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Conformational Polymorphism of Dimethyl 3,6-Dichloro-2,5-dihydroxyterephthalate. II. Structural, Thermodynamic, Kinetic and Mechanistic Aspects of Phase Transformations among the Three Crystal Forms

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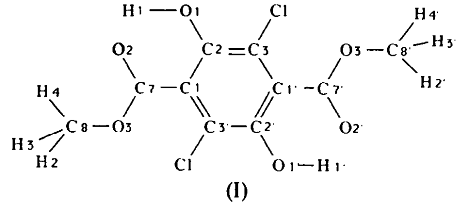
Abstract

The molecules in three polymorphic forms of the title compound – Y (yellow), LY (light yellow) and W (white) – are known to be conformational isomers with the ester groups approximately in the plane of the benzene ring (Y), nearly perpendicular to it (W), and in an intermediate orientation (LY) [Byrn, Curtin & Paul (1972). *J. Am. Chem. Soc.* **94**, 890–898; Yang, Richardson & Dunitz (1989). *Acta Cryst.* **B45**, 312–323, Part I]. Phase transformations among these crystal forms have been studied by simultaneous differential scanning calorimetry measurements and optical microscopy observations recorded with a video-camera. At room temperature and below, the order of thermodynamic stability is Y > LY > W; above 360 K, it is W > Y > LY. On heating, crystals of LY transform to W but sometimes first to Y; crystals of Y transform to W, often through the transient intermediacy of LY; crystals of W melt at 453 K to yield a yellow liquid that freezes (on supercooling) to give crystals of all three forms but mostly Y. The solid–solid transformations occur over a wide temperature range. They seem to be controlled by the presence of certain types of defect and to proceed by a nucleation and growth type of mechanism. These results are discussed in terms of the known crystal structures at several temperatures with particular reference to the atomic displacement parameters and their temperature dependence.

Introduction

The work to be described here is the second part of a contribution from our laboratory dealing with the remarkable conformational polymorphism of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate [(I), see structural formula for atom labelling]. This compound exists in three differently coloured crystal forms, designated as Y-(I) (yellow), W-(I) (white) and LY-(I) (light yellow). The study of the first two forms goes back to Hantzsch (1915), who observed that Y-(I) transforms to W-(I) on warming to about 410 K and suggested that the two forms are tautomers. Much later, from X-ray diffraction studies (Byrn, Curtin & Paul, 1972; BCP), it became clear that the molecules in these two forms are actually conformational isomers of (I). In Y-(I) the molecules are almost coplanar, with intramolecular hydrogen bonds to carbonyl O atoms; in W-(I) the methoxycarbonyl groups are rotated nearly perpendicular to the plane of the other atoms, with hydrogen bonds to carbonyl O atoms of different molecules. BCP also made detailed observations (mainly by optical microscopy and differential scanning calorimetry) on the solid-state transformational of Y-(I) to W-(I).



(I)

In Part I of this work (Yang, Richardson & Dunitz, 1989) we reported the existence of the third form [LY-(I)], which had apparently been overlooked by the earlier investigators; in this form the ester groups are neither nearly coplanar with the benzene ring, as in Y-(I) (torsion angle about 5°), nor nearly perpendicular to it, as in W-(I) (torsion angles

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about 85 and 70° for the two symmetry-independent molecules), but in an intermediate orientation (torsion angle about 40°). We also described results of new crystal structure analyses of all three forms, Y-(I) and LY-(I) at five temperatures and W-(I) at three temperatures between 100 and 350 K. Stereo drawings of the three crystal structures are shown in Figs. 1–3. In addition to the changes in crystal packing and hydrogen-bond arrangement, there are also significant differences in bond lengths and angles as the molecular conformation changes. One striking difference between the three types of molecule comes from the analysis of the atomic anisotropic displacement parameters (ADP's). [For recent reviews of the possibilities and limitations of deriving information about atomic motions from ADP's see Dunitz, Schomaker & Trueblood (1988), Dunitz, Maverick & Trueblood (1988) and Bürgi (1989).] From this analysis it was apparent that the molecules do not behave as rigid bodies in the crystals; the ester groups have an additional librational motion with respect to the rest of the molecule. The mean-square amplitude of this libration, $\langle\omega^2\rangle$, is much larger for Y-(I) than for the other two forms, and so is the temperature dependence of $\langle\omega^2\rangle$. In terms of a mean-field potential model, this means that the potential hindering libration of the ester group is much softer for Y-(I) than for the other two forms. In the present paper we discuss the relevance of these and other observations to structural, thermodynamic, kinetic and mechanistic aspects of the transformations between the various phases.

