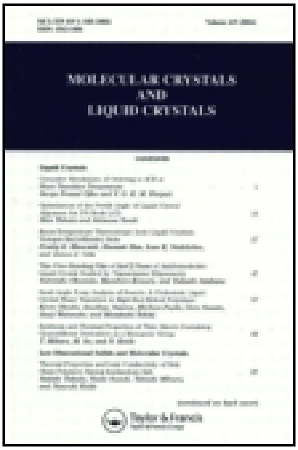

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Experimental Studies on the Single Crystal to Single Crystal Transformation of 5-Methyl-1-thia-5-azacyclooctane-1-Oxide (TACO) Perchlorate. Evidence for an Intermediate State

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Version of record first published: 20 Apr 2011.

To cite this article: Eileen N. Duesler, Karl E. Wiegers, David Y. Curtin & Iain C. Paul (1980): Experimental Studies on the Single Crystal to Single Crystal Transformation of 5-Methyl-1-thia-5-azacyclooctane-1-Oxide (TACO) Perchlorate. Evidence for an Intermediate State, Molecular Crystals and Liquid Crystals, 59:3-4, 289-298

To link to this article: http://dx.doi.org/10.1080/00268948008071429

Mol. Cryst. Liq. Cryst., 1980, Vol. 59, pp. 289–298
0026-8941/80/5903–0289$04.50/0

Printed in the U.S.A.

Experimental Studies on the Single Crystal to Single Crystal Transformation of 5-Methyl-1-thia-5-azacyclooctane-1-Oxide (TACO) Perchlorate. Evidence for an Intermediate State

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(*Received June 2, 1979; in final form August 14, 1979*

The single crystal transformation of the perchlorate salt of 5-methyl-1-thia-5-azacyclooctane-1-oxide (TACO) has been studied by X-ray, microscopic, and differential scanning calorimetric methods. The transformation from the α- to the β-form occurs in the range 8–11°C, and is reversible, topotactic, and takes place without apparent change in the shape, appearance, or ability to diffract of a single crystal. The heat of transition is 0.6 Kcals/mole. From an examination of the intensities of X-ray reflections as the transition takes place, it was shown that the transition α to β is much faster than the reverse process. Evidence was also obtained for the involvement of an intermediate state in the transformation β to α.

INTRODUCTION

It has been observed that the perchlorate salt of 5-methyl-1-thia-5-azacyclooctane-1-oxide (TACO) (1)[1] undergoes a reversible transformation from one single crystal form stable at 3° (α-form) to another stable at 25° (β-form) with retention of orientation and outward morphology.[2] The transformation may be more properly described as a phase transition rather than a chemical reaction,[3] although the question as to whether a molecular change accompanies the transformation has not been resolved. Crystal structure determinations were carried out on the same sample at both 3° and 25°.[2] The cell data showed a halving of one, with concomitant doubling of the other, of the *a*- and *c*-axial lengths. The structures of both forms were very similar in

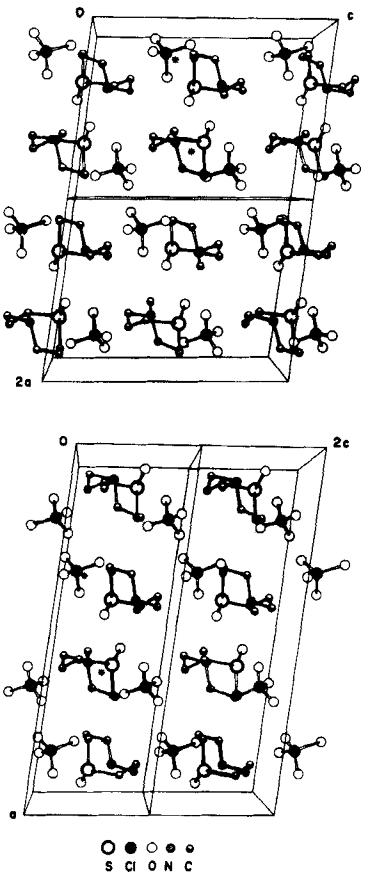
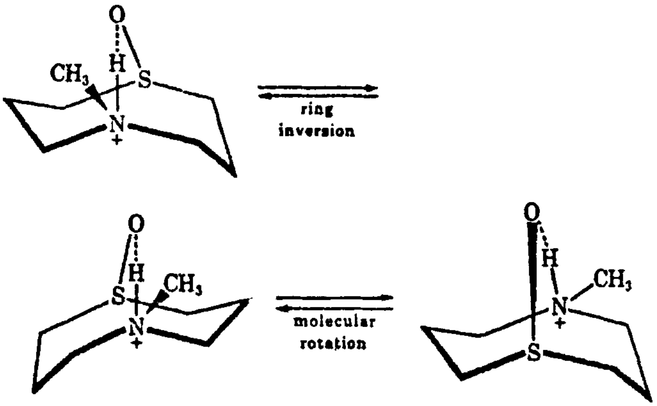


