

Reversible Chemical Reactions in the Solid State

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In this paper, it is demonstrated through a number of examples, beginning with that of a simple melting transition (order/disorder) that the observation of the idealised spontaneous, i.e., first order, transition is not to be expected. Other examples of reversible solid state transitions, including solid/solid (order/order) or solid/mesophase (order/semi-order) reactions of a number of organoboron compounds, confirm this notion. It is proposed that the deviations from the ideal transition have their origin in the multitude of lattice defects in the units making up the composite sample, polycrystalline or even 'single crystal'. While in each crystallite or domain first order transitions are to be expected, the assembly will naturally transform over a temperature range. This mechanism does not apply to hysteresis free solid state transitions or reactions in which the unit cell remains greatly unaffected by any transformation. Examples of this type are also presented and discussed.

INTRODUCTION

Studies of chemical reactions have traditionally been carried out in either gas or liquid phase. Although there have been sporadic reports on the observation of a reaction occurring in the solid state [1], it had been, in general, accepted that the solid state is the 'grave yard' of molecules in which, at most, the atoms or molecules librate or undergo minute translational motions about their lattice points [2]. A systematic study of one type of solid state reaction (photo chemical dimerization of a number of cinnamic acid derivatives) was only undertaken during the past 30 years, being mainly initiated by Schmidt [3]. Most of the relatively few observed and reported thermally induced reactions suffer from the limitation of being a one way affair. Those cases in which reversibility of a solid state transformation (not necessarily a chemical reaction) has been observed, are often complicated by accompanied hysteresis, which is a widely observed phenomenon in nature. The non-equilibrium reversals are not in line with thermodynamic laws of microscopic reversibility. This has been the cause of much headache for the solid state chemists who in the past have made many extensive efforts to find theoretical and mathematical rationalizations for it [4].

Overall, solid state reactions, with the exception of the photochemical dimerizations of suitably packed monomers, have, mainly because of the difficulty in

predicting their occurrence, retained their aura of mystery for organic chemists and, therefore, have generally been ignored. Furthermore, often, they have remained unnoticed. Thus, a solid which after a prolonged period at room temperature or upon thermal treatment has lost its original color, or changed its appearance, is often thought to have decomposed and is discarded. This is unfortunate, since when a reaction occurs in the matrix of a crystal lattice, it can be expected that only a single product, with a geometry predetermined by that of the matrix, is formed. At present, solid state chemists are far from being able to tailor-make crystals of one reactant or, as would be even more desirous, to co-crystallise two reactants with the suitable topology and contact distance of the molecules. In the meantime, research efforts should be concentrated on gaining fuller understanding of those rare examples of fortuitously discovered examples of intra-crystal reactions. Given the investigative techniques available nowadays, two parallel venues of approach can, at present, be suggested:

- (a) The study of molecular motion, at the onset, (librational as well as translational) within crystals known to undergo temperature dependent polymorphism or reactions. This can be done, as will be shown in the examples discussed below, amongst other techniques, by traditional X-ray diffraction or by the more modern solid state ¹³C NMR methods.
- (b) The study of the intermolecular forces involved in crystal lattices which lead to the particular molecular packing found in the unit cell. The quantization

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of these forces should lead to calculation of the lattice energies of each of the possible polymorphs and the prediction of the temperature of the crystal-crystal inter-conversion. An obvious method seems to be the modern technique of molecular modelling [5,6]. Up to now, however, very little effort has been made to quantify the intermolecular forces in crystals.

The present review of the state of knowledge is, therefore, restricted to examining the results of those cases which have been investigated by various spectroscopic methods and by X-ray diffraction of single crystals.

Assuming the phenomenological similarity of the initiation of an order/disorder (melting) process to that of an order/order transition, one has to view and compare the forces involved at the onset of a solid/solid phase transition with those leading to the melting of a solid. In both cases, the energy absorbed results in only a small entropy change and therefore it contributes to the rise of a metastable condition which culminates in spontaneous order/disorder or order/order transition.

The thermodynamic considerations of the melting transition are based on the general expression:

$$\Delta G = \Delta H - T\Delta S = 0$$

With this law, it is assumed that during melting any heat input leads only to a change of entropy S and none to a change of the temperature T . During everyday measurements of the melting point of samples purified laboriously, either visually by microscopy or by the modern thermo-analytical method of DSC, it is normally observed as mentioned above, that always a discrete melting range exists. Thus, in the strict sense, independent of the chemical purity of a sample, $\Delta T \neq 0$.

A crystalline solid is said to be pure if it shows a very narrow melting range (normally about 1–2°C). Melting points are usually measured using polycrystalline samples and not a homogeneous single crystal. In such an assemblage the individual crystals or crystallites present may have different degrees of lattice imperfections. That is why, as can be seen with the example of the melting transition of benzoic acid (99.9% purity), the DSC measurement, carried out with a polycrystalline sample, does not lead to a perfectly sharp melting endotherm even at the very low scanning rate of 0.2°C/min (see Figure 1), i.e., melting onset \neq peak apex. (Of course, sample impurities also add to lowering and further broadening of the melting temperature and range. It is obvious that foreign molecules will lead to an increase of the lattice imperfections and thus to the weakening of the crystal lattice.)

It seems that in the past, both thermodynamists

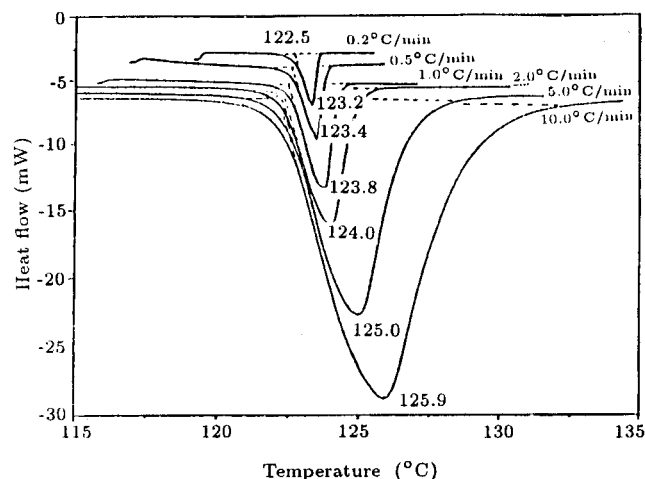
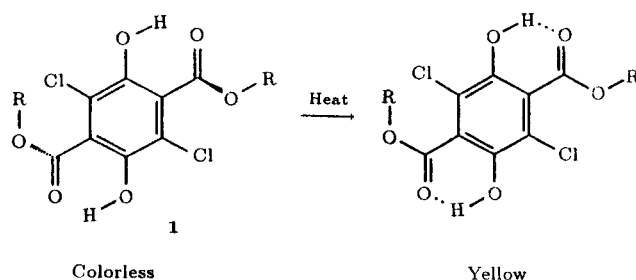


Figure 1. DSC scans of the melting endotherm of benzoic acid at different scanning rates.

and solid state chemists have in the their considerations, perhaps for the sake of convenience, or otherwise, ignored this small yet significant discrepancy which, as will be shown in the following, has also very important consequences for the understanding of hysteresis effects.

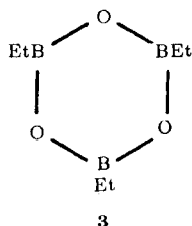
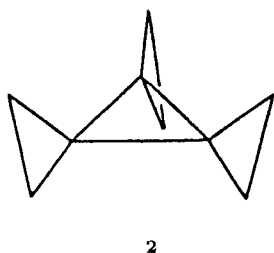
To gain a better insight into both of the phenomena introduced above, i.e., transitions and hystereses, one can in principle choose any molecular crystal which shows polymorphism. Yet not all of the numerous known examples are either convenient or suitable for this type of investigation. A great majority of the cases are those in which the polymorphs do not transform into each other on simple heating, rather they are obtained by different modes of crystallisations. For the sake of this paper, this type is disregarded.

Another large group is that in which the thermal transition is a one way process. Typically, it is only observed during heating. Therefore, they provide no information on the reverse process and, thus, on hysteresis. A typical example, which fits in this category and has been very extensively studied, is the thermochromic transformation of the terephthalic acid derivative **1** [7].



A third group, with still a substantial number of examples, comprises those reversible cases in which no

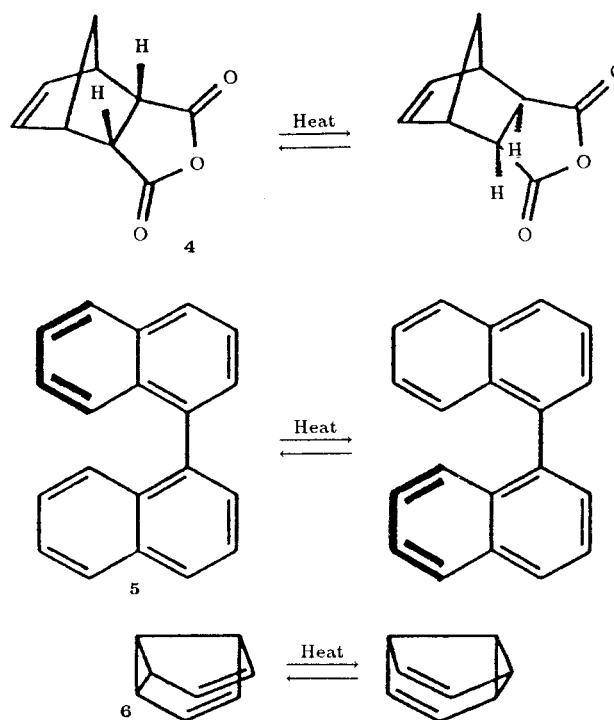
chemical change of the transforming molecules occur during the transposition. Only rotation or translation of the molecules to new sites within the lattice or a conformational change takes place with the concomitant change of the morphology of the crystal. These are generally unimolecular processes. Representative of this group are, e.g., the phase changes of [3] rotane **2** [8,9] and ethylboroxine **3**. In the latter case there is in addition to rotational and translational reorientation of the whole molecule, also a change of the conformation of the substituent ethyl groups [10].



