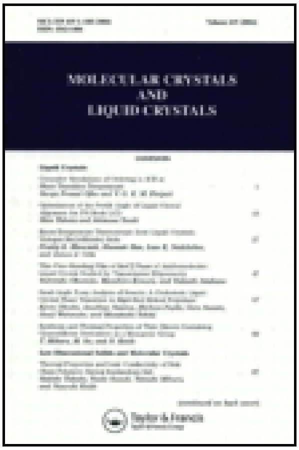

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A Single Crystal to Single Crystal Reversible Phase Transition Which Exhibits The "Hopping Effect"

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A SINGLE CRYSTAL TO SINGLE CRYSTAL REVERSIBLE PHASE TRANSITION WHICH EXHIBITS THE "HOPPING EFFECT"

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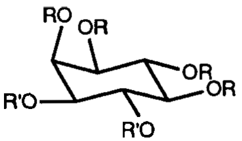
Abstract A reversible phase transition involving jumping of the crystal in the process of heating and cooling is described. If crystals are fixed to the heating area, physical expansion and contraction are observed when heated and cooled respectively. From the crystal structure of Form I and the powder diffraction of Form II it was found that the expansion and contraction occurs in the direction of the *b* axis.

INTRODUCTION

The phenomenon of "hopping crystals" or "jumping crystals" was first described by Gigg at al.[1] These terms are used to describe vigorous mechanical movements of a crystal on heating or cooling through a phase transition. From discussions we have had with colleagues, it is apparent that many have observed the phenomenon, but to the best of our knowledge it have been reported explicitly for only two systems; *myo*-inositol derivatives [1] (**1a**-$R=C_6H_5$-CH_2, $R'=CH_3$-CO,**1b**-$R=C_6H_5$-CH_2, $R'=H$), and *ttatt*-perhydropyrene [2] (**2**).



1a, 1b

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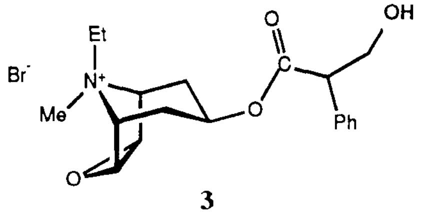
In the former case the close similarities between the packing in the structures of the starting and final phases prevented establishing a mechanism for the phenomenon.[3] For perhydropyrene the explanation for the jumping effect during the heating and cooling process is that the compound is packed in a layered structure and upon heating there are movements of the molecules within the layer, leading to a buildup of stress until the layers are shifted relative to each other in the course of phase transition which causes the crystal to jump.[2]

We present here preliminary results on a third compound, oxitropium bromide (**3**), which behaves in a similar fashion. The reversible phase transition involves physical expansion and contraction of the crystal during the heating and cooling process, respectively. Upon heating the crystal exhibits highly anisotropic parameter changes corresponding to about 4% volume expansion. The transformation of Form I to Form II is endothermic, observed in temperature range 56-58°C, with an enthalpy of transition of about 2.5 kJ/mole. The reverse transition is exothermic and exhibits hysteresis, occurring in temperature range of 34-36°C. The lower and upper temperature crystal forms I and II, both orthorhombic, have been characterized by their different IR spectra, DSC and powder diffraction patterns.



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RESULTS AND DISCUSSION

Lattice parameters of both forms[†] indicate the anisotropicity of the phase change. The b axis increases by 11% from 10.118Å to 11.254Å, while the c axis

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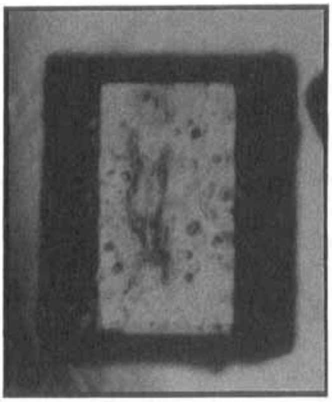
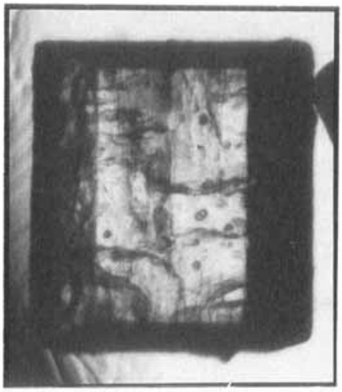
[†] *Crystal Data for Form I*: $C_{19}H_{26}NO_4Br$ M= 412, orthorhombic, space group $P2_12_12_1$, a= 7.388(2)Å, b= 10.118Å, c= 24.705Å, V= 1846.7Å^3, Z=4. 3241 unique reflections were collected with a Siemens P$\bar{1}$ diffractometer at 293K, .[λ(Mo-K$_\alpha$)=0.71069Å, graphite monochromator, $2\theta<50^\circ$]. R factor at the current stage of refinement is 3.1%.
Crystal Data for Form II: The lattice parameters were obtained by indexing the powder diffraction pattern (348K): orthorhombic, space group $P2_12_12_1$, a= 7.479Å, b= 11.254Å, c= 22.890Å,V= 1846.7Å^3, Z=4.

