffman (1954). (d) From Pemberton & Parsonage (1965). (e) From Cope & Parsonage (1969).

alkanes temperatures and energies decrease globally with  $n$  and nothing distinguishes compounds with even- or odd- $n$  alkanes.

The energies per alkane mole involved in the transitions of TANO-*n*-alkanes are 10 to 20 times larger than the corresponding value in urea-alkanes. Two structural features can be related to these results: in TANO-*n*-alkanes the distance between two channels (18 Å) is larger than in urea-*n*-alkanes (8·3 Å) and the interactions between adjacent alkanes are quite different - the TANO matrix is disordered, while the urea matrix seems to be ordered at room temperature.

### 3. X-ray study

#### 3.1. General study

The X-ray study was performed on an Explorer camera; we essentially took oscillation photographs ( $\pm 5^\circ$ ) around the  $b$  axis. We used a Philips four-circle diffractometer to obtain cell parameters and reflection intensities. We tested five TANO-*n*-alkanes but we will present the results concerning principally  $n = 7, 8, 9$  because they are the simplest.

Each experiment was carried out on several crystals because they did not resist successive cycles of temperature changes from 120 K to room temperature for long.

Oscillation photographs (Fig. 3) at 20-30 K below  $T_T$  after quenching for ten minutes with liquid nitrogen, all exhibit:

(a) the disappearance of the diffuse planes which existed on the HT photograph;

(b) the emergence of new Bragg peaks: the new LT  $b$  parameter [called  $b(\text{LT})$ ] is a multiple of the

HT one (called  $b$ ).  $b(\text{LT}) = b \times 2$  for TANO-*n*-heptane (Fig. 3),  $b(\text{LT}) = b \times 7$  for TANO-*n*-octane,  $b(\text{LT}) = b \times 5$  for TANO-*n*-nonane;

(c) the disappearance of the  $C$  lattice translation [the ( $h1l$ ) plane no longer presents  $h+k=2n+1$  extinction];

(d) the division by 2 of the  $a$  parameter. For TANO-*n*-heptane, this means that only 25% of the HT Bragg peaks remain in the same position as in the LT form.

So, as we explained in paper I, for TANO-*n*-heptane structures, these are both reconstructive and order-disorder transitions.

If  $n$  is the number of alkanes fitting in the LT phase with  $m$  periods of the TANO form, and if  $l$  is the length of an alkane supposed to be in a linear plane configuration, we get  $b(\text{LT}) = mb = nl$ . Taking  $l = 1·272(n-1) + D$  Å, we can deduce the  $D$  distance between two extreme methyls (Table 2).

So, for the three compounds in Table 2, we do not observe any shortening similar to that observed in other included compounds with alkanes. Indeed, the distance  $D$  is 3·74 Å in urea-*n*-alkanes (Laves, Nicolaides & Peng, 1965), 3·65 Å on average in PHTP (perhydrotriphenylene) compounds (Allegra, Farina, Colombo, Casagrande-Tettamanti, Rossi & Natta, 1967) and 4·06 Å (Teare, 1959) in pure alkanes.

#### 3.2. Evolution of the cell parameters and intensities of reflections as a function of temperature

*Experimental:* This analysis, which needs four-circle diffractometer measurements, was carried out in detail for TANO-*n*-heptane and more roughly for TANO-*n*-octane and TANO-*n*-nonane. The findings

Table 2. Values of  $b(LT)$ ,  $m$ ,  $n$  and  $D$  for several inclusion compounds

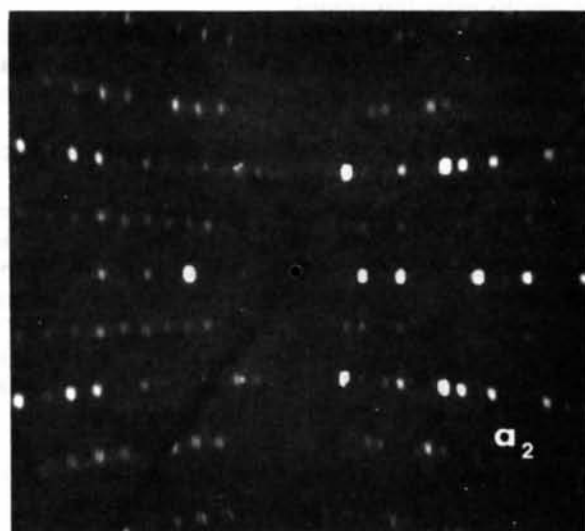
	$b(LT)$ at 140 K (Å)	Ratio $m =$ $b(LT)/b$	Number $n$ of alkanes in $b(LT)$	Corresponding length of alkane (Å)	Distance $D$ between two methyls (Å)
TANO- <i>n</i> -heptane	11.6	2	1	11.6	4.0
TANO- <i>n</i> -octane	40.5	7	3	13.5	4.7
TANO- <i>n</i> -nonane	29	5	2	14.5	4.3