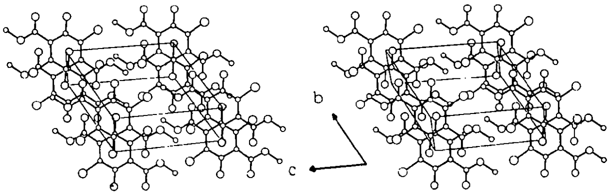

Fig. 1. Stereoview of the Y-(I) crystal structure on the plane of the benzene ring. The axes have been transformed from the published cell to one more comparable with the LY-(I) structure (see *Structural aspects*).

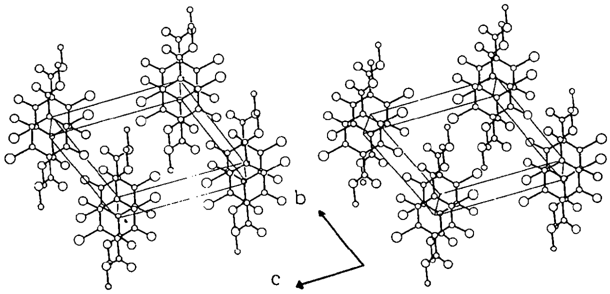

Fig. 2. Stereoview of the LY-(I) crystal structure on the plane of the benzene ring.

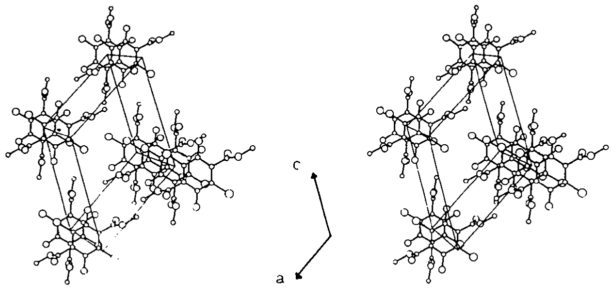

Fig. 3. Stereoview of the W-(I) crystal structure on the plane of the benzene ring.

Preparation and stability

As mentioned in Part I, slow cooling of (I) from ethanol and from ether frequently yields a mixture of crystals of all three polymorphs. This mixture can be separated by hand according to colour and morphology. Typical crystal morphologies of the three forms are shown in Fig. 4. At room temperature (and below) all three forms appear to be indefinitely stable; specimens have been kept for several years without detectable change. However, when crystals of the three forms are left to stand in a suitable solvent at room temperature, Y-(I) grows at the

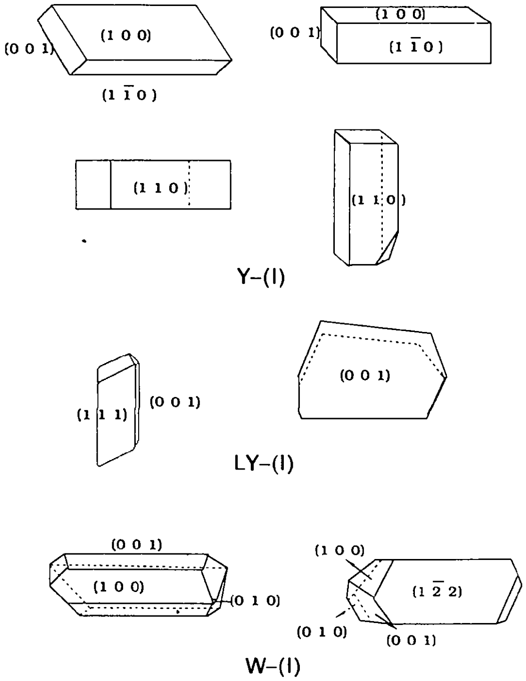

Fig. 4. Drawings of typical crystals.

expense of the other two; also, under these conditions W-(I) dissolves faster than LY-(I). Hence Y-(I) is identified as the thermodynamically stable form at room temperature, W-(I) as the least stable.

Attempts to grind or polish crystals of Y-(I) or LY-(I) often produce sporadic regions of W-(I), recognizable from the difference in colour. This is presumably due to the generation of local, transiently high temperatures by conversion of mechanical energy into heat.

Crystal morphology

In addition to the two crystal habits of Y-(I) described by BCP, we have observed several others. In fact, both Y-(I) and L-(I) show a bewildering variety of crystal habits, some of which are depicted in Fig. 4. Crystals of LY-(I) obtained from solution often exhibit rounded edges (owing to partial dissolution with enhanced solubility in some directions). From differences in colour and shape it is not difficult to distinguish crystals of Y-(I) from those of LY-(I), and we believe that the specimen photographed in Fig. 2 of BCP and described there as Y-(I) is actually LY-(I). (After a discussion with JDD in Urbana in 1987, BCP agree with this identification.) When crystals of LY-(I) transform to W-(I) the phase boundary moves along [110], which is usually the long direction of the crystal.

Crystals of W-(I) obtained from solution are typically needles elongated along [010] with (100) and (001) as zonal faces.