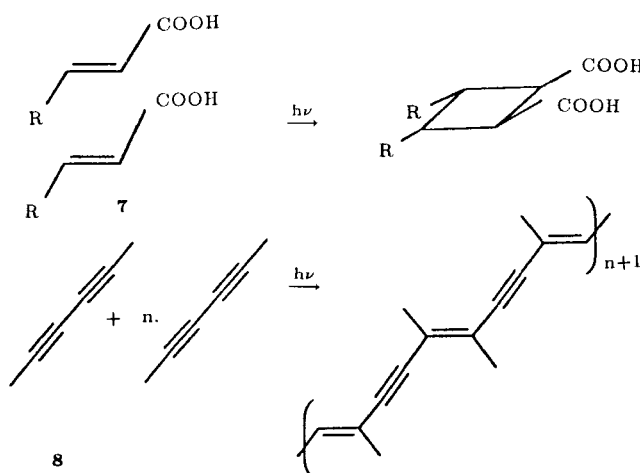
There is a substantial number of fully reversible crystal-crystal unimolecular transformations in which the morphological change is only indirectly the result of molecular reorientation. Rather, the phase transitions are the consequence, or occur concomitant with an intramolecular reaction. However, by their nature (unimolecularity), they occur, at least superficially, irrespective of the molecular topology in the crystal lattice. They can best be compared to monomolecular reactions in any solid matrix or indeed in any wholly inert medium, gas phase or in solution.

Forces holding molecules in a lattice can be ionic, polar or only of the van der Waals type (for the present discussion, only the latter two are considered, although any consequences drawn can easily also be related to ionic crystals). In unimolecular reactions occurring in the solid state, it can be envisaged that the intermolecular lattice forces only play a small and indirect role. An example could be a case where the intramolecular transformation will only result in an insignificant change of the molecular geometry. By nature this transformation may be marginally hindered or aided by the prevailing lattice and the onset of an intramolecular reaction may have become shifted to somewhat higher temperatures. The following three reversible isomerisation reactions of the norbornane derivative **4** [11], the 1,1-binaphthyl **5** [12] and the semibulvalene **6** [13] are typical of this type of transformation.

A meaningful study of the problems posed by crystal-crystal- or, by extension, a crystal-mesomorph transition has to include a significant interplay of the ensuing intramolecular chemical changes as well as the

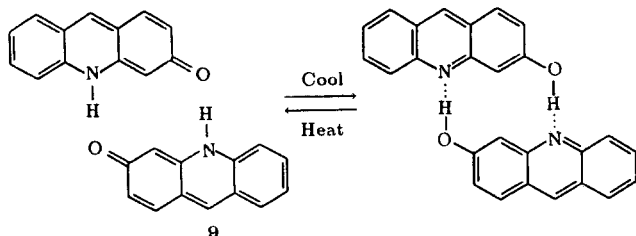


crystal lattice. Since, by definition, intermolecular forces play a greater role in bimolecular solid state transformations, the study of all aspects of phase transitions can be most fruitful if it utilises such reactions as models. Unfortunately, there are only very few known cases of solid state transformation in which the topology of the lattice dictates the course of the reaction. Among these is the already mentioned, very important and well known class of the photochemical dimerization of certain olefins, e.g., of **7** and the thermal polymerization of diacetylenes, e.g., of **8** [14,15].

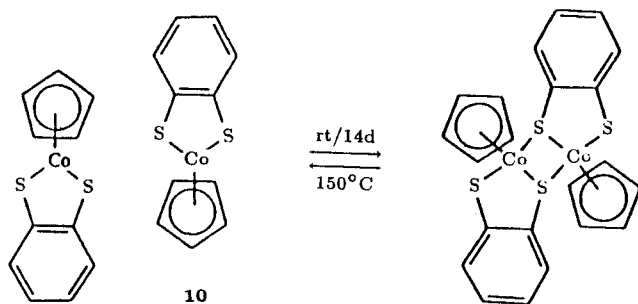


Both of the above reactions are, however, irreversible processes and the very extensive studies carried out with them, including the intralattice topological considerations, have served different aims. Other

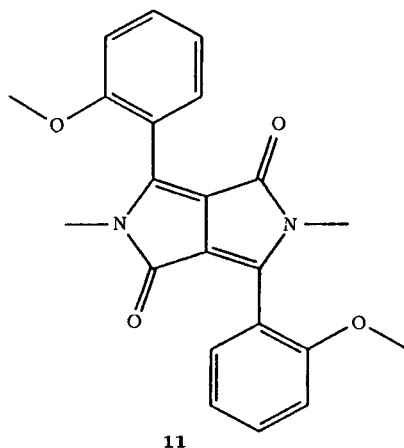
older examples have unfortunately as yet received little attention. Intensive involvement with them may result in further useful insights. One such case is the thermochromic, probably bimolecular lactim-lactam transformation of 2-hydroxy-5-phenylacridine **9** [16,17].



The case of the intralattice dimerisation of $(\eta^5 - \text{C}_5\text{H}_5)\text{Co}(\text{S}_2\text{C}_6\text{H}_4)$, **10** [18] is at first sight a very interesting case. However, in the forward direction at 25°C, it is a rather slow reaction.



A more recent example is the thermochromic transformation of the diketopyrrolopyrrole **11** [19].



It is reported that the thermochromicity is due to lattice controlled intermolecular interaction of the π -electrons of the chromophores [19]. However, since the transition temperature is rather high (196°C), it would pose experimental difficulties for detailed spectroscopic and X-ray studies.

DISCUSSION

In the past, two types of reaction have been fortuitously discovered that fit into this very narrow category and various aspects of the chemistry involved [20–33] have been studied. Most recently two other promising reactions have been encountered which are in the initial stages of being understood.

The purpose of the present article is to recount and sum up the past and current studies and views on the topic of the mechanism of phase transformation and hysteresis which continues to be extremely controversial among solid state chemists.

Thermochromism of a Boron Heterocycle;

A Case Study for a Spontaneous Crystal-Crystal Reaction

The boron heterocycles **12** are reversibly thermochromic yellow (LT) \rightleftharpoons colorless (HT) [20,21]. The transition temperatures for the heating and cooling cycles of the derivatives studied are shown in Table 1 [22].

In each case, a large hysteresis effect ($\Delta T_{\text{phase tr}} = 18\text{--}47^\circ\text{C}$) is observed. The attention here was mainly focused on the two thermochromic B-diethyl- and B-dipropyl derivatives **12b** and **12c** and the non-thermochromic B-diphenyl derivative **12j** (cooling of **12j** even to 4K did not result in a color change).

X-Ray Studies [21,22]

Molecular and crystal structures of **12b** were obtained at -30 and $+40^\circ\text{C}$, the LT and HT forms respectively and of **12j** at room temperature. These are shown in Figure 2, respectively. An attempt to elucidate the structure of **12b** also at room temperature failed because the X-ray reflexes found appears to be the sum of the LT and HT forms.

While **12b** HT and **12j** are planar molecules, the substituent B-ethyl groups in **12b** LT are significantly bent out of the molecular plane. The implications of this is best seen by comparison of the packing of the molecules in their respective cells. These are depicted in Figure 3.

It is readily seen that molecules of **12b** in the cooled crystals have polymerised and are packed as stacks of giant strings with a zigzag conformation. The B-ethyl substituents point out on both sides of the polymer string and are interlocked with those of the neighbouring string. Molecules of both hot **12b** and of **12j** are packed individually in a herring bone fashion.

The change of structure at low and high temperature is best viewed in the close-up representation in Figure 4.

It can be seen that in the low temperature form, bonding contacts are established between the oxygen atoms of one molecule of **12b** to the boron

Table 1. Thermal transition parameters for substituted 12.

12	Range of Measurement, °C	Heating		Cooling		Hysteresis ΔT_p	ΔH , J/g
		$T_{y \rightarrow c}^a$, °C	T_p , °C	$T_{c \rightarrow y}$, °C	T_p , °C		
a, CH ₃	-70 to +120	~ 25	25	~ -5 ^b		~ 30	c
b, C ₂ H ₅ ^d	-70 to +60	17	-30.5/+26	+5	-4/-43	30	55.4 ^d
c, n - C ₃ H ₇	-70 to +100	75	75	55	55	18	78.6
d, i - C ₃ H ₇	rt ^g to +165	150	150	106	103	47	112.0
e, i - C ₄ H ₉	rt to +115	72	84	48	43	41	56.1
f, c - C ₄ H ₁₁	rt to +115	88	91	49	44	47	67.0
g, n - C ₈ H ₁₇	rt to +110	75	70/90	55	81/50	20	56.0 ^e
h, n - C ₁₆ H ₃₃	rt to +125	11	118	85	81	37	
i, CH ₂ C ₆ H ₅	rt to +125	87/98 ^f	93	60/45	62	31	33.5 ^e

^a y = yellow; c = colorless. ^b Determined visually, no cooling run. ^c DTA runs only.

^d ΔH for the thermochromic transition only. ^e ΔH for sum of both transitions.

^f Color changes from orange to yellow to colorless. ^g Room temperature. ^h Not determined.