FIGURE 1 Views of the crystal structures of (top) the α-form and (bottom) the β-form looking along the *b*-axis. A reference molecule in the same configuration in each structure is marked by an asterisk. Molecules which have the same configuration in both structures are shown with blackened bonds. In order to generate one structure from the other, the molecules shown with open bonds must change configuration, *ie.*, D to L and *vice versa.*

projection down the *b*-axis, but molecules that were related by a glide operation in one form were related by a translation in the other, and *vice versa*. The space group description for the α-form was $P2_1/c$ while that for the β-form was $P2_1/a$. Views of the two structures are shown in Figure 1. One way of transforming the structure from the α to the β-form, would involve a "flipping" of the boat-chair (BC) conformation of the eight-membered ring, followed by rotation of the cation of one half of the molecules in the crystal. Such a procedure would convert translation-related molecules to glide-related molecules, and *vice-versa* (Figure 1); these changes involve the inter-



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conversion of D and L configurations. Such a mechanism, if it could be established, would be of particular interest because it might represent a rare example of a possible "homogeneous" solid state reaction in which a change from starting crystal A to product B would proceed by random conversion of A molecules to B; the crystal would thus pass through a continuous series of single crystalline states of intermediate structure.[4,5]

On the basis of an analysis of the two limiting crystal structures, Thomas and co-workers[6,7] have proposed an alternative mechanism that does not assume any molecular change, but involves a cooperative shear on alternate (102) crystallographic planes. Through the courtesy of Professor W. Kenneth Musker of the University of California, Davis,[8] we have recently obtained a sample of the perchlorate salt of TACO, and we now report for the first time an experimental investigation of the actual transformation.

EXPERIMENTAL SECTION

Crystals supplied by Professor Musker were used without further recrystallization.† X-ray diffraction data were measured on a Syntex $P2_1$ diffractometer (MoK_α, $\lambda = 0.7107$ Å), equipped with a Syntex LT-1 Low Temperature Attachment. Cell data were determined for both forms (α-form at 0°C, β-form at 22°C) by a least squares fit to the settings for fifteen high-angle reflections. The results are in Table I. Two or three different crystals were observed at temperatures above and below the transition. In the case of

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† These crystals had been sent to Illinois by air from California during the 1978–79 winter. Temperatures were such (even indoors because of the need for energy conservation) that it is probable that they had undergone one or two transitions before our study was initiated.

TABLE I

Crystal data for the two forms of TACO perchlolate (I)

	α-form (0°)	β-form (22°)
a (Å)	9.825(2)	19.827(5)
b (Å)	8.740(2)	8.770(2)
c (Å)	13.183(2)	6.644(1)
β (deg)	98.59(1)	98.00(2)
V (Å^3)	1119.3	1144.0
Z	4	
Space group	$P2_1/c$	$P2_1/a$

at least one crystal, four different passes through the transition temperature were made. The progress of the transition in each direction was followed by measuring the intensities of ten strong reflections ($k \neq 0$) in a 12.5-minute cycle while the temperature was changed such that the transition would occur. Five of these reflections would be present only for the α-form and five of them would be present only for the β-form. The intensities of the reflections were measured by a 2θ scan at 5.9° per minute.

Crystals in their transmission positions between crossed polarizing filters on a thermoelectric cold stage were cooled to 0° for 18 hr. and then to −20° for 1 hr. There was no marked change in the appearance of the crystals. No frontal migration could be observed and the crystals continued to transmit in approximately the same way after cooling as before. On warming to room temperature there was some indication that extinction upon rotation of the crystals was less complete than had been the case before heating but otherwise there was no marked change. Differential scanning calorimeter (DSC) runs were made using the DuPont 900 Thermal Analyzer. Several runs were made on the same sample (13.5 mg), with an initial temperature of *ca.* −20°C, a heating rate of 10°C/min, and a final temperature of 40°C. The instrument was calibrated to the heat of fusion of benzoic acid ($\Delta H_f = 33.9$ cal/g).[9] The areas under curves were measured with the aid of a planimeter, taking the average of four readings.