Phase transformations

In our work on the various phase transformations we have been greatly aided by a device allowing simultaneous differential scanning calorimetry (DSC) measurements and microscopic observations recorded with a video-camera, as described by Wiedemann & Bayer (1985). The basic unit is the Mettler FP800 Thermosystem, consisting of the hot stage FP84 and the control unit FP80, connected to a personal computer *via* an RS 232C interface (Fig. 5). The hot stage is viewed through a microscope fitted with a video-camera, so that the visual observations can be recorded and shown on a video-screen. A second video-camera records the temperature of the sample, which can be shown on the video-screen together with the image of the crystal. In our experiments samples of 0·5–5 mg were used with heating (and cooling) rates in the range 1–10 K min^{-1}.

Typical DSC curves for Y-(I) are shown in Fig. 6. In general, the slower the heating rate, the lower the onset temperature and the broader the peak. Indeed, with our materials, certain phase transitions could be followed only with high heating rates. With slower heating rates, the transformations occurred over such a wide temperature range (long time span) that the onset could hardly be discerned above the background curve. With fast heating rates, on the other hand, the transformation temperature may be very variable and in any case much higher than the thermodynamic transition point. In our work, the accuracy of the measured transition enthalpies was limited by these factors and also by sublimation of the samples, which were enclosed in a transparent (sapphire) cell.

We can confirm that the melting and phase transformation behaviour of a crystalline substance depends not only on the crystal size and form but also on other factors, such as the thermal history of the crystal and the rate of heating. Visual observations can sometimes be more sensitive indicators of phase changes than the DSC measurements; on heating or cooling the sample, one can *see* that changes are happening in and on the surface of the crystals while the DSC trace remains featureless. The video-record secures the permanency of these ephemeral events.

Our observations can be summarized as follows:

Thermal transformation of Y-(I). As observed also by the earlier investigators, the Y-(I) to W-(I) transformation can occur over a considerable temperature range, between about 375 and 415 K, depending on many factors such as crystal size and perfection as well as the heating rate. (If the crystals are held at a

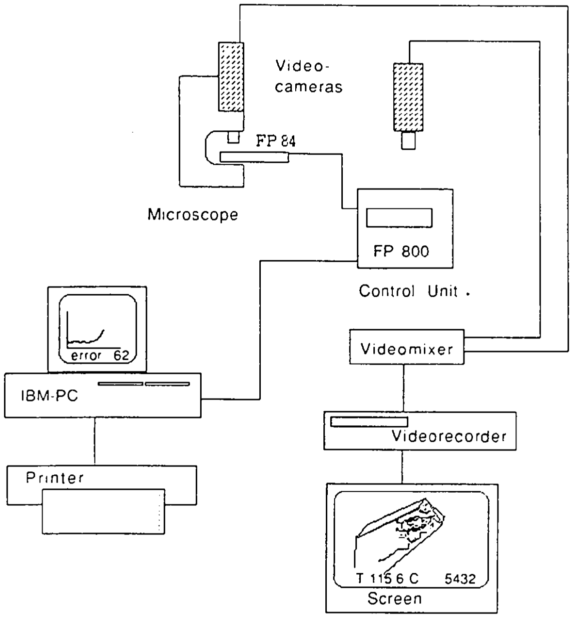

Fig. 5. Schematic description of the apparatus for simultaneous visual and DSC observations using the Mettler Thermosystem FP800.

temperature of 375–385 K for 1–2 min, this is usually enough to initiate the transformation.) The transition is associated with a rather broad, ragged endotherm in the DSC record that is difficult to integrate exactly; from many experiments we estimate a ΔH around $+1{\cdot}7$ kJ mol^{-1}, corresponding to a ΔS of about $+4$ J deg^{-1}. On further heating to 455 K the white form [W-(I)] melts ($\Delta H_f \simeq 40$–42 kJ mol^{-1}, $\Delta S_f \simeq 90$ J deg^{-1} mol^{-1}) to a yellow liquid that generally supercools to yield on freezing not W-(I) but rather a conglomerate consisting mainly and sometimes almost exclusively of Y-(I). The Y-(I) material obtained from the melt in this way (sometimes as single crystals) does not revert to W-(I) on rewarming through the transition temperature region but melts directly – at around 435 K, some 20 K lower than W-(I). However, if the Y-(I) crystals obtained from the melt are cooled rapidly to room temperature and then heated, they transform normally to the W-(I) modification. This kind of erratic behaviour points to the importance of crystal defects in initiating the various transformations, and, indeed, if defects are introduced artificially by touching the crystal surface with a sharp needle, the Y-(I) to W-(I) transformation starts at the scratch and proceeds outwards from there, along the [100] direction, as observed by BCP.