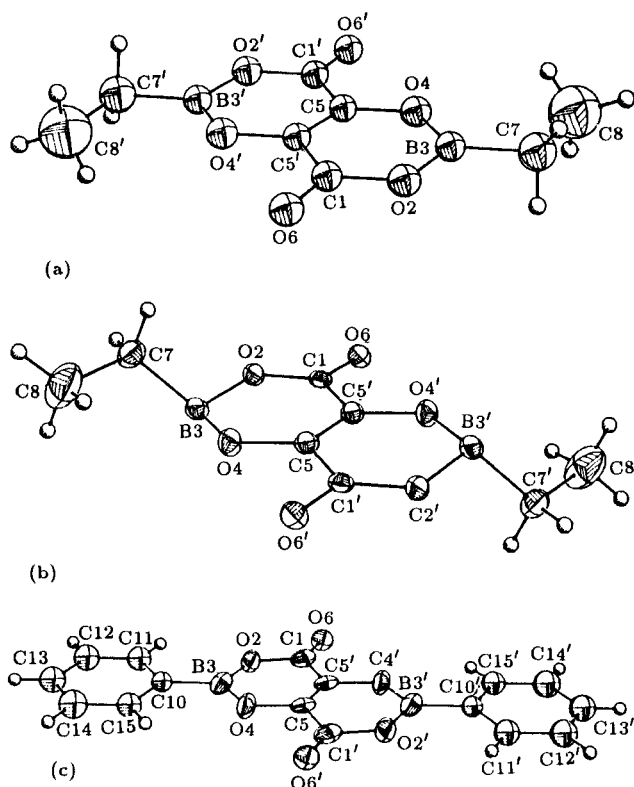
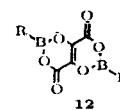


Figure 2. Molecular structure of 12b; (a) hot form (at 40°C), (b) cold form (at -30°C) and (c) of 12j at rt.

atom of the next molecule (B-O bond length = 1.656 Å). As a result, the inter-planar angle between the two adjoining molecules is increased from 73° for the HT form by about 13° to 86.1° in the LT form. These changes also result in a drastic increase in the monoclinic angle β from 90.0 to 96.01°. This occurs without breaking down of the crystal, provided the cooling or heating rate beyond the transition temperature is very low.

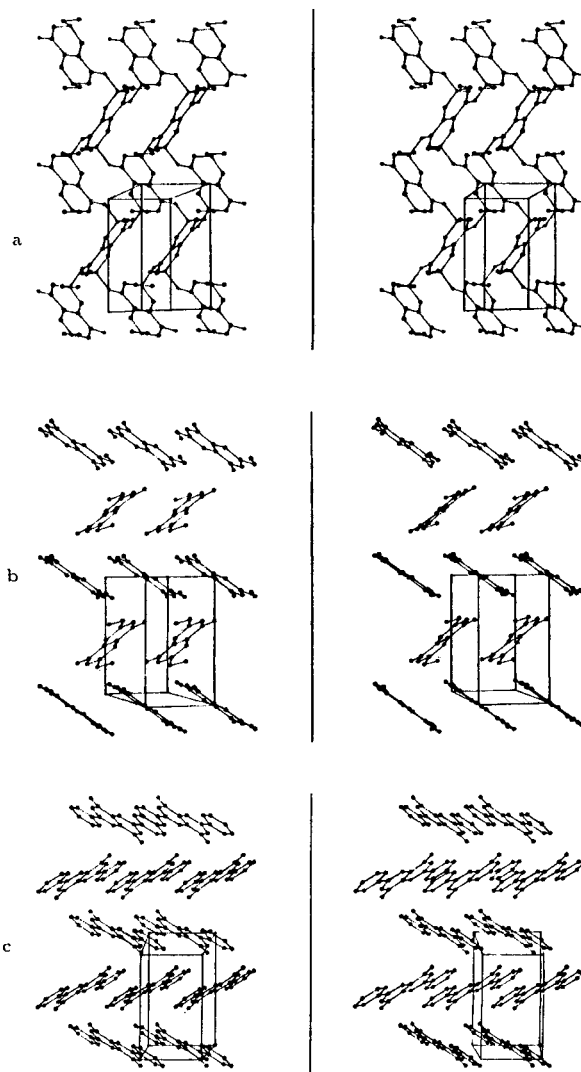


Figure 3. Stereoscopic view of molecules of 12b; (a) LT, (b) HT and (c) 12j in the crystal (seen along the a-axis).

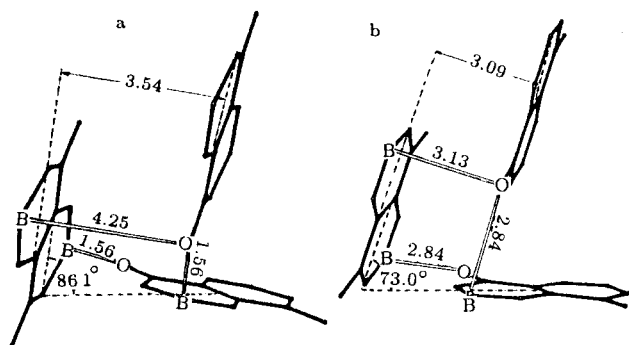


Figure 4. Contact distances and interplanar angles for molecules of **12b** in (a) cold and (b) hot crystal modification.

DSC Analysis [22]

The phase transition can also be monitored by thermochemical DSC analysis. Parts a and b of Figure 5 shows the heating and b the cooling thermograms of **12b** obtained directly from the pure polycrystalline material as separated from the reaction mixture. Two solid/solid endothermic transitions are observed during the heating scan. The lower, low energy, transition is non-thermochromic and it is proposed that at this juncture the polymer chains are pulled apart and the ethyl groups get untangled from the neighbouring chains. This becomes evident by a rather substantial lengthening of the crystal 'a' axis (from 10.12 to 11.25 Å) [21] when the crystal is heated from -73 to -30°C (just above the lower phase transition). This change is deemed to be a critical first step towards the progression to the HT phase (see also below). The next stage of the transition (the thermochromic) is probably the narrowing of the angle β (see above), followed or accompanied by a tighter packing of the polymer chains (the crystal 'a' axis shortens from 11.25 to 11.00 Å).

The cooling thermogram in Part b of Figure 5 shows the full reversibility of the transition, including the full energy balance. A hysteresis of 30°C for the high and 13°C for the low temperature transition is also evident. Interestingly, the lower transition temperature is missing in the thermograms of all the other derivatives of **12**. Obviously, in the crystal packing of these, assuming they are similar to **12b**, the intertwining of the substituents plays an insignificant role. This is perhaps due to the greater flexibility of the substituents in some cases and their larger bulk in others.

From the understanding which has been so far gained of the arrangement of the molecules of **12b**, LT and HT, the extra large contraction/expansion of the cell volume at the transition temperature and the probable mechanism by which they transpose into each other, it is easy to predict that it should also be piezochromic. Indeed, when, in a specially constructed DSC cell, mechanical pressure was exerted onto crystals of **12b** and heating and cooling curves were measured

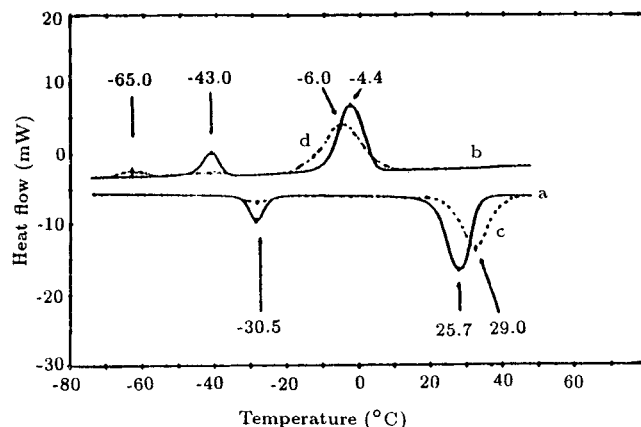


Figure 5. DSC curves showing the phase changes of **12b** at ambient (---) and under mechanical pressure (—).

by DSC, the results (shown in parts c and d of Figure 5) were unambiguous. Pressure elevates the temperature of the upper transition and lowers that of the reverse process. Significantly, both transitions are broadened and shifted to lower temperatures. In the case of the lower transition, it is shifted by 20° to -85°C in the cooling curve.

The manner by which pressure was exerted on the sample does probably not transmit it uniformly throughout the polycrystalline mass and, therefore, it is to be expected that the transition peaks appear broadened. Furthermore, the reasons for the observed elevation of the thermochromic transition temperature (in the heating scan) are also easy to anticipate: It is more difficult to break the B-O bond and increase the chain separations and thus the cell volume. More difficult is the rationalization of the increased stability of this phase when being cooled. It is plausible that the monomer molecules have a new topology in the high pressure arrangement (HP-HT) from which the collapse to the new HP-LT phase is hindered. Similarly, the return to the original state, with intertwined substituents is also hindered, since it probably requires relative shifts of the polymer chains. Therefore, the low temperature transition at -43°C is also hindered.

Even more wide spread lattice stabilities are observed when vacuum sublimed crystals are subjected to DSC analysis. Figure 6 depicts the thermograms of crystals of the B-propyl derivative **12c**, before and after sublimation. Clearly, sublimation, although it results in a chemically more pure material, produces a polycrystalline mass which has a lowered and considerably broadened transition temperature range.

Infrared Studies [22]

Another approach to a fuller understanding of this reaction was made by infrared spectroscopy. Figure 7 spectacularly demonstrates the reversibility of the appearance and disappearance of complexed and uncomplexed carbonyl bands.

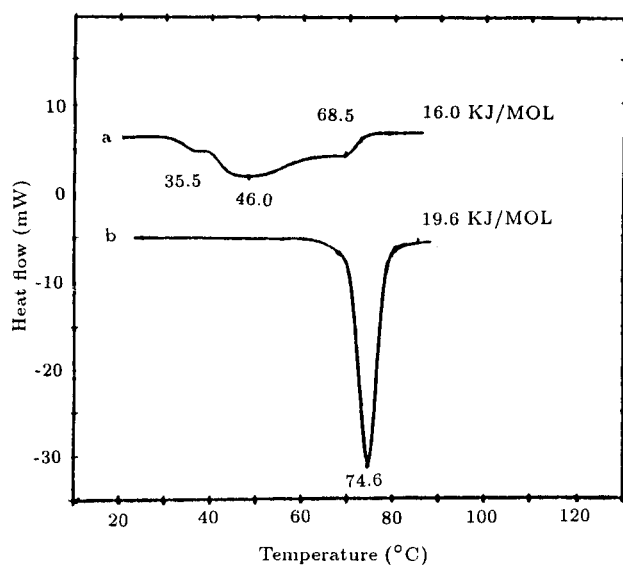


Figure 6. Effect of sublimation on the DSC heating scan of (a) sublimed crystals, compared with that of (b) crude crystals of **12b**.

