Role of Imperfections in the Dimerization of Substituted Anthracenes. Part II.[1] 1,8-Dichloro-10-methylanthracene

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Optical and electron microscopic examination of the (010) (*ac*) faces of the orthorhombic crystals of 1,8-dichloro-10-methylanthracene, together with supporting differential-enthalpic and dielectric measurements, have been employed with a view to explaining how the topochemically forbidden *trans*-photodimer is produced in the solid state upon u.v. irradiation. It is shown that dimer nuclei appear at emergent dislocations and tend to be aligned along the [001] and, to a lesser extent, the [100] directions. Two slip systems which would account for these observations are $(210)[\bar{1}20]$ and (011)[121], both of which yield space-symmetries at the dislocation cores such that a *trans*-relationship exists between neighbouring molecules. The possible importance of stacking faults on $(41\bar{1})$ and $(40\bar{1})$ planes is discussed, and so also is the general significance of our results in relation to the recently evolved technique of crystal engineering.

ALTHOUGH the detailed three-dimensional crystal structure of the dimer produced by irradiating 1,8-dichloro-10-methylanthracene (1,8-Cl_2-10MA) (Figure 1) has not yet been elucidated (owing partly to its extreme insolubility and the consequential difficulty in obtaining single crystals of adequate quality), there is little doubt that it has the *trans*-configuration (Figure 2). The detailed arguments leading to this conclusion have been chronicled elsewhere [2,3]—we need recall here only the fact that *meso*-substituted (*i.e.* with substituents at the 9-, or the 10-, or both the 9- and the 10-positions) anthracenes yield exclusively the *trans*- (*i.e.* centro-symmetric or head-to-tail) dimer upon u.v. irradiation.[4] The crystal structure (Figure 3) of 1,8-Cl_2-10MA, like those of other photosensitive substituted anthracenes (*e.g.* 9-cyanoanthracene),[5-7] would lead us to expect, on the basis of the topochemical theory summarized in Part I [1] and discussed fully elsewhere,[7,8] the production of *cis*- (mirror-symmetric or head-to-head) dimers, yet it is the *trans*-dimer which is produced.

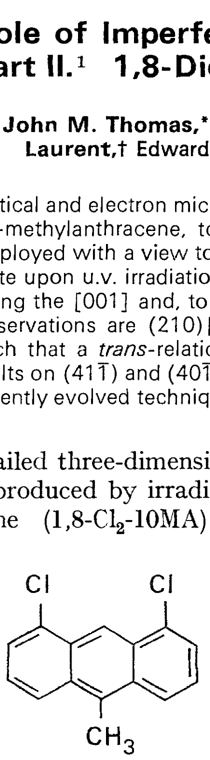

FIGURE 1 Molecular structure of 1,8-dichloro-10-methylanthracene

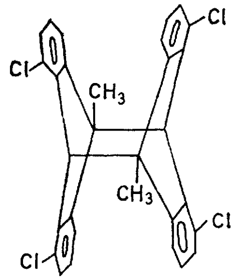

FIGURE 2 Schematic illustration of the *trans*-dimer of 1,8-Cl_2-10MA

This apparently anomalous situation raises the question of the relative importance of the ideal lattice on the one hand and the structurally imperfect ones

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on the other as the loci of photochemical activity. Dislocations are unquestionably important as sites of preferred photodimerization for both anthracene[6] and 1,8-Cl_2-9MA[1] where, in each case, the spacings and orientations of the molecules in the ideal structures are inconducive for ready dimer formation. Also, in other solids such as 9-cyanoanthracene where the ' wrong ' dimer is formed, it is not difficult[5,6] to conceive of stacking faults (resulting from the dissociation of unit strength dislocations into separated partial dislocations on particular planes, see *e.g.* Figure 12 of ref. 5) which would facilitate the production of the *trans*-dimer within a monomer matrix where the neighbouring molecules are in an incipient *cis*-orientation. This is one reason why we have endeavoured to elucidate the nature of line defects in 1,8-Cl_2-10MA.