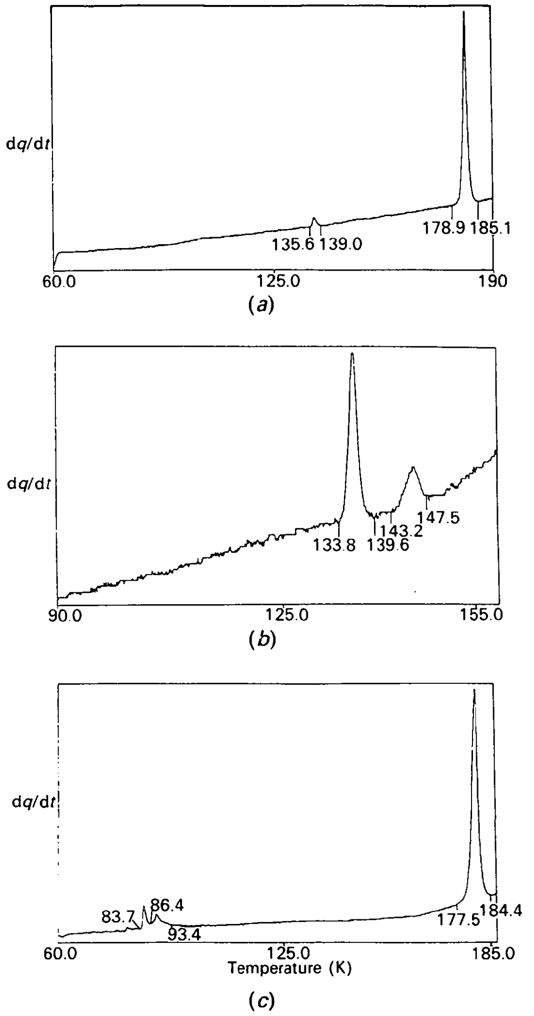

Fig. 6. Typical DSC curves measured for (I). (*a*) Y-(I) heating, 3 K min^{-1}, single crystals, weight $\simeq 2{\cdot}5$ mg. (*b*) Y-(I) heating, 3 K min^{-1}, single crystals, weight $\simeq 8$ mg. (*c*) LY-(I) heating, 3 K min^{-1}, single crystal, weight $\simeq 4{\cdot}2$ mg.

Thermal transformation of LY-(I). Crystals of LY-(I) usually transform to W-(I), again over a wide temperature range, between 360 and 380 K ($\Delta H \simeq 2{\cdot}5$ kJ mol^{-1}), as observed in DSC runs. With crystals held at constant temperature, the transformation has been observed to occur as low as 340 K. Occasionally, an LY-(I) crystal (or part of it) may be seen to transform to Y-(I). In contrast to the other transformations, which all yield polycrystalline products, this yields quite large translucent regions of Y-(I), an indication that it is a single-crystal to single-crystal transformation.

Thermal transformation of W-(I). As mentioned already, W-(I) melts around 455 K to give a yellow melt that supercools and freezes around 435 K to yield mainly the Y-(I) form, even though this is well above its usual range of stability.

From visual observations during the Y-(I) to W-(I) transformation, the colour change seemed to occur in two stages, first a change from deep to light yellow, followed almost immediately by a second change to white, suggestive of the transient appearance of LY-(I) as an intermediate. This was confirmed by the video-microscopical observations. As the transformation often takes place over a wide temperature range, it can happen that in some portions of a crystal the Y–LY–W transition may be complete while other portions are still unreacted. As a check on the intermediacy of LY-(I), the powder diffraction pattern was recorded for a crystal that had been heated until the first signs of transformation began to appear at about 395 K and then rapidly cooled to room temperature; it showed that the material was a mixture of Y-(I), LY-(I) and W-(I).

Thermodynamic aspects

What do we know about the relative stabilities of the three forms? At high temperature, above 375 K, W-(I) must be the thermodynamically stable form since Y-(I) and LY-(I) both transform to it. Also, W-(I) has a higher melting point than Y-(I) – 455 *versus* 435 K. At room temperature the thermodynamically stable modification must be Y-(I) because a single crystal of this form grows at the expense of the other two forms when all three are present in a suitable solvent. W-(I) dissolves more rapidly than LY-(I) and hence can be identified as the least stable at this temperature. By 360 K the LY-(I)/W-(I) free-energy curves must have crossed, since on warming to this temperature LY-(I) is converted into W-(I). We also know that at this temperature LY-(I) is still less stable than Y-(I) since it is occasionally converted into it instead of W-(I). Thus, there appears to be no temperature where LY-(I) is the most stable form; hence the system is *monotropic*, according to McCrone's (1965) classification.

The crossover in the Y-(I)/W-(I) free-energy curves must be between room temperature and 343 K according to the following observations made with the video-microscope. A single crystal of Y-(I) was placed in contact with one of W-(I) and covered with a layer of saturated ethyl benzoate solution. At 348 K, after 3–4 h, small crystals of W-(I) could be observed on the exposed surfaces of the slowly dissolving Y-(I); after 2–3 days at this temperature the Y-(I) crystal had been completely replaced by a polycrystalline mass of W-(I). In a second run, after 2 days at 343 K the W-(I) crystal had become slightly larger at the expense of the Y-(I), which had dissolved. At 338 K there was no change in the appearance of the crystals after 10 days.