RESULTS

The previous findings[2] regarding retention of single crystal character and crystal orientation after three or four passes through the transition were confirmed. The cell data (Table I) for the β-form are slightly different from, and are undoubtedly more accurate than, those reported previously. The ratios of the three axial lengths, (with appropriate correction for doubling

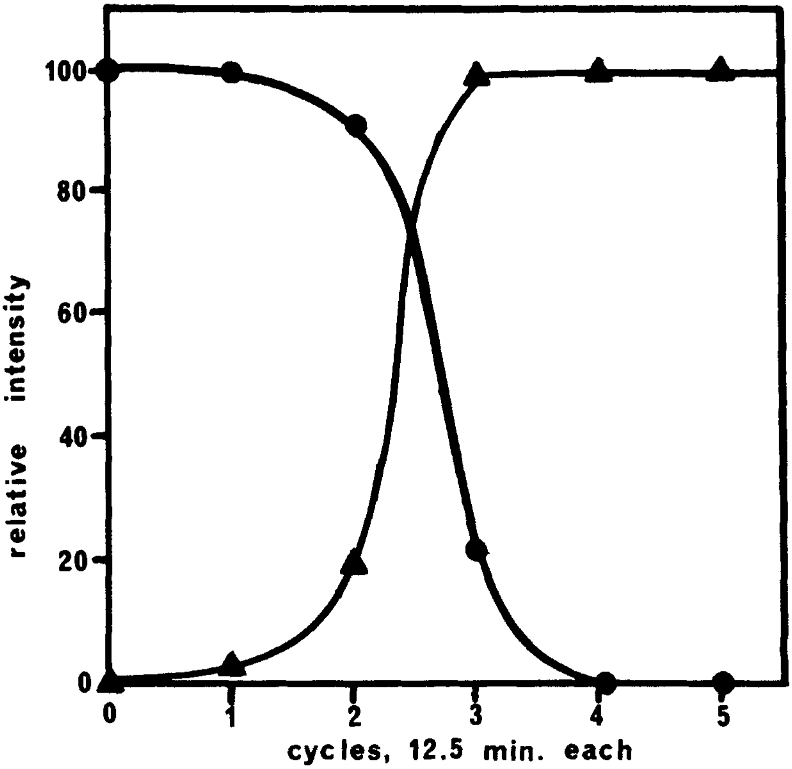

FIGURE 2 The combined normalized intensity of five reflections for each form of TACO perchlorate measured on 12.5 minute cycle as the crystal is taken through the α- to β-transition. The triangles correspond to the intensities of the reflections that are specific to the β-form, while the circles correspond to the intensities of reflections of the α-form.

and halving) are now β/α 1.009, 1.003, and 1.008 for *a*,*b*, and *c*, respectively.

In the case of one crystal of TACO perchlorate, additional reflections along the c^*-axis were observed on an axial rotation photograph taken on the diffractometer when the transition α to β was effected; these reflections corresponded to a number of repeat distances in the range 25–40 Å and were observed each time that the α to β transition was carried out on this particular crystal.

Careful control of the temperature of a crystal on the diffractometer has led us to believe that the transformation takes place in the temperature range 8–11°C. A crystal initially in the high temperature β-form takes a few hours to change completely to the α-form when held between 0–8°, whereas the same crystal, raised above 11°, reconverts to the β-form in a much shorter time. One crystal has been recycled through four transitions without apparently affecting its crystallinity, ability to diffract, orientation, or outward appearance.