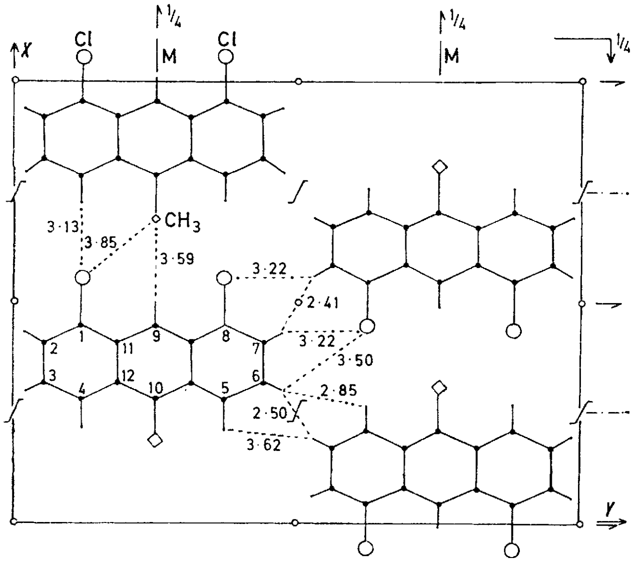

FIGURE 3 Projection on the *ab* plane of the crystal structure of 1,8-Cl_2-10MA; separation distances between chlorine (denoted ○) and other atoms given in Å; methyl group symbolized by ◊

It is particularly important to understand how it comes to be that the topochemically forbidden photodimer is produced upon irradiating 1,8-Cl_2-10MA, since this opens the whole question of the reliability of the recently discovered technique of ' crystal engineering ' pioneered by Schmidt and his co-workers.[7,8] The considerable synthetic potential of crystal engineering, in which, by the simple expedient of mono- or di-chloro- aromatic substitution, it becomes possible to induce potentially dimerizable molecules to crystallize in well overlapped and closely juxtaposed arrangements conducive to the production of a given desired dimer species, has been discussed elsewhere.[7,8] It has already proved of great value in synthesizing molecules which are otherwise impossible to prepare. But 1,8-Cl_2-10MA crystallizes, as expected from the existence of the so-called halogen bond (see ref. 9), in the overlapped mirror-symmetric mode, yet, unlike almost all other similarly packed chloro-substituted aromatic molecular crystals it yields the *trans*-centrosymmetric dimer. This, therefore, is the other main reason for examining the role of imperfections in the photochemistry of 1,8-Cl_2-10MA.

It had been hoped that, by transmission electron microscopy,[10—12] we might have readily seen, as a result of diffraction- and stacking-fault-contrast, the particular dislocations favoured in this solid and the extent of their dissociation into partials. Such studies are, however, rendered extremely difficult in organic solids generally because of their ready susceptibility to electron-beam damage.[13,14] They have not yet proved totally successful for 1,8-Cl_2-10MA even though some progress in this direction has been achieved electron microscopically with anthracene itself,[15-18] and with *p*-terphenyl,[14] which is, however, photochemically rather inactive. Optical microscopy has, therefore, played a large part in the studies to be described here. A few results of electron microscopy (sufficient to demonstrate the rather unusual nature of the solid-state phase transformation) are presented. Further aspects of the electron microscopic studies will be discussed elsewhere.[15]

EXPERIMENTAL

1,8-Cl_2-10MA was prepared by the method of de Barry Barrett *et al.*[19] Purification, culminating in chromatographic isolation, was achieved as previously described.[2] After crystallizing samples from benzene–ethanol, pale yellow single crystal specimens (Figure 4) could be produced by microsublimation, their dimensions being typically 1 × 2 × 0·05 mm, just large enough for optical microscopic study, before and after brief immersion in ethanol which served as an effective etchant for dislocations emergent at (010) faces.* To generate the photodimer, which was always produced heterogeneously within the monomer matrix (Plate 1), it was necessary to irradiate the samples with light from a high-pressure mercury

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* Crystallographic identity was established by X-ray (Weissenberg) methods and by electron diffraction. 1,8-Cl_2-10MA belongs to the space-group *Pnma* with $a = 15{\cdot}26$, $b = 18{\cdot}97$, $c = 4{\cdot}00$ Å, $Z = 4$.

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lamp, filtered through a solution of copper sulphate, for at least 1·5 h at *ca.* 300 K.