The way the relative free energies of the three polymorphic forms vary with temperature is shown schematically in Fig. 7.

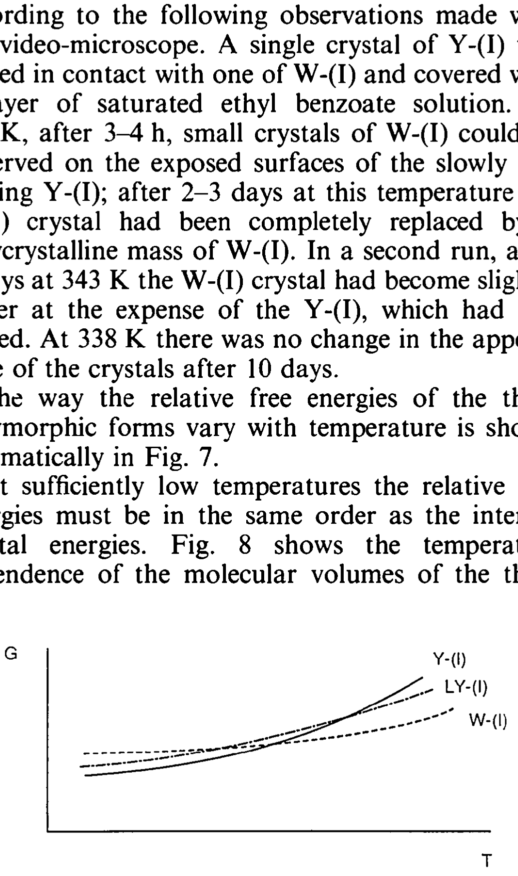

Fig. 7. Schematic drawing of crystal free energies.

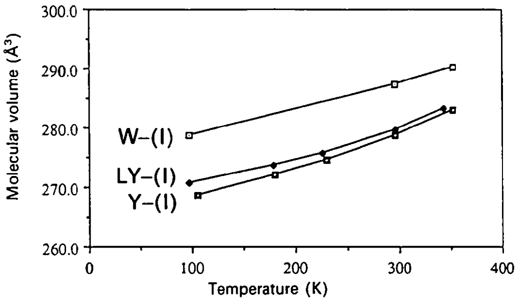

Fig. 8. Molecular volume as a function of temperature.

Table 1. *Cell dimensions of the room-temperature (296 K) crystal structure*

The space groups are all $P\bar{1}$.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
Y-(I)	9·582	4·292	7·950	114·23	94·93	106·22	278·7
LY-(I)	3·898	8·034	9·491	70·42	89·09	86·68	279·6
W-(I)	9·843	7·847	10·573	116·40	124·18	88·96	574·8 = 2 × 287·4

At sufficiently low temperatures the relative free energies must be in the same order as the internal crystal energies. Fig. 8 shows the temperature dependence of the molecular volumes of the three polymorphs; evidently, the denser the crystal, the lower its internal energy. (This can be considered as a general rule, but there are many exceptions.) As shown in Part I, the mean-square libration amplitude of the ester group, $\langle\omega^2\rangle$, in Y-(I) is much larger than in the two other forms and so is the temperature dependence of this motion. In fact, all the atoms in the Y-(I) crystal have larger displacement parameters than the corresponding atoms in the other two forms (see Table 4, Part I). From this, one might have guessed that the Y-(I) crystal would have the largest entropy of the three. However, this is not so. As we have seen (see *Phase transformations*), the Y-(I) to W-(I) transformation at 395 K is endothermic and hence associated with an entropy *increase*. In this respect, the relative molecular volumes seem to be a better guide.

Why has our intuition led us astray in expecting that the crystal with the larger atomic ADP's should have the greater entropy? One factor may be that the ADP's represent sums of squared displacements over *all* the lattice vibrations of the crystal, not just the ones on which we happen to concentrate our attention. Perhaps the fact that the W-(I) cell is bimolecular while the Y-(I) cell is unimolecular may be significant. It means that for W-(I) there are twice as many lattice vibrations over which the available energy can be distributed. The problem is left to the theoreticians.

Structural aspects

The changes in molecular conformation in the three crystal structures have been described in Part I and summarized in the *Introduction*. These changes are accompanied by changes in the hydrogen-bonding patterns – intramolecular in Y-(I) and LY-(I), intermolecular in W-(I) – that are also dealt with in Part I. Here, we concentrate on the intermolecular packing in the three phases. For convenience, we reproduce in Table 1 the cell dimensions and space groups of the room-temperature (296 K) crystal structures given in Part I. The e.s.d.'s are 0·001–0·002 Å for the lengths and 0·01–0·02° for the angles.