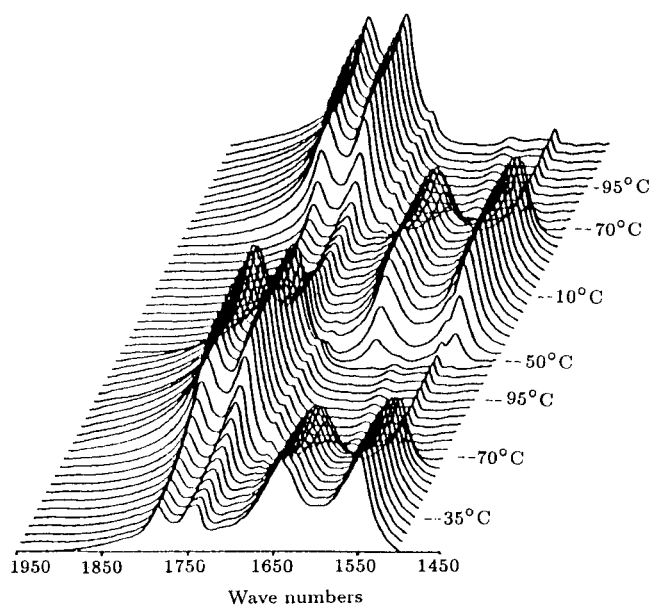


Figure 7. Segment of infrared spectrum of **12c** cycled between the HT and the LT forms.

Using the intensities of the carbonyl absorption maxima, hysteresis loops can be drawn. These are shown in Figure 8.

In Figure 8a, the hysteresis loops are from a sublimed polycrystalline sample of **12c**. It shows a broad range ($\Delta T \approx 30 - 85^\circ\text{C}$), whereas on recycling (Figure 8, dotted lines), a slightly narrower range ($\Delta T \approx 30 - 75^\circ\text{C}$) is obtained. Clearly, tempering of the polycrystalline material removes some lattice defects. From a sample of **12c**, aged for a long period and tempered, the hysteresis loop shown in Figure 8b is obtained. In this case a transition range of $> 15^\circ\text{C}$ is seen.

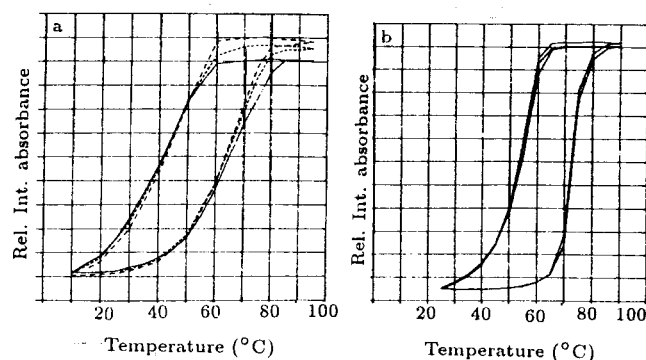


Figure 8. Hysteresis loops of (a) sublimed and (b) aged crystals of **12c** through three heating and cooling cycles (relative intensities are those of the carbonyl bands at 1760 and 1735 cm^{-1}).

Matrix Isolation Studies [22]

The above mentioned results demonstrate very convincingly the relationship of crystal make up, its history and broadness of a phase transition. It was therefore of no surprise that the yellow crystals of **12c** when sublimed under high vacuum and collected on the tip of a cold finger cooled to -196°C by liquid N_2 , initially formed a film which was a perfectly colorless amorphous solid. As the thickness of the film on the cold finger increased, first a tingle of, then a full yellow colored solid layer was formed.

These purely visual observations were further underpinned by carrying out a detailed matrix isolation investigation of **12c**. Figure 9a shows the infrared spectrum of molecules of **12c** co-deposited with argon onto the optical window cooled down to 12 K. Whereas the IR spectrum of **12c** as bulk has two carbonyl absorption bands at 1780 and 1745 cm^{-1} in the HT form [22], that in an argon matrix has only one very sharp band at 1791 cm^{-1} . The ultraviolet spectrum of **12c** shows an absorption maximum at 255 nm and none above 350 nm.

An IR spectrum of **12c** deposited, as a film, at 12 K on the optical window without a matrix is shown in Figure 9b. Virtually no absorption band due to associated carbonyl bands at 1635 and 1545 cm^{-1} are visible. The ultraviolet spectrum of this film again shows no absorptions above 350 nm. When this film is warmed to 300 K, the spectrum shown in Figure 9c appears which clearly shows the simultaneous presence of both the LT as well as the HT forms. Re-cooling of this sample gives a spectrum in which only a small broad unassociated carbonyl frequency is visible. In its ultraviolet spectrum an absorption maximum is present at 390 nm, an indication that the sample is colored in this state.

For the purpose of understanding reactions in the solid state, the results of depositing a film without a matrix at the higher temperature of 170 K are

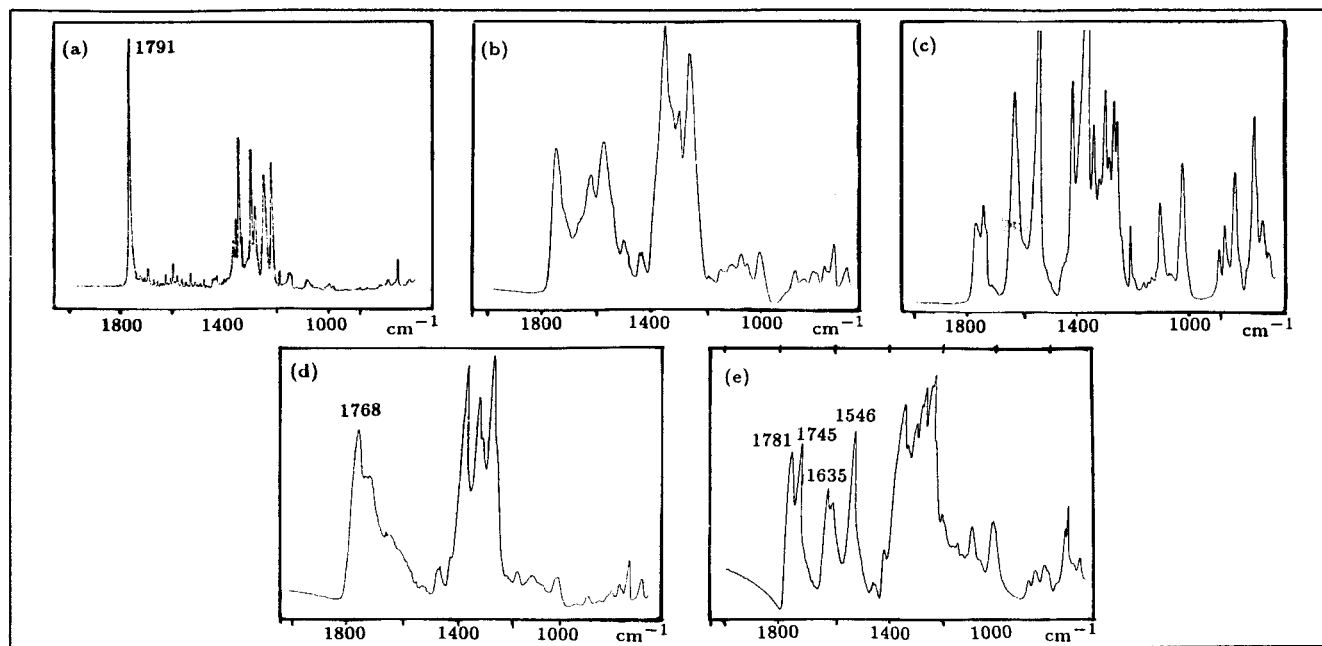


Figure 9. The infrared spectra of **12c** in the region of 2000–600 cm^{-1} . a) 2h codeposition with argon at 12 K; b) sublimed for 2.5h as a film at 12 K, subsequently annealed to 260 K and c) then warmed to 300 K; d) sublimed for 3.5h as a film at 170 K then annealed to 300 K and e) recooled to 12 K.

of particular interest. At this temperature, it can be expected that molecules forming a film on the optical window will receive sufficient energy to move subsequently from the site of arrival to a potentially more stable one with, or approaching, a close packing. In this way, it can be expected that in the micro crystalline regions formed, there will be relatively large numbers of surface molecules. In the micro crystallites, many of these surface molecules cannot have both of their carbonyl oxygen atoms coordinated to the boron atoms of the underlying layer of molecules of **12c**. It can be anticipated that in the infrared spectrum obtained at this temperature, a significant intensity of 'free' carbonyl groups should remain alongside the absorptions for the associated groups. This appears to have been realized, as seen in Figure 9d [23]. The relative intensities of the 'free' and associated carbonyl absorptions should roughly reflect the ratio of surface molecules and those at the sites of lattice defects to those at the sites within the crystallites. More interesting are the results observed when the above crystallite film was once warmed to room temperature and then re-cooled to 12 K. In this case, in the spectrum shown in Figure 9e, the continued presence of the sizeable intensity of the 'free' carbonyl intensity is an indication for the presence of very small crystallites with large surface area. Since progressive heating of these crystallites from 12 K to room temperature results in a uniform increase of the intensity ratio of the 'free' to associated carbonyl absorption maxima, it

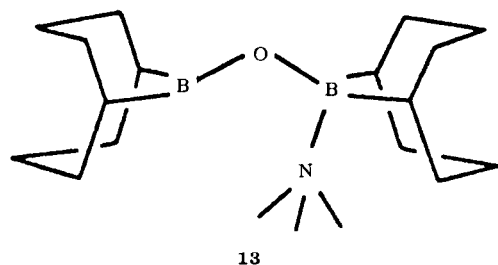
appears that the phase transition is a gradual process extending from 12 K to room temperature and beyond.

Transition to Fluctuational Crystals; The Case of N-Base Adducts of Bis-(1,5-cyclooctanediylboryl)oxide

Fluctuating molecules have always fascinated chemists [24,25]. The author has observed and reported on several examples of molecules containing two or more boron atoms and a nitrogen base which interchange between the boron atoms [26–32]. However, with few exceptions, fluctuation has only been observed in solutions. There are examples of such reactions also occurring in the solid state, e.g., [11,12], but since they are generally intramolecular, they do not affect the crystal lattice beyond 'softening' it to the point of plastic crystallinity.