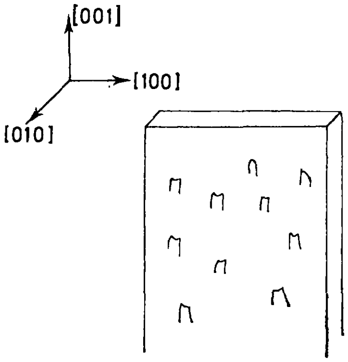

FIGURE 4 Illustration of morphology of the crystals grown from solutions in benzene–ethanol

Ultra-thin crystals were required for the electron microscopic bright-field and dark-field studies (at liquid nitrogen temperatures on a goniometer stage of a Philips EM 300 instrument). These were produced by allowing dilute solutions of the monomer, in xylene, to evaporate slowly on a water surface, and later transferred to metallic grids.

Calorimetric measurements were made by use of a Perkin-Elmer DSC-1B for differential enthalpic analysis.[20] It was necessary to use sealed sample holders.[21] Dielectric measurements, on an apparatus kindly provided by Dr. G. Williams, enabled the permittivity of the monomer to be recorded as a function of temperature up to its m.p. (427 K).

RESULTS

Optical microscopic examination of etched and/or irradiated (010) faces revealed dislocation-etch-pit alignments along [001]. There was strong evidence (Plate 2) that nuclei of photodimer were formed preferentially at sites of emergent dislocations. Nuclei were aligned mainly along [001], but there was a slight tendency for alignments also to occur along [100]. Dimer formation was, to some extent, also facilitated at surface steps running across (010) faces.

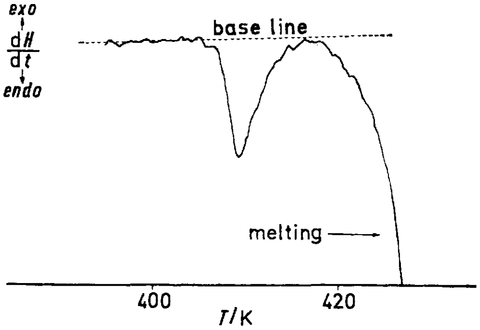

FIGURE 5 Typical differential enthalpic trace showing occurrence of endothermic peak below the m.p. of 1,8-Cl_2-10MA

Electron micrographs of thin platelets with (010) faces dominant [Plate 3(a)] rarely show up any dislocations (see, however, ref. 15). We do, however, see some well identified lamellae [Plate 3(b)] running in distinct crystallographic directions. Attempts to operate at higher magnifications invariably resulted in beam damage, as evidenced by the loss of diffraction pattern and contrast in the direct image.

The enthalpic analyses, typified by Figure 5, showed a prominent endothermic peak generally starting at *ca.* 407 K. The magnitude of this peak is variable and depends to some extent on the rate of cooling from the melt in a previous run. Often with freshly sublimed samples the peak was absent. Permittivity measurements showed no sign of any sharp or smooth dielectric changes at the ' transition temperature ' either at increasing or decreasing temperatures up to or down from the m.p.

DISCUSSION

The most important fact relating to the photodimerization of 1,8-Cl_2-10MA is that, contrary to the expectations of the topochemical theory which is now embodied in the powerful synthetic procedure known as crystal engineering, the centrosymmetric (*trans*) rather than the mirror-symmetric (*cis*) dimer is formed. It is obvious, however, from the distribution of product nuclei at the *ac* face, that the dimerization process is itself heterogeneous and displays all the symptoms [18,22] of being facilitated by structural imperfections. We are therefore led to the conclusion that excitation energy transfer (whether through the singlet- and/or triplet-exciton or even through the excimer manifold) is a relatively efficient process, at least in comparison with chemical relaxation, leading to the stereochemically unfavourable ' *cis* ' mirror-symmetric dimer. The excitation therefore functions as a kind of ' probe ' (*cf.* ref. 23) for the structural defects, at which the orientations of contiguous molecules may be incipiently *trans* or centrosymmetric.

Although line defects (dislocations) are clearly of importance as preferred sites of dimerization, some of these defects are more favourable than others. Indeed, from an analysis of the crystal structure (Figure 3), certain families of dislocations, for example (100)[010] or (010)[001], are seen to lead to less conducive configurations of neighbouring molecules situated at the dislocation core than those in the ideal structure. It is also apparent that a particularly helpful dislocation family, so far as facilitation of production of the *trans*-dimer is concerned, would be (011)$\frac{1}{4}$[121], which would bring neighbouring molecules into the registry shown schematically in Figure 6(a) and (b). Note that two types of orientation are possible [(a) and (b)], one more favourable than the other as a result of a translation slip vector of $\frac{1}{4}$[121] shown schematically in Figure 6(c),