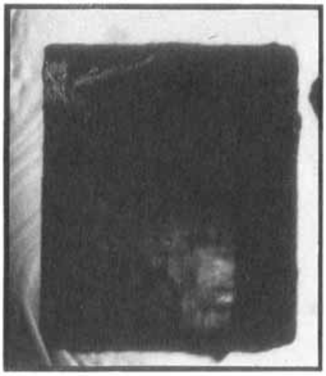
decreases by 7%. This directionality is readily observed while heating the crystal under the microscope (the crystals are prevented from jumping off the hot stage by a small amount of Vaseline in contact between the crystals and the glass); during the phase change the crystal expands along the *b* axis by approximately 10%. Upon cooling it contracts by the same amount, as illustrated in Pictures 1-3. Picture 1 shows a crystal before the phase transition, whose width is 0.50mm, Picture 2 shows the same crystal at 56.6°C after the phase transition with width of 0.55mm, and Picture 3 shows the crystal after cooling to 35°C with reduced width of 0.50mm. From this it is possible to infer that the microscopic change in the unit cell dimension (*b* axis) is manifested as a macroscopic one in the physical crystal dimension.



PICTURE 1



PICTURE 2



PICTURE 3

The crystal habit is given in Figure 1. As shown in pictures 1-3 the observed dimensional change of the phase change is in the width, as can be seen in Figure 1 as the *b* axis. There is a very slight expansion of the *a* axis and correspondingly no observable physical change in the crystal in that direction. The *c* axis contracts in going from Form I to Form II. Figure 2 shows the packing of the molecules parallel to *ab* plane. The packing consist of layers of molecules parallel to the *ac* plane, with anions tending to be in the vicinity of the areas between layers.

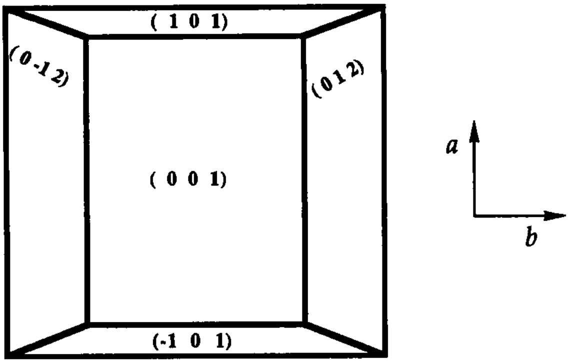


FIGURE 1 Crystal habit of 3.

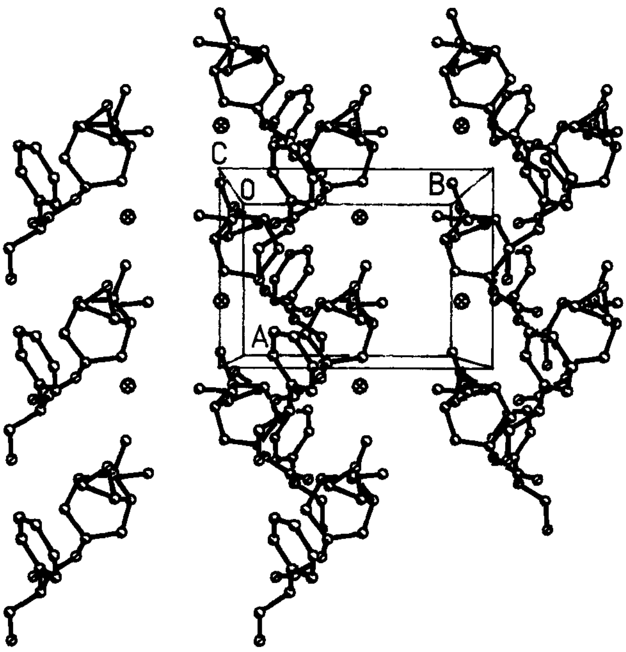


FIGURE 2 Packing diagram of 3.