Some information on the rate and extent of the transition was obtained by monitoring the intensities of ten reflections, five being present in only the α-form ($\bar{1}\bar{1}3$, $\bar{1}\bar{1}5$, $\bar{1}\bar{2}1$, $\bar{2}\bar{2}3$, $2\bar{2}1$) and the other five being present in only the β-form ($\bar{1}\bar{4}1$, 312, $1\bar{2}3$, $\bar{1}20$, $1\bar{1}1$), as the crystal passed through the transition. The results are shown in Figures 2 and 3. Figure 2 illustrates the change in total intensity of the two groups of five reflections as the crystal was heated from 0° to 30°. The intensities of each reflection were normalized so that each reflection had a maximum intensity of 100, and the averages of the five reflections common to each form were plotted. It is seen that transition is complete over a relative short time period (< 1 hr.) after the temperature is above 12°C. Also, the decrease in intensity of the reflections present only in the α-form is virtually matched by the increase in intensity of the reflections characteristic of the β-form. In Figure 3 is illustrated the

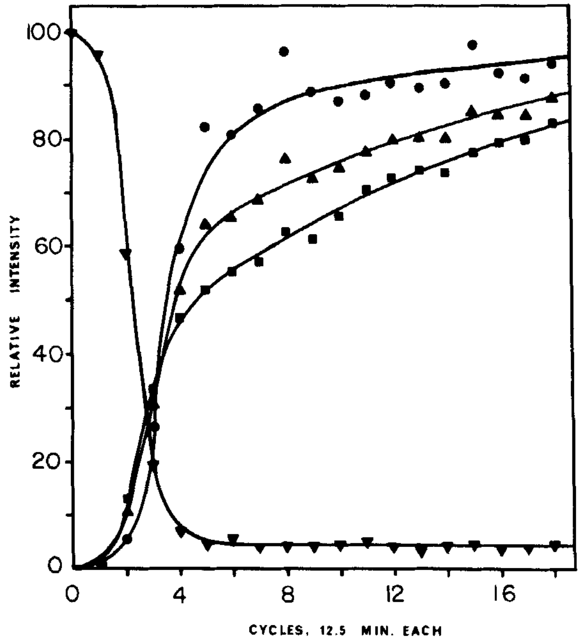

FIGURE 3 The combined normalized intensity of reflections for each form of TACO perchlorate measured on a 12.5 minute cycle as the crystal is taken through the β- to α-transition. The inverted triangles (▼) correspond to the combined normalized intensity of five reflections that are specific to the β-form; the normal triangles (▲) correspond to the combined normalized intensity of five reflections that are specific to the α-form; the squares (■) correspond to the intensity of three of these latter reflections with $k = 2$, while the circles (●) correspond to the intensities of the two reflections with $k = 1$.

TABLE II

Data on DSC runs as crystal is taken through transitions α to β

Run	Hrs. at −20°C	Onset (°C)	Peak (°C)	Area (in^2)[a]	ΔH (kcal/mole)[b]
1	0.1	16.5	25.0	0.34(3)	0.09
2	0.5	23.5	28.5	1.30(1)	0.35
3	2.0	26.5	30.5	1.87(1)	0.51
4	6.0	26.0	33.0	2.14(4)	0.58
5	7.5	25.5	29.5	2.21(2)	0.60

[a] Measured by a planimeter; average of 4 readings.

[b] Calibrated to heat of fusion of benzoic acid (ΔH_f = 33.9 cal/g)[9].

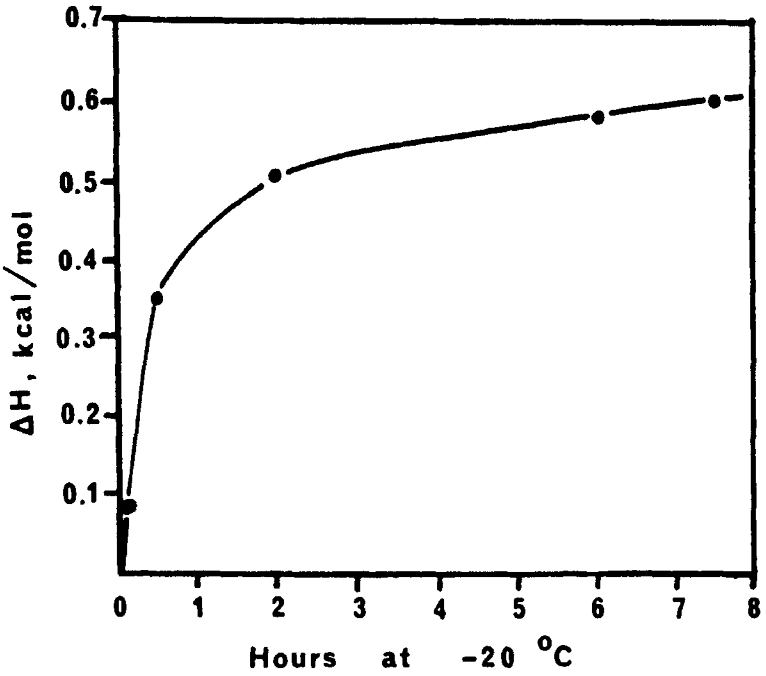

FIGURE 4 Effect of cooling time on enthalpy change for transition of α-form to β-form.