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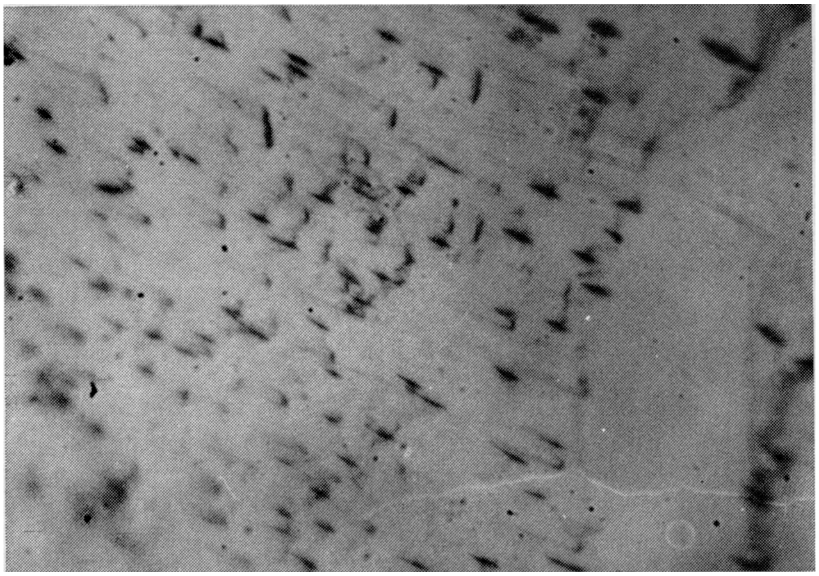

Plate 1 Optical (interference-contrast) micrograph showing typical heterogeneous nucleation of dimer on the (010) faces (magnification × 350)