The packing arrangements in the Y-(I) and W-(I) phases have been described by BCP and there is little to be added to their description. Both structures contain stacks of molecules along the respective **b** axes (Figs. 1 and 3), but whereas the molecules in Y-(I) are related by simple translation, there are two crystallographically non-related molecules in the W-(I) stacks, one at 0,0,0 (molecule *A*) and one at 0,$\frac{1}{2}$,0 (molecule *B*), linked by hydrogen bonds between a hydroxyl group of one molecule and the carbonyl O atom of its neighbour [O(H)···O(2) distances 2·72 Å (from *A* to *B*) and 2·80 Å (from *B* to *A*)]. To form these hydrogen bonds the ester groups need to be twisted strongly out of the planes of the benzene rings, the twist angles being about 85° in molecule *A* and about 70° in molecule *B* (as mentioned in Part I, these angles are markedly temperature dependent). Note that the two molecules in W-(I) have opposite senses of rotation with respect to the sequence of the substituents, *i.e.*, opposite senses of two-dimensional chirality; if the order Cl, OH, COOMe is clockwise for a given molecule in the stack, it is anticlockwise in the two neighbouring ones. This is important since it means that the transformation Y-(I) to W-(I) cannot be achieved by a mere change in hydrogen bonding accompanied by rotation of the ester groups; in addition, every other molecule has to be flipped upside down.

Although the cell dimensions given here of the Y-(I) and LY-(I) phases look very different, the crystal structures are actually quite similar, as seen by comparing the stereoscopic packing drawings shown in Figs. 1 and 2. The unit cell of LY-(I) is in the reduced form (Santoro & Mighell, 1970), whereas, to avoid unnecessary duplication in the literature, those of Y-(I) and W-(I) have been left in the orientations described by BCP. In fact, by applying the transformation $0\bar{1}0/0\bar{1}\bar{1}/100$ to the above cell for Y-(I) we obtain (in the same order as Table 1): 4·29, 7·32, 9·58 Å, 75·2, 73·8, 81·9°, now more similar to the reduced LY-(I) cell. Note, however, that this transformed Y-(I) cell is still not reduced. (Any similarity that may exist between triclinic structures is not necessarily seen to best advantage by transforming the cells to their reduced form.) Like Y-(I) (Fig. 1), the LY-(I) structure (Fig. 2) contains stacks of translation-related molecules. Although the translation distance in LY-(I) is less than in Y-(I) (3·90 *versus* 4·29 Å), the stacking angle (the angle between the mean aromatic ring plane normal and the stacking axis) is also less (24 *versus* 38°), with the result that the shortest distances between atoms of successive molecules along the stacks are not very different in the two structures. In Y-(I) successive molecules along the stack are displaced along the direction of their hydroxyl groups so that the centre of one ring lies almost over a hydroxyl O atom of its neighbour (Fig. 9). This brings C(2) and C(2′) of adjacent molecules into register at a distance of 3·28 Å. There is another close contact of 3·33 Å between the Cl atom of one molecule and C(7′) of its neighbour (and between the centrosymmetrically related pair). In LY-(I) the displacement is different, adjacent molecules in the

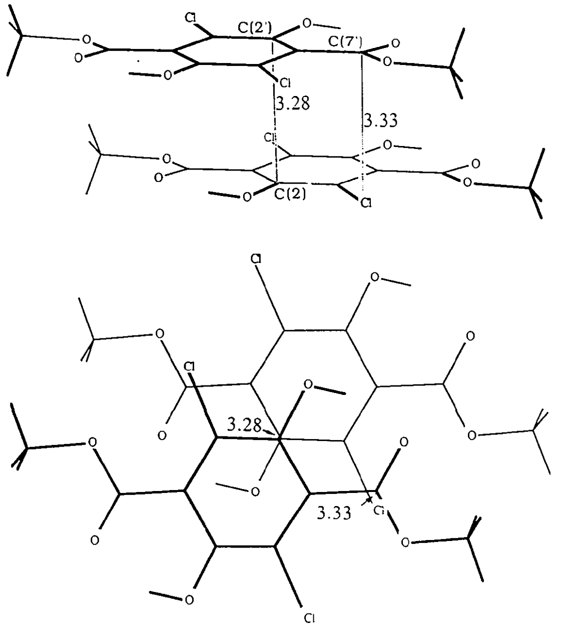

Fig. 9. Stacking diagram of Y-(I); interatomic distances (at 105 K) in Å in two different projections about 90° apart, the lower projection being on the mean plane of the aromatic ring.