are similar and we will present the results only for TANO-*n*-heptane.

Measurements were done between 130 and 318 K, using 12 strong reflections with sufficiently high angle values ( $\theta \sim 20^\circ$ ). Each time, we centred two symmetric positions of the peak  $\theta$ , and  $-\theta$ , to avoid zero inaccuracies.



(a)



(b)

Fig. 3. Oscillation photographs around  $b$  axis of a TANO-*n*-heptane crystal. (a) HT phase 295 K. (b) LT phase 170 K.

As the lattice parameters  $b$  and  $a$  are different in the two phases, and in order to avoid fractional values of  $h$  or  $k$ , we have chosen to give the results with the  $a$  parameter of the HT form ( $\sim 36$  Å) and the  $b$  parameter of the LT form ( $\sim 11.6$  Å).

In parallel with the study of the parameters, we observed the intensities of the following reflections:  $\bar{1}2,0,16$  of the  $2n,4n,l$  type, the only kind of reflection which exists in the two phases.

$13,2,1$  of the  $2n+1,4n+2,l$  type. These only exist in the HT phase and vanish when the transition occurs.

$\bar{1}2,2,19$  and  $634$ , respectively, of the  $2n,4n+2,l$  or  $2n,2n+1,l$  type, which exist only in the LT phase.

**Results** (Fig. 4): The four cell parameters  $a$ ,  $b$ ,  $c$ ,  $\beta$  decrease. The volume decreases in a significant manner:  $\Delta V/V = 1.6\%$  at the transition. The hysteresis phenomenon is confirmed. As for the DSC curve (straight peaks when the temperature increases, wide peaks when it decreases), the variation of cell

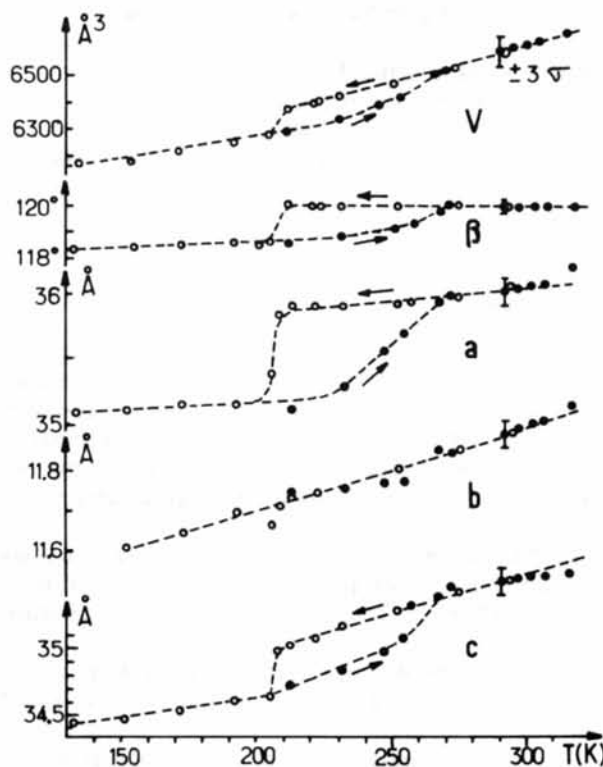


Fig. 4. TANO-*n*-heptane: cell parameters as a function of temperature. (Values are given in the cell  $a, 2b, c$ , where  $a, b, c$  are the parameters of the HT phase.)

parameters is abrupt at the descent (less than 3 K) and broad at the ascent (30 K for the  $a$  parameter). Transition temperatures are higher than DSC temperatures by about 20 K but this is not significant because the temperature calibration of the diffractometer has not been tested.