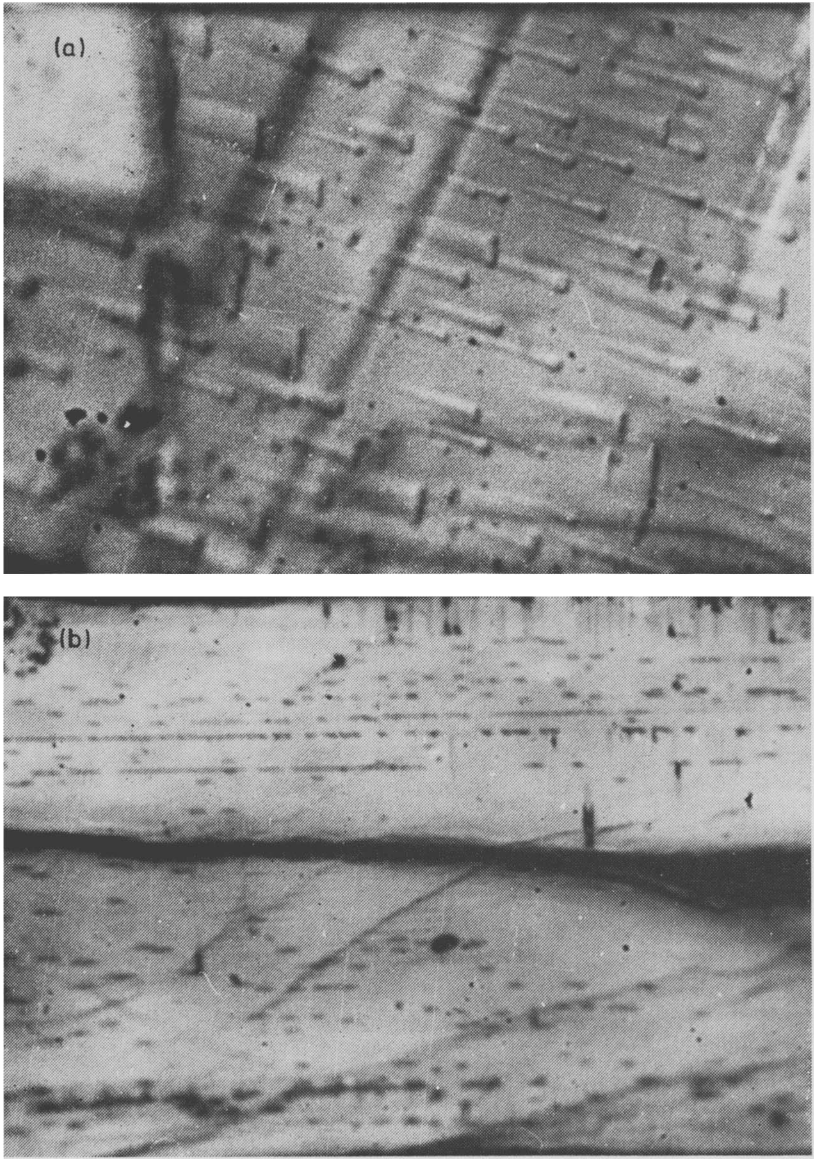

Plate 2 (a) Micrograph showing that dimer nuclei are formed preferentially at emergent dislocations and that dislocation etch-pits tend to align along $[00\bar{1}]$. (b) Illustration of a typical [001] alignment of dimer nuclei following u.v. irradiation; the crystallographic face is (010), and the magnification × 350, for (a) and (b)

PLATE 3 (a) Typical electron micrograph, with associated diffraction pattern the symmetry and spacing of which shows that the zone axis is [010], of $1,8\text{-Cl}_2\text{-10MA}$; no dislocations are visible and the dark lines are bend extinction contours (magnification × 9000). (b) Another micrograph showing striations running closely parallel to [301] directions and signifying existence of planar faults separating two distinct crystallographic phases (see text) (magnification × 11,000) which depicts the (011) plane of the crystal structure of 1,8-Cl_2-10MA. However, there is no etch-pit or slip-trace evidence that such a dislocation occurs, although poisoning by impurities at the defects could render their detection by etching very difficult. The observed slight tendency for dimer nuclei to be aligned along [100] on the (010) face may be interpreted in terms of the occurrence of a (011)[121] slip system.

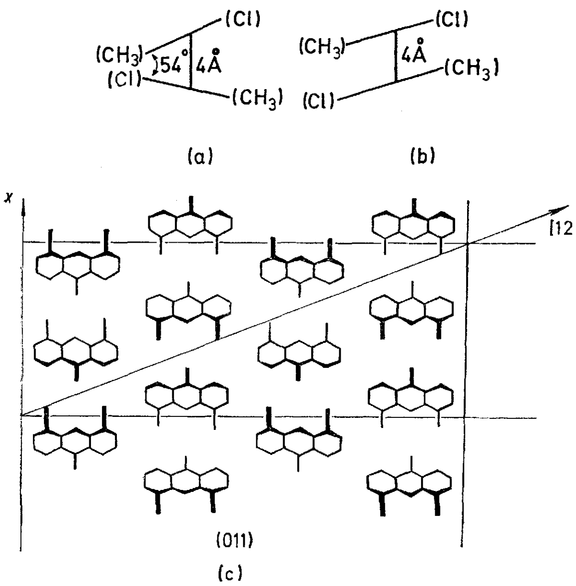

FIGURE 6 (a), (b) The two distinct types of orientation (viewed along [100]) that incipiently *trans*-related pairs of molecules take up as a result of a $\frac{1}{4}[121]$ translation on the (011) plane. (c) This illustrates how $[\bar{1}21]$ translation on a (011) plane leads to a sequence of *trans*-related molecular pairs at the dislocation core (for simplicity the Cl atoms and CH_3 groups are represented by short rods)

To account for the occurrence of dislocation etch-pits aligned along [001] on the (010) faces, a number of reasonable slip systems may be postulated. The most plausible of these are those that have (210) as the active plane in which the dislocations may glide: *e.g.* $(210)[\bar{1}20]$, $(210)[\bar{1}21]$, (210)[011], and $(210)[01\bar{1}]$. It is noteworthy that the slip system $(210)[\bar{1}20]$ brings about an incipient *trans*-configuration (see Figure 7), and it would account fully both for the observed preferential dimerization at non-basal dislocations emergent at (010) faces and for the alignments of nuclei along [001].