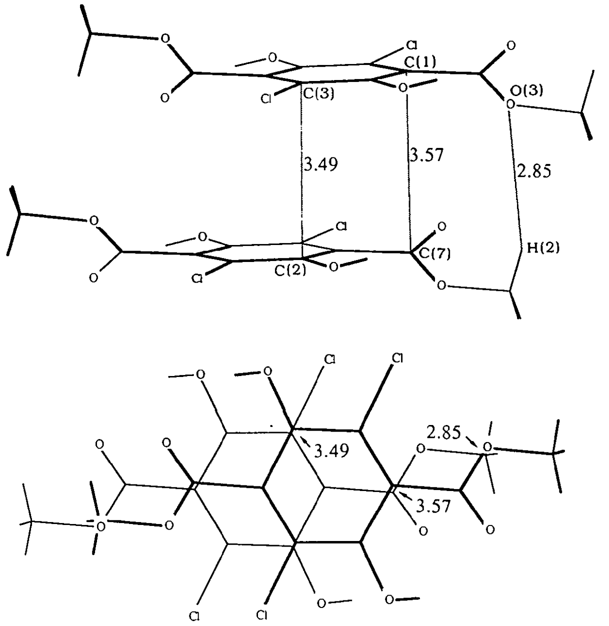

Fig. 10. Stacking diagram of LY-(I); interatomic distances (at 97 K) in Å in two different projections about 90° apart, the lower projection being on the mean plane of the aromatic ring.

stack being displaced along their long directions to put C(1) and C(3) of one molecule nearly in register with C(7) and C(2) of its neighbour at interatomic distances of 3·56 and 3·49 Å, respectively, and correspondingly for the centrosymmetrically related pairs (Fig. 10). With the 40° tilt of the ester groups in LY-(I), this displacement leads to a contact distance of 2·85 Å between methyl H(2) and the ester O(3) atom of a neighbouring molecule (the corresponding C—H···O angle is 158°).

The two structures show similarities and differences with respect to the interstack packing. In both, there are short contacts involving carbonyl O(2) atoms of different stacks: in Y-(I), O(2)···O(2)($-x$, $2-y$, $-z$) = 2·76 Å; in LY-(I), O(2)···O(2)($-1-x$, $1-y$, $-z$) = 2·78 Å; in LY-(I) the corresponding O(2)···O(1) distance is only slightly larger, 2·87 Å, in Y-(I) it is 3·05 Å. In Y-(I) molecules related by the inversion centres at $\frac{1}{2},0,\frac{1}{2}$ (those in the centre of Fig. 1) are in contact *via* their methyl groups [C(8)···C(8′) = 3·31 Å], and those related by the inversion centres at $\frac{1}{2},0,0$ (those at the top and bottom of the figure) *via* their Cl atoms (Cl···Cl = 3·46 Å). The corresponding contacts in LY-(I) are much looser.

Kinetic and mechanistic aspects

As mentioned earlier, DSC measurements yield very variable results for the transition temperatures of Y-(I) and LY-(I) crystals. Optical microscopy shows that these solid-state transformations spread out from specific points, which often correspond to scratches and other recognizable defects and irregularities on the crystal surface. These points are presumably nucleation sites for the new phase. Observations with slow heating rates show that such events occur at different defects at different temperatures. Once the new phase has begun to grow from a given point, it spreads within a short time (a few seconds to a few minutes) to cover a portion of the crystal (sometimes the entire crystal) and then stops. Further spread of the new phase has to await the start of growth at another nucleation site. For the complete transformation of a single crystal, the whole process can extend over a temperature range of 20–30 K. These results are in accord with views of Mnyukh (1979), who proposes that each defect suitable for nucleation of a new phase has its own characteristic 'pre-coded' transition temperature.

As mentioned earlier, Y-(I) crystals obtained by cooling the melt behave anomalously in that they do not usually transform to W-(I) on re-warming but undergo melting instead; presumably they lack the right kinds of defect for the polymorphic transition. Also, the nucleation and growth rate of Y-(I) formally obtainable from LY-(I) or W-(I) in the temperature range where they are thermodynamically unstable must be very slow indeed. We have never observed any indication of solid-state phase transformation of metastable LY-(I) or W-(I) on cooling. At room temperature and below, all three phases can be kept indefinitely.

Given the crystal structures of the three polymorphs (Figs. 1–3), it is tempting to assume that the transitions occur by the simplest imaginable deformation of one structure into the other, involving translations and rotations of the individual molecules. For the transformation of Y-(I) and LY-(I) to W-(I), there is no feasible pathway for such a 'least-motion' mechanism; starting from these structures, half the molecules would need to be rotated 180° about an axis in the plane of the benzene ring, a process that would require a very high activation energy and which can hardly be imagined without total disruption of the existing structure. On the other hand, the Y-(I) and LY-(I) structures are sufficiently similar that the transformations LY-(I) $\longleftrightarrow$ Y-(I) could be imagined to proceed by the kind of deformation mechanism just described. Such a notion might even be encouraged by the observation that the forward process sometimes occurs by a single-crystal to single-crystal transformation. However attractive this notion might appear, it seems highly unlikely to be correct. The optical and thermal observations leave little doubt that the transitions involve nucleation and growth of the new phase outside the domains of the existing one. In other words, molecules must be transferred somehow from the unstable phase to the growing, stable one, across the phase boundaries. At the present state of our knowledge, there seems little point in proposing any kind of detailed mechanism for such a process. We have no possibility for checking it.