The author has recently reported on what is believed to be the very first case of a solid-mesophase transition in which the anisotropic mesophase is held together by a rapid intermolecular motion [33]. Such a mesophase is therefore different from that of liquid and plastic crystals. As will be shown below, it resembles the former one in some of its thermal behavior, as observed by DSC and the latter in its appearance under the microscope. Because of this unique feature, this 'solid' is called a fluctuational crystal. Since the transition to this mesophase appears to be controlled by the topology of the molecules in the respective original lattices, it falls within the scope of this discussion and

will be treated here in some detail. The molecules involved are the series of N-base adducts of bis-(1,5-cyclooctanediylboryl)oxides **13** [31].



- | | |
|------------------------------------|---------------------|
| a = pyridine | b = quinuclidine |
| c = 4-methylpyridine | c = 3-bromopyridine |
| e = 4-(N,N-dimethylamino)-pyridine | |

Rapid intramolecular fluxional motion can be observed by NMR spectroscopy in solution. Except for the pyridine and the quinuclidine adducts **13a** and **13b**, respectively, all others show a 'normal' thermal behavior up to their melting points, by microscopy or DSC analysis. Both **13a** and **13b**, however, showed a large pre-melting endothermic transition in their DSC thermograms (see Figure 10) and in the mesophase, under an optical microscope, the crystals acquire an opaque and plastic like appearance [26–32]. In this phase they can be deformed by exerting pressure on them.

The structures of **13a**, **13b** and three other derivatives (**13c–e**) which show no thermal transitions were determined by X-ray techniques. All six compounds have very similar molecular structures and

also superficially the packing of the molecules in their respective cells are similar in that they appear as head to tailed pairs. These are shown in Figure 11. The intermolecular distances between the pair (N-B2') range from 5.19 to 7.19 Å. Both **13a** and **13b** fall within this range. In all cases the distance is far beyond the proposed threshold centre-centre separation of about 4.2 Å for topologically controlled intra-solid reactions [34].

The decisive insight obtained is that in **13a** and **13b** the oxygen atoms are located on the periphery, while in **13e** they are pointing towards each other and in **13c** and **13d** the N-base molecule is located between the pair. In **13e** the non-bonding electron pairs of the oxygen atoms and in **13c** and **13d** the orientation of the N-base molecule are in the way and hinder the ensuing of intermolecular interactions. In the fortuitous topology found in **13a** and **13b**, it can readily be seen that only a slight movement of the N-base is sufficient for it to jump from one diboroxane molecule to its neighbor. If this movement is rapid enough, a network constituting a mesophase can be established throughout the crystal. In principle such a network of intermolecular interaction is, of course, also possible in all other adducts and should be expected.

Why then is such behavior not universal for all such adducts in the pre-melting temperature range?

A further observation which may help in understanding this process is the rough proportionality of the melting points of the adducts with the Lewis base strengths of the corresponding N-bases. In the series under study, the 2- and 3-bromopyridine adducts respectively, with 88° and 106°C have the lowest and the 4-dimethylaminopyridine derivative at 222°C, the highest melting points. It is thus evident that a major contributor to the lattice stability is the strength of the adduct -B-N- bond. If the intermolecular

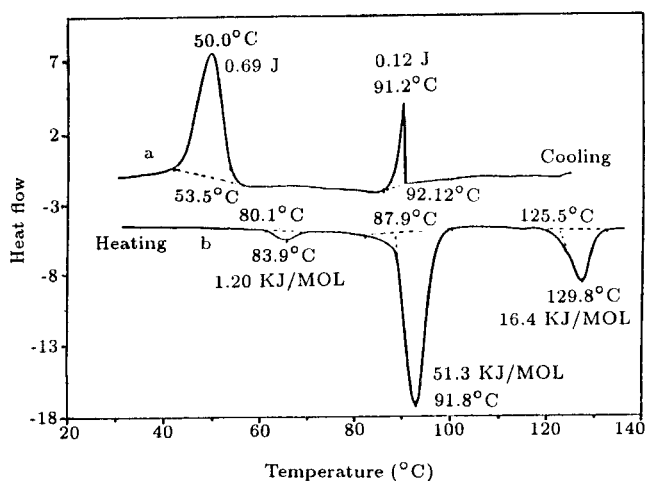


Figure 10. DSC scan of **13b** (a) heating and (b) cooling.

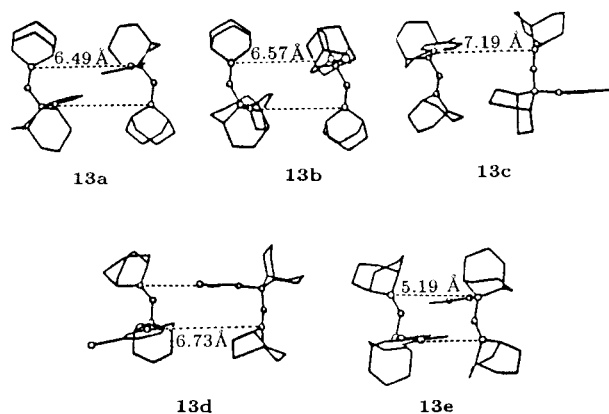


Figure 11. Molecular structures of the pyridine, quinuclidine, 4-methyl-, 3-bromo-, 4-methylpyridine adduct pairs (**13a–e**)₂.

attraction between these dipoles is larger than the strength of the intramolecular -B-N- bond (weak N-base), then, once melted, the two molecules making up the adduct also become dissociated. Indeed, the intramolecular dissociation may contribute to, or even initiate, the melting transition. Only in molecules with intermediate -B-N- bond strength and especially in only those which have the correct and favourable topology, a measure of lattice coherence is retained in the pre-melting phase. Conversely, in adducts with a strong intramolecular -B-N- bond, the collapse of the lattice structure appears to have an intermolecular origin. The intermediate situation is only found in **13a** and **13b**.

These ideas are verified by an NMR experiment [35]. The presence of two boron atoms initially in a different bonding environment was to provide a sensitive probe. In the relatively mobile matrix of the mesophase, only one ^{11}B signal was expected to be found with a time averaged chemical shift midway between that for a trigonal and that for a tetra-co-ordinated boron atom. The success of the planned NMR experiments depends, of course, as previously observed with plastic crystals [11,36], on the presence of significant molecular motion within the lattice. Figure 12 shows the NMR spectra of a sample of **13b**, heated in steps from just below its first solid/solid phase transition, through the mesophase, to the melt.

At 75°C, a relatively narrow signal at $\delta \approx 56$ resulted (Figure 12a). This is just above the low energy solid/solid phase transition. This chemical shift can, with certainty, be assigned to an unassociated mobile dialkyloxyboron atom. The absence of a visible second signal for the N-base complexed boron atom is assumed to be due to the lack of internal motion of this moiety (see also the discussion on the results of a high temperature X-ray structure determination, below). At 85°C (Figure 12b), just below the solid-mesophase transition, a second broad peak appears at $\delta \approx 40$. In the temperature interval of 90–105°C (Figure 12c and 12d), only a single signal is observed at $\delta \approx 30$. Above this range and yet below 125°C, the temperature which is the equivalent to the clearing point in liquid crystals, one peak appears at $\delta \approx 56$ and one at $\delta \approx 41$ when a 1:1 intensity ratio is formed (Figure 12e). Finally, above 125°C only one very sharp peak at $\delta = 57$ is present in the spectrum (Figure 12f). These results are rationalized in the scheme shown in Figure 13.

The molecular assembly making up the mesophase thus has a uniform structure only at the lower end of the temperature range ($\sim 90^\circ\text{C}$). As the temperature is raised above $\sim 90^\circ\text{C}$, the B...N interactions weaken the network (as seen by the slight shift of the ^{11}B chemical shift to $\delta \approx 41$) and in a non

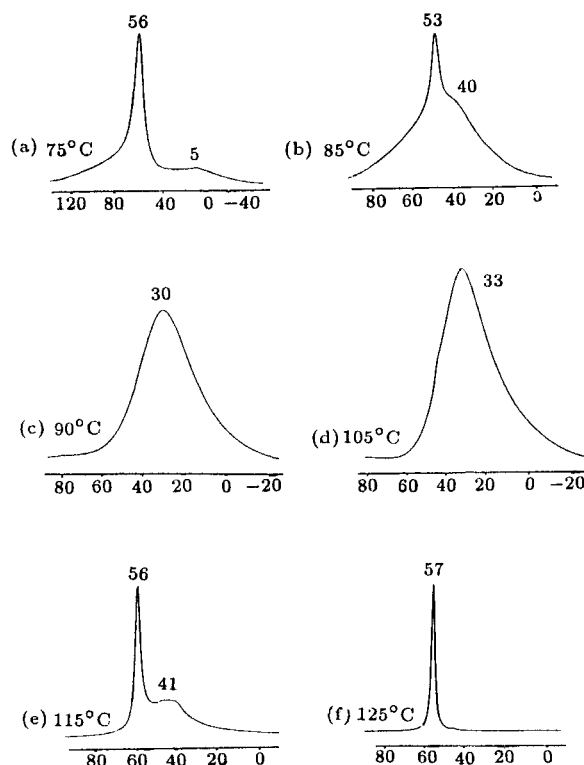


Figure 12. ^{11}B NMR signals of solid and 'solid' **13b** at various temperatures (values at peak points are chemical shifts in ppm).

degenerate equilibrium, in part completely dissociate (the ^{11}B NMR signal at $\delta = 56$).

Evidence for the existence of extensive molecular motion in the mesophase can also be obtained by inference from a detailed X-ray single crystal analysis [33]. Figure 14 shows the increase of the librational movements of the atoms in each section of the **13b** molecule. Clearly, of the two 1,5-cyclooctanediylboryl groups, the one uncomplexed to an N-base (Figure 13b) shows the greatest increase of librational motion as the crystal is warmed to $+50^\circ\text{C}$. Unfortunately, above this temperature the quality of the single crystal rapidly deteriorated, so that further investigations became impossible. However, it is predictable that as the temperature reaches $+85^\circ\text{C}$, the latter boryl group begins a free rotation about the B-O bond and thus the observed ^{11}B NMR signal is made possible. At this temperature the tetra-co-ordinated boryl group is still prevented from major movements. Therefore, no signal, or only an extremely broad one, can be observed for this boron atom.