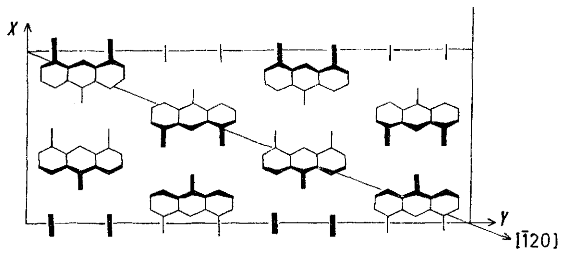

FIGURE 7 Illustration of how a $(210)[\bar{1}20]$ slip system would lead to *trans*-related molecular pairs; such a system would also give rise to alignments of nuclei (and dislocation etch-pits) along [001] on the (010) faces (as seen in Plate 2)

Pursuing the idea [5,22] that partial dislocations, and in particular associated stacking-fault ribbons, can facilitate production of the *trans*-dimer—by acting both as exciton traps and as regions where contiguous molecules are in the appropriate configuration—we may readily propose (*cf.* analogous formulations for 9-cyanoanthracene [5]) dislocation reactions at certain specific planes which would lead to the necessary favourable conditions within the monomer structure for ready photodimerization. Such reactions, occurring on $(41\bar{1})$ and $(40\bar{1})$ planes, are

(i) on $(41\bar{1})$ planes:

$$[104] \longrightarrow \tfrac{1}{4}[126] + \tfrac{1}{4}[3\,\bar{2}\,10]$$

and

$$[011] \longrightarrow \tfrac{1}{4}[126] + \tfrac{1}{4}[\bar{1}2\bar{2}]$$

(ii) on $(40\bar{1})$ planes:

$$[104] \longrightarrow \tfrac{1}{4}[124] + \tfrac{1}{4}[3\,\bar{2}\,12]$$
$$[010] \longrightarrow \tfrac{1}{4}[124] + \tfrac{1}{4}[\bar{1}2\bar{4}].$$

Figure 8 illustrates the nature of the stacking faults characterized by the dissociation summarized in (ii).

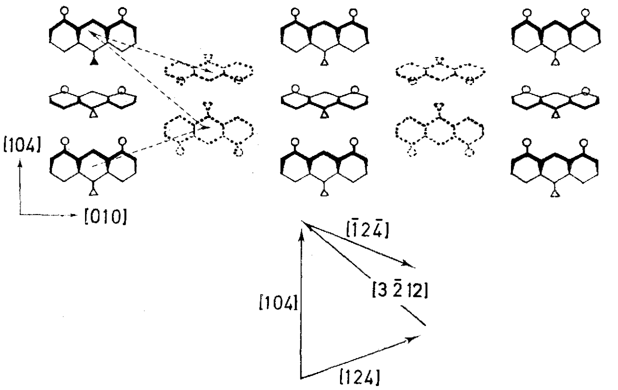

FIGURE 8 Diagrammatic representation of the nature of stacking faults that may be produced on the (401) plane following the dislocation reaction: $[104] \longrightarrow \frac{1}{4}[124] + \frac{1}{4}[3\,\bar{2}\,12]$. It can be seen that, between the partial dislocations, molecules situated either side of the (401) plane will be *trans*-related

We have no definite proof of the existence of such faults.

Electron microscopy has, however, shown up a fault the trace of which on the (010) plane runs in essentially the [103] direction [Plate 3(b)]. By selected-area diffraction and beam tilting we have established that these faults are indeed planar but not of the stacking-fault variety. (They involve a shear deformation and lead to new structures—indeed to a new phase—akin to, but distinctly different from, those characteristic of twin boundaries.[24,25]) Though the precise microstructure at the interface of the parent phase and these faults is not yet fully clear, it is evidently not going to

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lead to favourable incipient *trans*-orientations amongst neighbouring molecules. We have demonstrated that no enhanced dimerization occurs at these faults, a conclusion which is expected from our interpretation [25] of their general nature.

The new phase, which is always introduced when a melt of 1,8-Cl_2-10MA is rapidly cooled, but which does not extend through the entire parent monomer, is clearly responsible for the rather anomalous differential thermal analysis data. Since most samples of the monomer are, to a variable degree, biphasic, and since we have not yet been able to isolate the pure second phase (also orthorhombic), it is impossible to quantify the results relating to the enthalpy and entropy of transition.

The permittivity measurements clearly cannot detect the phase change, presumably because only a negligible fraction of the molecules execute dipolar reorientational changes during the transition. They also rule out the possibility that the topochemically forbidden *trans*-dimer is formed in the monomer matrix as a result of ready rotation of the individual molecules at their regular lattice sites about an axis parallel to the crystallographic *c*-direction.

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