Nevertheless, the motional analysis described in Part I may throw light on one aspect of the mechanism – the conformational changes between the three polymorphs and particularly between Y-(I) and the other two. We recall that although the molecules in Y-(I) show a slightly greater translational and librational motion than in the other two crystal forms, by far the greatest difference is in $\langle\omega^2\rangle$, the torsional motion of the ester group about the exocyclic C—C bond. This is much larger for Y-(I) than for the other two forms (190 deg^2 compared with 40–70 deg^2 at 350 K) and also has a larger temperature dependence (see Fig. 4, Part I).

If we assume that the quantity $\langle\omega^2\rangle^{1/2}$ corresponds to the half-width of a parabolic energy well at the height $RT/2$ above its minimum (Shmueli & Kroon, 1974), then we can construct potential-energy curves for the torsional motion of the ester group for each of the three modifications from the available experimental data. These are shown in Fig. 11, where the horizontal lines represent $\varphi \pm \langle\omega\rangle^{1/2}$, φ being the mean twist angle of the ester groups. The curve for W-(I) represents an average over the two independent molecules. As mentioned in Part I, φ changes perceptibly with temperature; in Y-(I) it is (e.s.d. 0·4°) 4·1, 4·4, 4·8, 5·1 and 5·7° at the five measurement temperatures; in LY-(I) 38·2, 38·7, 38·9, 39·4 and 40·0°; and in W-(I) 85·0, 86·3 and 86·7° for molecule *A* and 69·8, 72·4 and 73·1° for molecule *B* at the three measurement temperatures. This systematic variation is an indication of anharmonicity in the potentials describing the ester-group rotation, as seen in Fig. 11.

The relative displacements of the three curves in Fig. 11 along the energy coordinate have no well defined meaning. We have drawn them so that the energy minima correspond approximately to the relative thermodynamic stabilities of the three phases around 375 K, where W-(I) is the most stable and Y-(I) and LY-(I) are roughly equienergetic. Thus, although the energy wells themselves rest on experimental data, their vertical displacements in the figure are less secure, and the dashed curves that connect them are purely hypothetical. Fig. 11 may be taken to portray, in a rough way, the energy dependence of φ at a defect in the crystal (around 375 K) and, in an even rougher way, the energy profiles for the phase transformations. Admittedly, the whole process must be much more complicated than that suggested by the one-dimensional profile of Fig. 11, but the φ coordinate presumably represents an important component. At the temperatures where Y-(I) transforms to W-(I), the extrapolated value of $\langle\omega^2\rangle^{1/2}$ is quite enough to carry a methoxycarbonyl group across the barrier to the orientation it has in LY-(I), which, as we have seen, can often be observed as a transient intermediate on the way to W-(I).

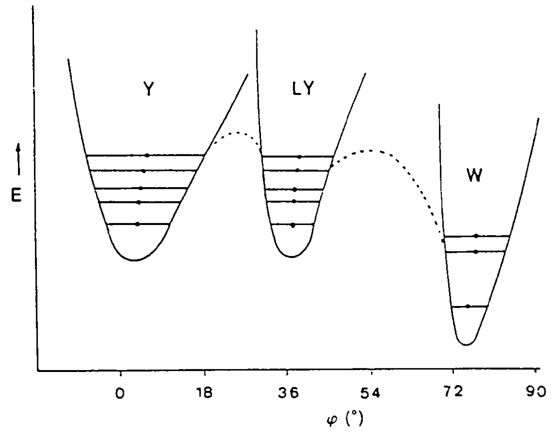

Fig. 11. Potential energy as a function of torsion angle φ of the ester group. The solid curves are based on the experimental data and show the potential-energy curves for Y-(I), LY-(I) and W-(I). The horizontal lines show $\varphi \pm \langle\omega^2\rangle^{1/2}$, and the point in the centre of each line shows the value of φ at a given temperature. The dashed curves crudely represent the energy changes accompanying methoxycarbonyl group rotation at a defect in the appropriate crystal structure.

Concluding remarks

The experimental study of polymorphic transitions is very difficult. The phenomena are complex and seldom reproducible, and our understanding of them leaves much to be desired. Our observations on the transformations among the three polymorphic forms of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (I) suggest that these occur by nucleation and growth of the new phase outside the domains of the old one; they do not occur by deformation of one structure into another. Nevertheless, at the molecular level, large-amplitude internal motions of the molecules in the Y-(I) modification can be detected, and it is possible these may help to trigger the crystal transformations.

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