Two DSC consecutive heating cycles of a single crystal were taken (Figure 3). The first heating cycle exhibits a sharp endothermic peak corresponding to the phase transition I→ II at 57.8°C. The exothermic peak of the cooling curve is not sharp due to breaking of the single crystal into several smaller crystals; when several crystals are heated or cooled it is expected that each crystal will transform at different temperature. This may be due to the non uniformity in size and shape of different crystals, to the variety of faces and surface areas in contact with the heating surface, to the anisotropicity of the thermal conductivity of the crystals, and to the rate of heating. While the phase change is reversible it suffers from hysteresis, so that phase change II→ I occurs at about 35°C The second heating cycle exhibit lowering of the temperature of the phase transition I → II of about 2°C.

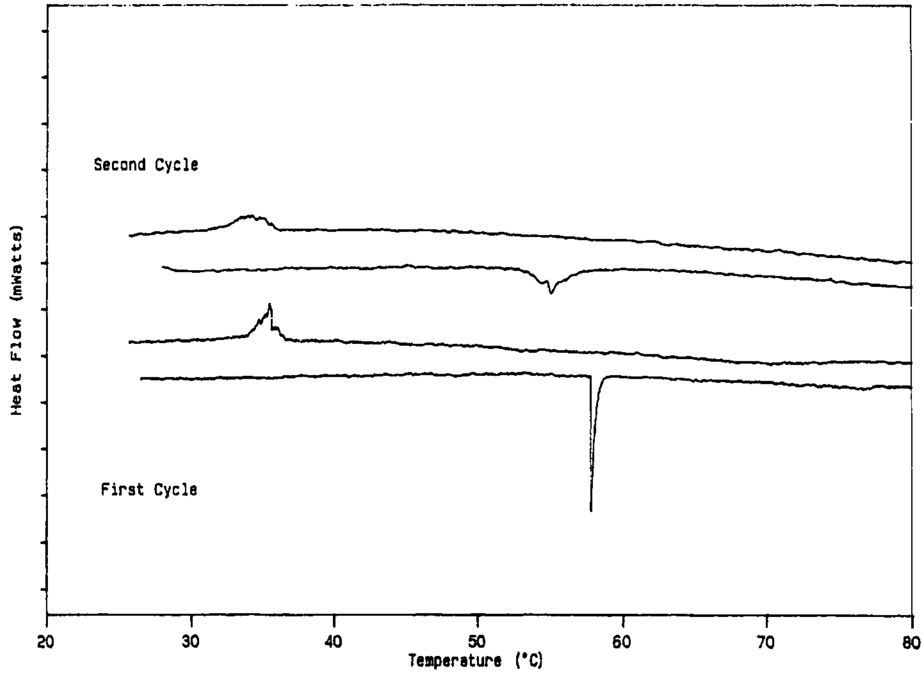
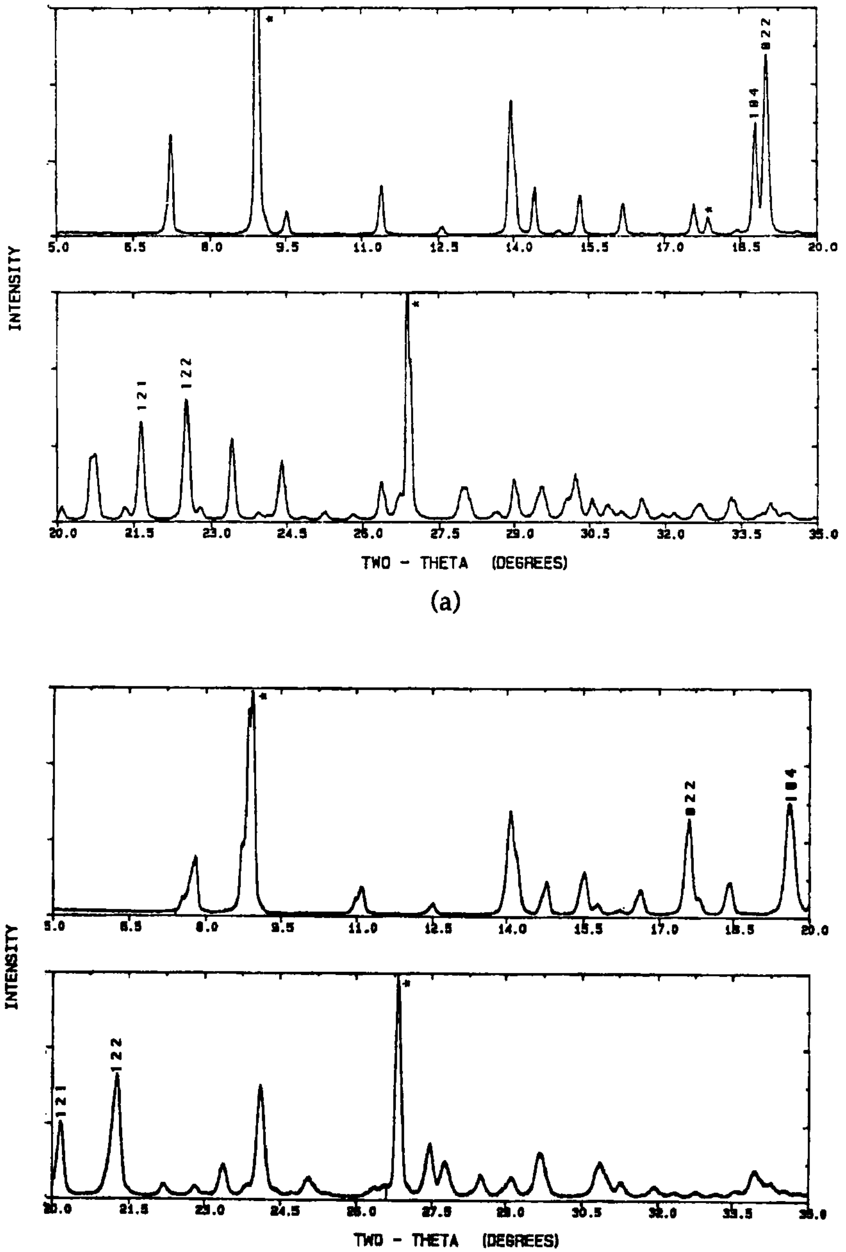