We can find the same behaviour (Fig. 5) in the evolution of the intensities of one category of reflections, which exists only in the LT phase:  $\bar{1}2,2,19$  and 634. They appear rapidly over less than 10 K, but vanish slowly over about 40 K. On the other hand, the  $\bar{1}3,2,1$  reflection which exists only in the HT phase behaves similarly at the ascent and at the descent. We have no interpretation.

In Fig. 5 we can see that the intensity of the  $\bar{1}2,0,16$  reflection, which exists in the two phases, curiously decreases by 30% both in descent and in ascent. Often the intensity of reflections increases during a transition because of a better mosaicity of crystals which lowers the secondary extinction. We find the opposite and it may be due to the relatively large shifts of TANO molecules at the time of the transition equivalent to a large disorder.

### 3.3. Structure hypothesis

The general observation of low-temperature rotating-crystal photographs along  $b$  immediately shows that layers observed in the HT phase are outstandingly

intense. Among the other layers, some are not observed, the others are more or less visible:

(a) for TANO- $n$ -heptane,  $b$  is multiplied by 2, intermediate layers are faint (Fig. 3);

(b) for TANO- $n$ -octane,  $b \times 7$ , only layers with  $k = 7m \pm 3$  ( $m$  integer) are observed;

(c) for TANO- $n$ -nonane,  $b \times 5$ , the layers with  $k = 5m \pm 2$  are noticeably more intense than those with  $k = 5m \pm 4$ .

The above observations are in agreement with the hypothesis of small helical displacements of previously superimposed TANO molecules, when the transition occurs. The helix would have its axis parallel to  $b$ , and there would be three (for TANO- $n$ -octane) or two (for TANO- $n$ -nonane) pitches of the helix for every repeated distance  $b(LT)$ . The only possible observed layers would be  $k = 3n + 7m$  ( $n, m$  integers) and  $k = 2n + 5m$ . It has been shown (Cochran, Crick & Vand, 1952) that, if the radius of the helix is small, the intensity of layers, which involves Bessel functions, decreases rapidly with  $n$  and is negligible for  $n > 2$ , which is effectively observed.

So we can make the assumption that TANO molecules, superimposed in the HT phase, undergo displacements so as to sit on a helix of small radius, which has its axis parallel to  $b$ , with a pitch equal to the length of the alkane guest. This could be a starting point for the resolution of the LT structures.

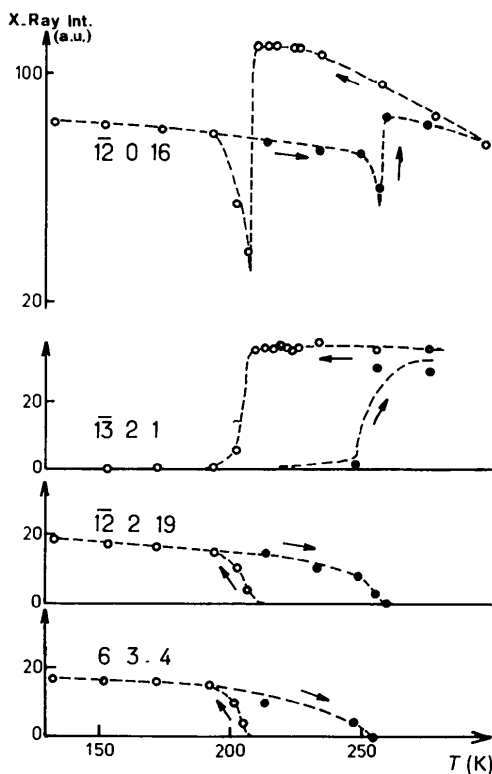


Fig. 5. TANO- $n$ -heptane: the intensity of some reflections versus  $T$ .

### 4. Concluding remarks

Although we do not present the results of the X-ray study for two other TANO- $n$ -alkanes ( $n = 14, 16$ ) because it reveals intermediary complex phases not yet understood, we can say that, at low temperatures, superstructures also exist. So in five different TANO- $n$ -alkanes, we have found superstructures, although *a priori* the repetition period of TANO molecules (5.8 to 5.95 Å according to the temperature) has nothing to do with the periodicity of alkanes in the channels. How does the competition between these two characteristic lengths - periodicities of TANO and of alkanes - take place to lead to lock-in transitions when the temperature is lowered? Do lock-in transitions exist for all lengths of the included alkanes? What happens in the vicinity of transitions? All these problems have to be elucidated.