change in intensity of the same reflections when the reverse process takes place, as the crystal is cooled from 32 to 0°C. In this case, the results are somewhat more complex. The decline in intensity of the five reflections characteristic only of the β-form is quite rapid and uniform. However, the growth of the intensities of the five reflections common to the α-form is considerably slower and takes several hours to reach a maximum value. Also the behavior of two of the reflections ($\bar{1}\bar{1}3$ and $\bar{1}\bar{1}5$) is somewhat different from the other three ($\bar{1}\bar{2}1$, $\bar{2}\bar{2}3$, $\bar{2}\bar{2}1$); the growth of the latter three reflections is significantly slower than that of the first two. There was no correlation of the different behavior of these two groups of reflections with either integrated intensity or peak breadth.

The examination of crystals under the microscope between crossed polarizing filters indicated no definite change either after 18 hr. at 0°, or after the crystal was returned to room temperature.

The results of the DSC studies are given in Table II. In each of the several runs made on a single sample at a heating rate of 10°C/min, an endotherm was observed, but the peak position, shape, and area depended upon how long the sample was maintained at *ca.* −20°C before the run was made. As the sample is held at −20°C for longer periods of time, the onset and peak temperatures increase, and the peak sharpens. In addition, the area of the peak increases substantially as the sample is cooled longer. The enthalpy change associated with the transition approaches a limiting value of *ca.* 0.6 kcal/mole for the transformation of the α-form to the β-form (Figure 4).

DISCUSSION

Our results indicate the unique nature of this transformation when compared to those of other organic solids that have been studied. While transformations such as that of monoclinic to triclinic *p*-dichlorobenzene exhibit single crystal to single crystal character, in that case the daughter crystal grows in an orientation that is random and the growth from a nucleation site can be followed microscopically.[10] A somewhat different view of this transition has also been described.[11] The reactions of iodobenzoyl peroxides studied by Gougoutas and co-workers[12] exhibit topotaxy, but of a much more complex nature than that described for TACO perchlorate. Other phase transitions such as that of β to α-*p*-nitrophenol result in microcrystalline products with little or no preferred orientation.[13] In many regards, the behavior of TACO perchlorate is somewhat similar to those of "plastic" crystals,[14] but in these cases a highly disordered phase is usually the product of the phase transformation.

The limiting value of *ca.* 0.6 Kcal/mole for the enthalpy change in TACO perchlorate is indicative of the difference in crystal packing and is in the usual range for the energy differences between crystalline forms.[15,16]

Because of the reversible topotactic nature of this transformation, we were able to study some aspects of the kinetics of the change by monitoring the intensities of the X-ray reflections. The data on the change in intensity of reflections as the transition occurs show that the change α to β is rapid and no information pertaining to the mechanism is apparent. The data for the conversion β to α, however, show that the growth of single crystal character as defined by the lattice of the α-form is slower than the loss of such character relative to the lattice of the β-form. This effect requires the presence of at least 20% of an intermediate; possibly microcrystalline, or one with single crystal character that does not give rise to reflections based on the reciprocal lattice of the α-form. This latter possibility received some additional support from the observation of additional reflections in the c^* direction when one of the crystals was cooled below the transition. Clearly, the possibility of the presence of some such crystalline intermediate is not inconsistent with a mechanism of the type proposed by Thomas and co-workers.[6] The explanation of the difference in behavior of the two sets of reflections of the growing α-phase is not evident with the data available.

That no change is observed with the polarizing microscope might be considered surprising. However, as the crystals tend to be plate-like with (100) being the face of the plate, and are generally elongated along the b-axis, a change taking place in a direction normal to the [010] direction, might not be obvious.

In conclusion, while our results do not provide all the answers necessary for delineation of the mechanism of the transition that occurs for TACO perchlorate, they do emphasize the extremely unusual nature of this transition. It is hoped that they will lead to further studies of this remarkable compound.

Acknowledgement

This work was supported in part by the National Science Foundation. We thank Professor W. K. Musker from the University of California at Davis for generously supplying us with the material.

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