FIGURE 3 Two concecutive DSC cycles of single crystal of **3** in the region of the phase transition.

The powder diffraction patterns of two forms (Figures 4a and 4b) differ markedly. Indexed reflections 022, 104, 121, 122 are marked for comparison.



(a)

(b)

FIGURE 4 Powder diffraction patterns of the two forms of 3. (*) indicate reflections of the standard fluorophlogopite. (a) Form I, (b) Form II.

The melting range of **3** is 202-205°C. At about 5°C below the melting point bubbles appear within the bulk of the crystal, and upon continued heating are released, while the crystal maintains its physical integrity. This phenomenon is also evidenced by the presence of a shoulder on the low temperature side of the melting peak in Figure 5. An NMR investigation of a solution of the melt indicates that the gas released consisted of 70% methyl bromide and 30% ethyl bromide.

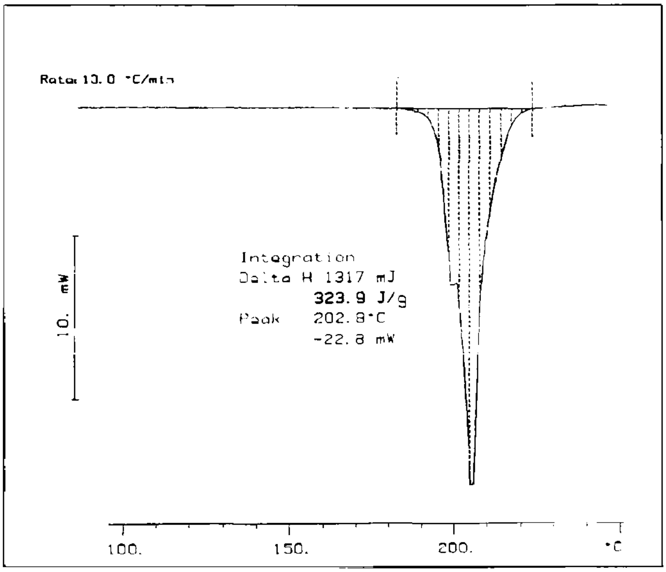


FIGURE 5 DSC of **3** in the region of the melting point.

CONCLUDING REMARKS

Final elucidation of the mechanism of the phase transition awaits the determination of the crystal structure of form II. However, the structure of Form I (Figure 2) suggest the possibility of relatively facile movements of molecules (or parts of molecules) across the boundary between layers. It is hoped that the crystal structure of Form II will also provide evidence to suggest a mechanism for the evolution of ethyl bromide and methyl bromide in the proportions observed.

ACKNOWLEDGMENT

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