A Liquid Crystalline Boron Heterocycle; Another Case of a Reversible Polymerization

Among a large number of derivatives of the boron-nitrogen heterocycles (**14**)₂, only (**14a**)₂ and (**14b**)₂ show an abnormal pre-melting phase transition [37].

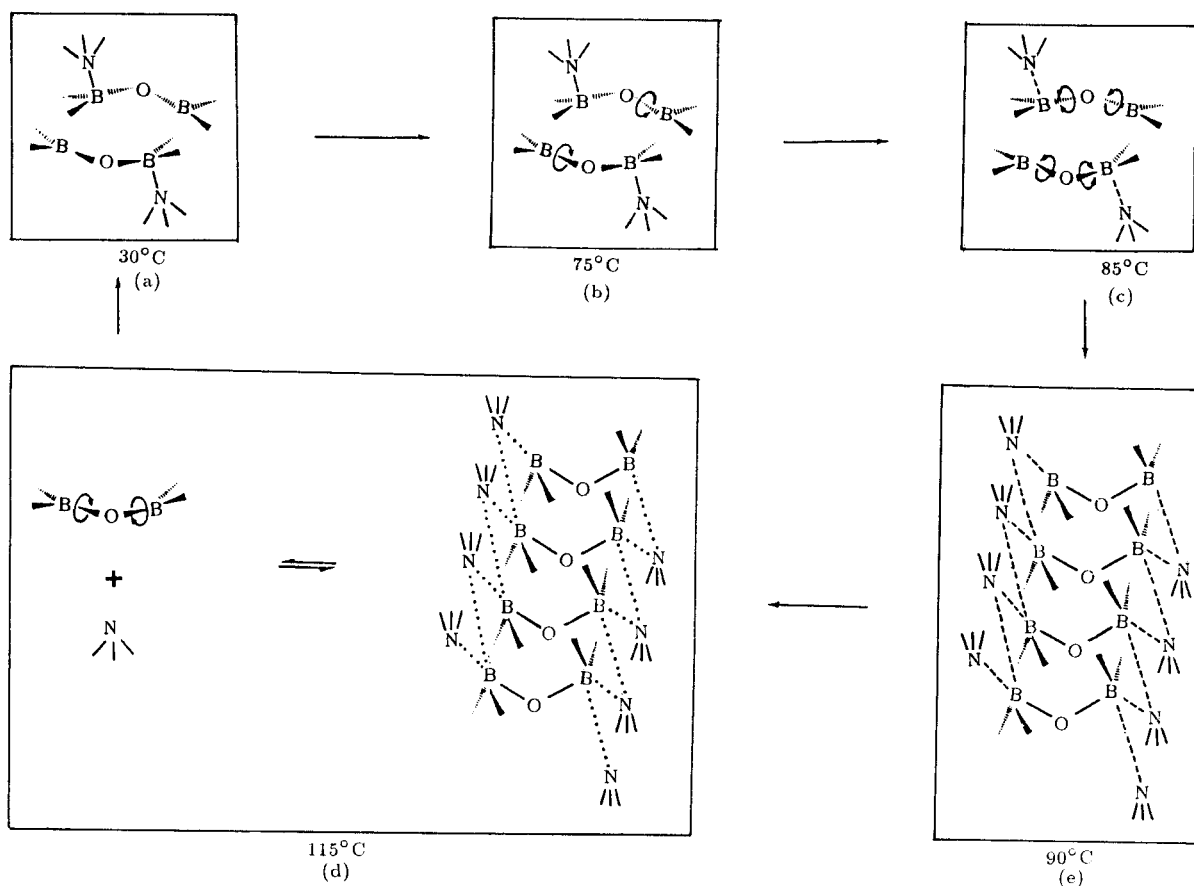


Figure 13. Schematized molecular packings and motions in solid and 'solid' 13b.

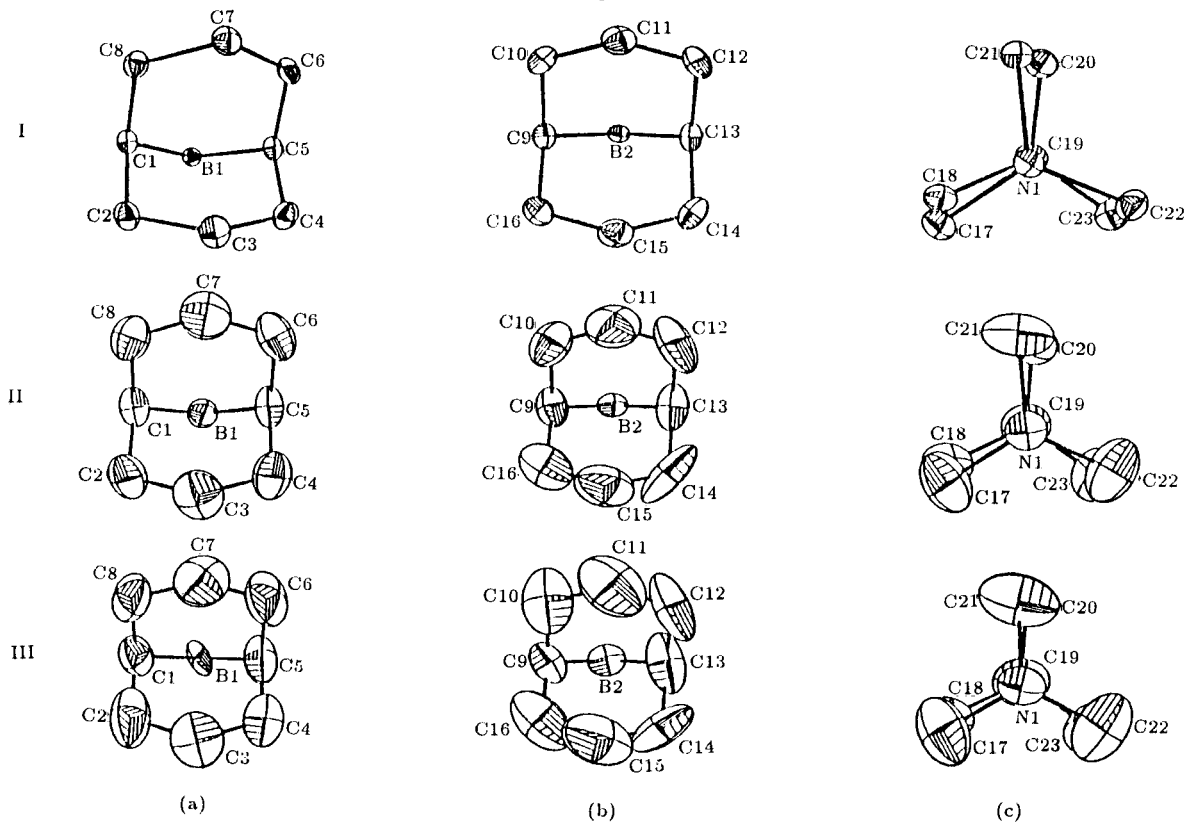
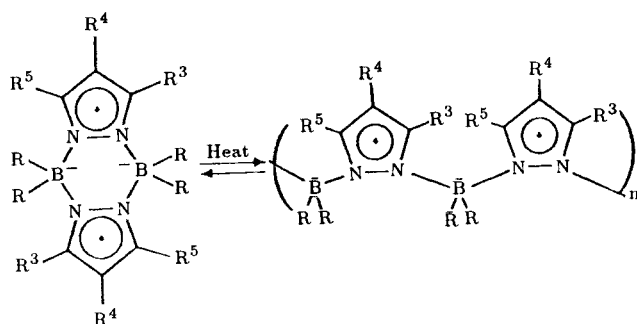


Figure 14. ORTEP drawings displaying vibrational ellipsoids of 13b, end-on views of (a) the quinuclidine bound, (b) the free 9-BBN moieties and (c) the top-on view of the quinuclidine moiety of the I LT, II RT and III HT forms.



14	R ¹	R ²	R ³	R ⁴
a	H	H	H	Et
b	Me	H	Me	Et
c	Me	Me	Me	Et
d	Me	Et	Me	Et
e	Me	H	Ph	Et
f	Ph	H	Ph	Et
g	i-Pr	H	i-Pr	Et
h	H	H	H	Pr
i	Me	H	Me	Pr
j	Me	Me	Me	Pr
k	Me	Et	Me	Pr

The DSC thermograms of these two compounds, as can be seen in Figure 15, both show pre-melting endotherms which are larger than the respective melting transitions.

When viewed under a polarizing microscope, a mesophase can clearly be observed. In this phase the material is plastic like and flows under slight external pressure. Figure 16 show color photographs of (14a)₂ and (14b)₂ in their respective mesophases, taken under crossed-polarized light.

The observed textures appear to belong to smectic phases, by comparison [38]. The crystal structure determination of both 14a and 14b revealed (as can be seen in Figure 17) that the molecules are packed in stacks. The center to center molecular distances > 6 Å are, however, far apart and in the habitat as found at room temperature there is no indication for a ready topo-tactical transition to an anisotropic liquid in which intramolecular forces may be effective in maintaining a degree of molecular order. Based on the observation that when mixtures of (14a)₂ and (14b)₂ are heated above a common melting point at 150°C the pyrazole rings interchange and the crossover product (14a)(14b) is formed (by GC-MS analysis), it is proposed that in the mesophase the central B₂N₄ six membered rings open up and B-N bonds to the neighbouring molecule are formed. Polymeric materials with alternate dipoles would result.

Preliminary CP-MAS spectra of (14a)₂ at room temperature and 75°C are also in agreement with this interpretation. Thus whereas below the mesophase, in conformity with the molecular structure as shown in Figure 17a, there are two types of B-ethyl groups, just above the transition into the mesophase only one type of B-ethyl group is found [39].