Another aspect of the study of the transitions is in progress: to get a better understanding of the phase transition in TANO- $n$ -heptane, we are looking into the dynamic character of the problem. At the present time, preliminary incoherent quasielastic neutron-scattering experiments performed at ILL in Genoble have proved the dynamic character of the disorder of molecules in TANO- $n$ -heptane. We must characterize the corresponding motions and try to study their evolution as a function of temperature.

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### Structure Determination of Benzil in its Two Phases

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#### Abstract

Benzil,  $C_{14}H_{10}O_2$ ,  $M_r = 210.2$ ,  $Mo\ K\alpha$ ,  $\lambda = 0.7107 \text{ \AA}$ . In the high-temperature phase ( $T > 83.5 \text{ K}$ ), trigonal,  $P3_121$ ,  $Z = 3$ ,  $F(000) = 330$ ,  $\mu = 0.90 \text{ cm}^{-1}$ . At 294 K,  $a = 8.402(4)$ ,  $c = 13.655(9) \text{ \AA}$ ,  $V = 835(2) \text{ \AA}^3$ ,  $D_x = 1.253 \text{ g cm}^{-3}$ ,  $R = 0.043$  for 390 reflections. At 100 K,  $a = 8.356(3)$ ,  $c = 13.375(6) \text{ \AA}$ ,  $V = 809(1) \text{ \AA}^3$ ,  $D_x = 1.294 \text{ g cm}^{-3}$ ,  $R = 0.041$  for 443 reflections. In the low-temperature phase ( $T = 70 \text{ K}$ ), monoclinic,  $P2_1$ ,  $Z = 6$ ,  $F(000) = 660$ ,  $a = 14.380(7)$ ,  $b = 8.373(4)$ ,  $c = 13.359(22) \text{ \AA}$ ,  $\beta = 88.82(5)^\circ$ ,  $V = 1608(4) \text{ \AA}^3$ ,  $D_x = 1.302 \text{ g cm}^{-3}$ ,  $R = 0.066$  for 1893 reflections. The resolution of the low-temperature phase ( $T = 70 \text{ K}$ ) was possible owing to a new low-temperature attachment for the X-ray four-circle diffractometer. Contrary to what has been previously assumed, the transition corresponds to a doubling of the unit cell. A discussion is developed with these new structural results in order to explain published Raman scattering experiments.

#### Introduction

In the last few years, considerable efforts have been devoted to the study of the crystalline phase transition of benzil ( $C_6H_5-CO$ )<sub>2</sub> which occurs at 83.5 K. The room-temperature structure has rhombohedral symmetry (Brown & Sadanaga, 1965; Solin & Ramdas, 1968). The space group is  $P3_121$  (or the enantiomorph  $P3_221$ ). The benzil molecule has a permanent dipole moment (Higashi, 1938) which coincides with the

twofold molecular axis. The hexagonal cell contains three molecules related by the  $3_1$  screw axis and there is no spontaneous polarization in this phase. Optical birefringence appears near 84 K (Esherrick & Kohler, 1973), which indicates a lowering of the symmetry. The transition is reversible with an extremely low latent heat and leads to a twinned crystal (Esherrick & Kohler, 1973). Calorimetric investigation (Dworkin & Fuchs, 1977) shows a peak in the heat capacity at 84.07 K and the form of the specific-heat anomaly suggests the first-order nature of the transition. Electron nuclear double resonance (ENDOR) spectroscopy (Chan & Heath, 1979) confirms the presence of domains separated by angular deviations of the order of  $1.55^\circ$  at liquid-helium temperature and the disappearance of the  $3_1$  screw axis in the low-temperature phase. X-ray studies (Odou, More & Warin, 1978) report that symmetry breaking leads to the triclinic space group  $P1$  with a fourfold expansion of the primitive unit cell corresponding to the doubling of the parameters along **a** and **b**. Domain arrangement occurs in such a way that the crystal acquires a pseudo-threefold screw axis and macroscopic polarization vanishes. However, Raman scattering experiments (Sapriel, Boudou & Perigaud, 1979) display a soft optical mode of *E* symmetry in the high-temperature phase which splits into two (*A* and *B*) components in the low-temperature phase, consistent with a monoclinic phase without change in the number of molecules of the unit cell. According to the observation of this optical soft mode and theoretical