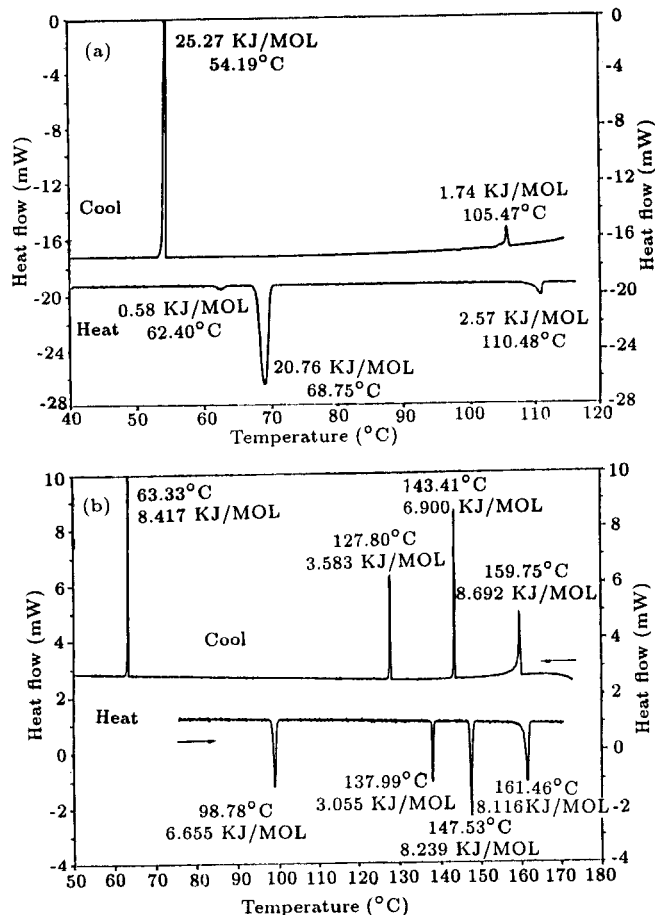
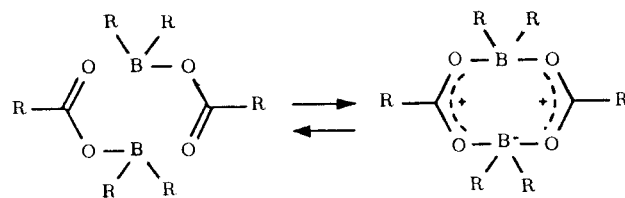


Figure 15. DSC scans, heating and cooling of (a) 14a and (b) 14b.

Hysteresis-Free Continuous Transitions Dimer-Monomer Transformation of Acyloxyboranes

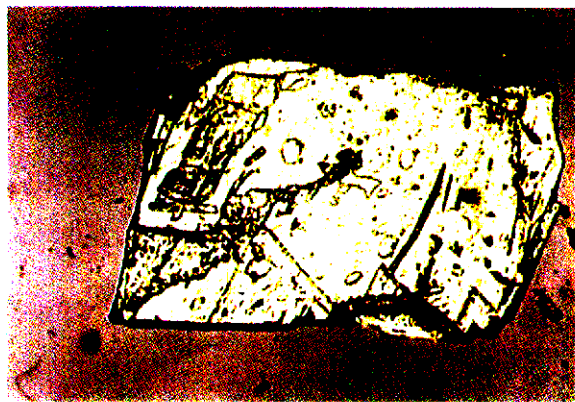
The solid acyloxydialkylborane 15 at room temperature consists of either dimers or mixtures of dimers and monomers [40].



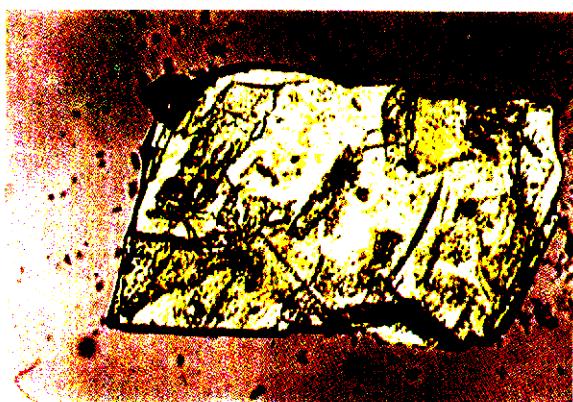
15

The dimers when heated in the solid state convert to the corresponding monomers. The process can be followed by IR or Raman spectroscopy and by the appearance of a free carbonyl absorption band (see Figure 18).

The reverse process sets in when cooled. In this case, a gradual disappearance of the carbonyl



20°C



61°C



65°C



85°C

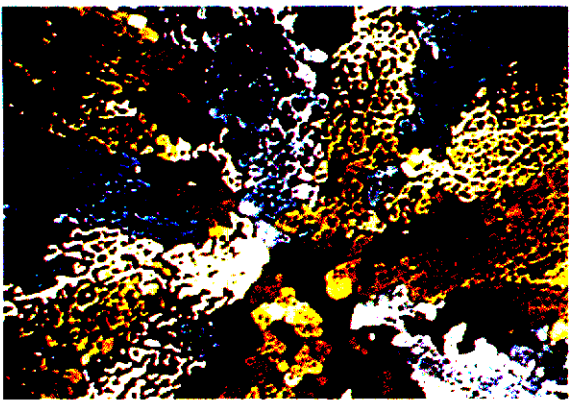
(a)



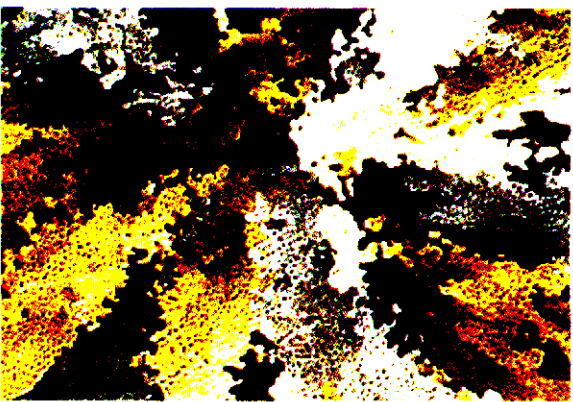
105°C



138°C



158°C



155°C

(b)

absorption band is observed. At any temperature, irrespective of the direction of approach, the same spectrum is obtained, provided that enough time is allowed for the establishment of equilibrium. So far, the X-ray structure of only the benzoic acid derivative

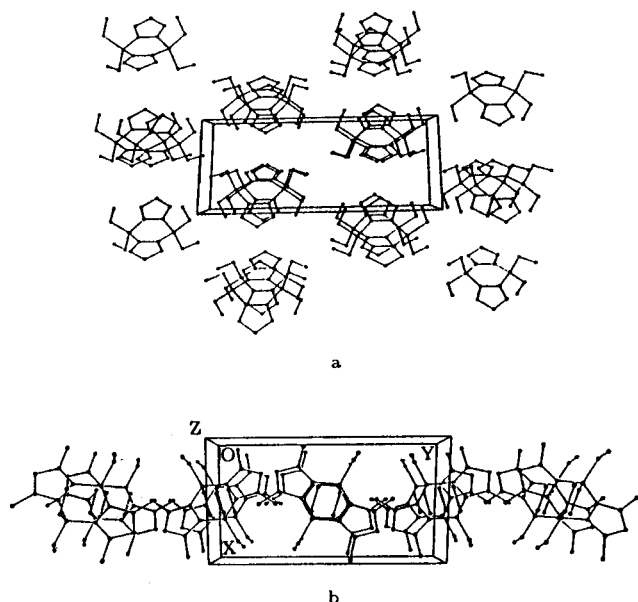


Figure 17. Molecular packing of (a) 14a and (b) 14b.

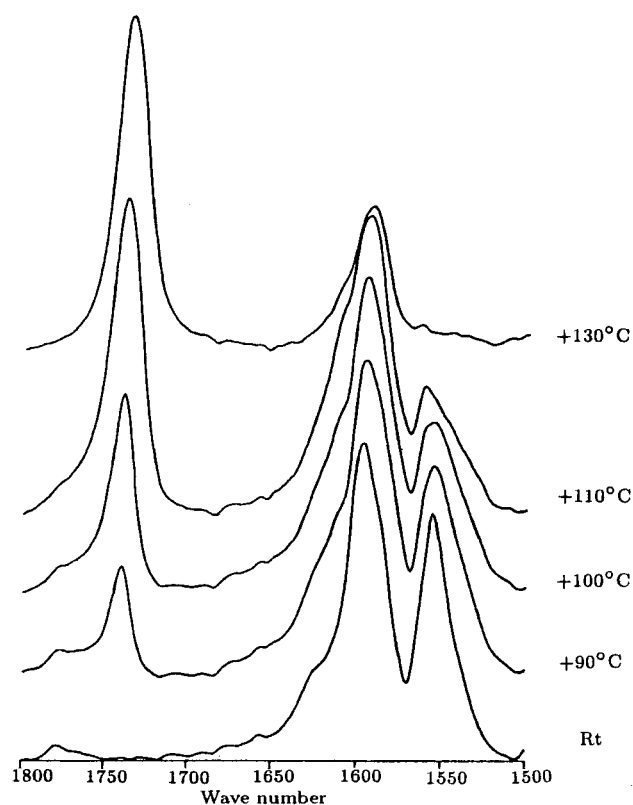


Figure 18. Infrared spectra of $(15)_2$ at different

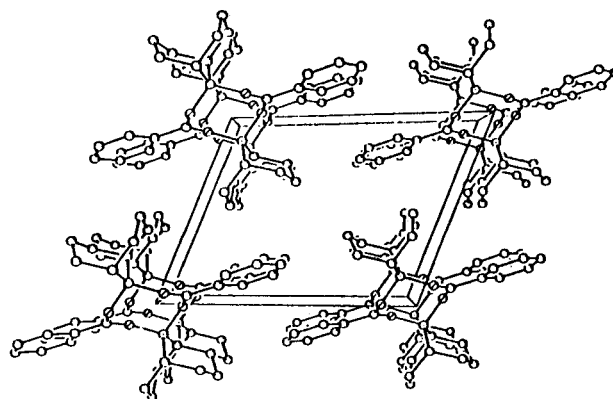


Figure 19. Molecules of $(15)_2$ in the cell.

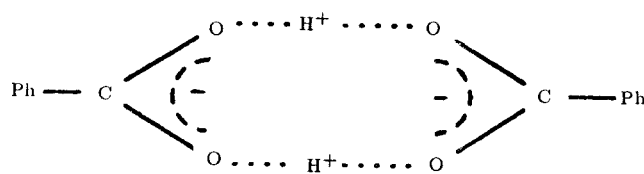
15 has been determined. As shown in Figure 19, it packs as stacks of dimers.

It can be expected that when heated, the intermolecular separation of the acyloxyboryl groups, i.e., only one of the cell axis, should undergo a larger thermal expansion. This would, in a thermodynamic equilibrium, lead to the breaking up or reforming of the intermolecular B-O bonds. The authors are currently continuing their investigations of this reaction.

Solid State Transformation of Benzoic Acid

Similar to the acyloxyboranes $(15)_2$, the parent carboxylic acids are also mostly dimeric in solution or in the solid state. The molecular structure of the benzoic acid dimer $(16)_2$, determined at room temperature by X-ray diffraction, shows that both C-O bonds are at 1.270 Å of nearly the same lengths [41,42]. This has been interpreted to indicate a disordered packing of the carboxyl groups with localized C=O and C-O bonds [41], or with symmetrical electron delocalized dimeric structure with the acidic hydrogen atoms situated equidistant to the two carboxyl groups [42]. The carboxyl group frequency of benzoic acid appears at 1688 cm^{-1} in the solid phase but is shifted to 1750 cm^{-1} as a monomer in an argon matrix [43]. The solid state carbonyl frequency is gradually shifted to 1710 cm^{-1} when an oriented crystal is cooled from about -126°C to liquid helium temperature [42,44-46]. A similar shift to 1705 cm^{-1} is observed when benzoic acid is heated between 70 – 120°C [42]. The high temperature effect can be due to the increase of the intra-dimer ($\text{C}_{\text{carboxyl}}-\text{C}_{\text{carbonyl}}$) distance without monomer formation [42]. The low temperature effect has been interpreted to indicate 'a proton transfer along the two hydrogen bonds of the dimer, thus changing the relative orientation of the C=O groups, of the dimer molecule to the crystal a and b axes' [44-46]. The results of extensive temperature dependent X-ray

(313–40 K) show that the transformation is truly gradual [42].



16

Whither Mechanism of Solid/Solid Phase Transition and Hysteresis?

Phase Transition

Since the phenomenological classification of phase transitions into orders such as first, 2nd, diffuse, lambda and so on, by Ehrenfest in 1933 [47], numerous attempts have been made by chemists and physicists to rationalize the observed anomalies, i.e., the inadequacy of classical thermodynamics to describe those transformations which occur over a wide temperature range [48–52]. Basically, the underlying question concerns the chronology with which the molecules leave one lattice and enter a new one. Do they do this in unison, or gradually? In the spontaneous case, a first order transition is implied. However, considering very small steps, or in the extreme case, one by one, the transition is gradual and by definition of the *n*th order. In Figure 20, two alternative pathways are schematically represented.

Along path (a) the molecules in the crystal react and transform in unison to the new lattice. In path (b) the molecules depart from the lattice one by one at a reaction front, then react and form the nucleus of a

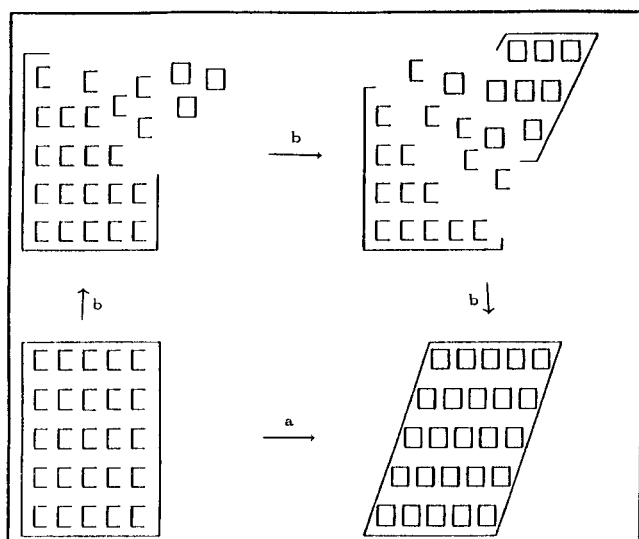


Figure 20. Schematized representation of alternate mechanisms for solid/solid phase transitions.

new lattice. This pathway could in principle be simply treated by a sequence of rate-equilibrium expressions: (1) for the sublimation; (2) for the reaction; and (3) for the condensation steps. Each of these should obey the classical thermodynamics laws. Unfortunately, there is one important flaw in this argument: The systems in question do not normally consist of molecules which can be expected to readily sublime at the temperatures involved, specially at the rapid rates normally observed.

According to a model called the 'contact mechanism' [53], nucleation of the daughter phase begins at the site of 'lattice defects in the form of a thin crack in the original crystal'. This picture also requires an individual molecule to separate from a site in an otherwise intact old phase and to move to a new location. It is again not clear how the required energy is transferred to the leaving molecule and whether the mass has to be transported through the gas phase. Furthermore, it is difficult to visualize transitions which also involve intermolecular reactions.

A third mechanism proposes the formation of solid solutions within the parent crystal [54]. This suggestion is in part based on the observation under optical microscope of regions in which the product has been formed within the matrix of the old crystal. The existence of many examples of guest solute solutions within the host crystal, e.g., of anthracene in acridine [54], also contributed the background for this proposal. Again, for the case of phase transition with or without the accompanying intra-solid reaction, the question of the energy transfer mechanism to the site of solid solution formation, or of the driving force remains unclear. Furthermore, as it has been found for the cases of **12**, **13** and **14**, the topology of the molecules in the parent phase is very much a determining factor in phase transitions. This aspect has also been previously amply exemplified [3,24,25]. It is not at all clear why, e.g., **13c** or **14c** should not form solid solutions and also show a phase transformation.

Born out of the experimental evidence accumulated and described above, the contention is that, whenever a phase change takes place in which noticeable energy is transferred only one phase change mechanism is involved. This rules out all gradual transitions, such as the case of **15** and **16** or those in which only slight reorientation of molecules within the lattice takes place. On the microscopic level, i.e., within the individual crystallite or domain, all abrupt transitions are, therefore, first order.

Once loaded with a sufficient quantity of energy the whole molecular assembly, making up that crystallite or domain, will in unison flip or react and flip into the new lattice form. On the everyday macroscopic level of operations, normally an assembly of polycrystalline mass is confronted, composed of particles of different size and, therefore, different ratios of surface

(edge/defect) to intra-crystallite molecules. Even in the 'ideal' case of a single crystal the reality that at a given temperature both parent and daughter phases may be simultaneously present has to be faced. In the case of **12b** at room temperature (near the transition temperature) the reflexes of both phases were observed by X-ray diffraction which shows that many domains are present in a single crystal and at or near a transition temperature both of the respective LT and HT forms exist side by side.

Therefore, for the transformation of each domain transferring exactly that package of energy that is required by a domain to break its former lattice and transforming its molecular content to a new one is necessary. In this process, the original crystal or domain may remain intact or break up into yet smaller crystallites or domains. Therefore, in a polycrystalline assembly there is a spectrum of 'energy levels' and hence, different temperatures are required for complete transformation of all the component crystallites. This was very clearly demonstrated by the very broad transition range in the case of sublimed crystals of **12b** (Figures 6 and 8b) compared to the very narrow temperature range for the aged and tempered crystals (Figure 8b).

Finally, it is obvious from the foregoing that also for the case of order/disorder transitions at the melting point (e.g., of benzoic acid in Figure 1) similar arguments apply and, therefore, in a strict sense for macroscopic systems isothermal transitions cannot, as required by thermodynamics, be expected.

Hysteresis

The above discussion on phase transitions was concentrated on the mechanism of lattice changes. Another consequence of a spontaneous phase change mechanism is that in a crystallite destined to undergo a transition, enough internal excess energy has to be accumulated until the transition temperature T_{tr} is reached [22]. Starting from a temperature T_0 , when T_{tr} is reached a lattice is metastable. In this temperature range the molecules making up the lattice have acquired the potential energy to undergo the predestined rotation, or reaction. However, the energy gained is not sufficient to overcome the statics of the parent lattice. In Figure 21 a hypothetical temperature dependent equilibrium shift is shown. Curve (a) follows the reaction in absence of the opposing lattice forces (in case of a phase transition with concurring chemical reactions, the molecules involved naturally have to also overcome the corresponding activation barrier). Curve (b) is to represent the spontaneous transition of molecules of phase A to phase B. By nature the onsets of the two processes do not coincide. That of the latter type is retarded by the opposing lattice forces.

The reverse process, starting from the new parent

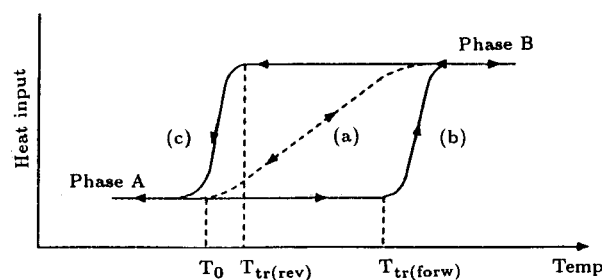


Figure 21. Schematic representation of solid/solid phase transformation and hysteresis.

lattice B, will generally not retrace either of the curves (a) or (b). Rather, in the case of a concurring solid state reaction the molecules have to pass the inverse activation barrier and, in any case, also overcome the lattice forces of phase B. The overall result is that the return to phase A will follow the hypothetical path (c). The extent of hysteresis is then given by:

$$\Delta T_{tr} = T_{tr(for)} - T_{tr(rev)}$$

In those cases where a phase transition appears to be monotropic, the reverse process may be hindered by either a high activation barrier of the reacting molecules, or by the stability of, e.g., the high temperature phase.

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