

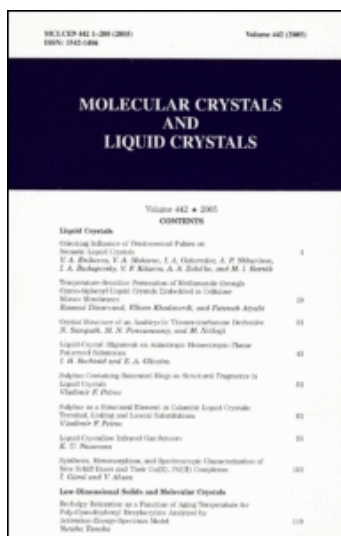
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Solid Crystalline Polymorphism in M-24

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Infrared absorption, differential scanning calorimetric, microscopic and X-ray diffraction studies of 4-cyano-4'-octyloxy biphenyl (M-24) has brought out clearly the solid crystalline polymorphism in this compound. There are at least three solid crystalline forms SCI, SCII & SCIII with the following transitions SCI $\xrightarrow{46^{\circ}\text{C}}$ SCII $\xrightarrow{51^{\circ}\text{C}}$ SCIII \longrightarrow smectic $\xrightarrow{67^{\circ}\text{C}}$ nematic $\xrightarrow{80^{\circ}\text{C}}$ isotropic liquid. The appearance and the preponderance of these solid crystalline forms depend critically on the manner in which liquid crystalline melt solidifies. Each of the phases has its characteristic I.R. absorption in the C—N stretching band. Solid crystalline phase SCII shows a doublet in the C—N stretching region and this seems to arise out of Devydov or correlation splitting.

INTRODUCTION

Recently, there have been several reports on the solid crystalline (SC) polymorphism¹⁻⁶ in various liquid crystalline materials exhibiting different mesogenic phases, such as smectic, nematic and cholesteric. Solid crystalline polymorphism has been interpreted differently by different workers. Some have attributed it to the coexistence of a metastable phase and a stable phase. Some others have speculated that different polymorphs represent the frozen short range order exhibited by the material in the liquid crystalline phase. Indeed, Ogorodnik⁷ contended that SC polymorphism is a necessary condition for the material to exhibit liquid crystalline properties. Although SC polymorphism in many cases appeared to be strongly related to the structure and short range order in the mesogenic phases, it does not totally exclude the conformational changes of the molecules. If SC polymorphism were to reflect the arrangement of molecules in the mesogenic phases, the

structure of the solid phase cooled from the melt (liquid crystalline melt or the isotropic liquid melt) would depend upon the rate of cooling, thermal history etc. Secondly, the study of SC polymorphism would give an insight into the nature of short range order in the liquid crystalline phases.

Most of the studies on SC polymorphism in liquid crystals have been carried out using Raman spectroscopy. Indeed any vibrational spectroscopy could be used to study this phenomena. In the present paper we report SC polymorphism as revealed by the infrared spectral, differential scanning calorimetric, X-ray diffraction and optical microscopic studies in 4 cyano-4'octyloxy biphenyl (M-24). Our studies have clearly shown that the substance crystallizes in SCI, SCII and SCIII crystalline phases: the structures observed depending strongly on the heat treatment. These three structures have characteristic C—N stretching vibration frequencies; SCI corresponding to 2235 cm^{-1} , SCII giving a doublet centered at 2228 and 2236 cm^{-1} and SCIII giving a peak at 2239 cm^{-1} with a long tail on the low wave number side. The observation of C—N stretching doublet seems to arise out of correlation or Davydov splitting and is similar to the observation of Gray and Mosley¹ of doublet in the Raman spectra of solid sample of 5CB (Cyanobiphenyl) in the C—N stretching region.

EXPERIMENTAL

The liquid crystalline sample M-24 was purchased from M/s BDH England, and was used as such without any further purification. The transition temperatures were determined using a hot stage polarizing microscope and differential scanning calorimeter. The material exhibits a smectic phase between 54.5°C and 67°C and a nematic phase between 67.0°C and 80°C .

Infrared spectra of this material, subjected to a variety of heat treatment, were recorded on Perkin Elmer model 399 spectrophotometer covering the region from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 0.5 cm^{-1} at 1000 cm^{-1} and abscissa accuracy of $\pm 1\text{ cm}^{-1}$. The spectra of solid samples were recorded either in KBr pellets or in between KBr windows using mylar spacers of thickness varying between 10–20 microns. A variable temperature cell was used for heating the sample and the temperature of the sample could be controlled to within $\pm 0.1^{\circ}\text{C}$. An identical hot cell was kept in the reference beam for compensation.

Each of the spectra were recorded five times and the spectra reported here are representative and typical.

Differential scanning calorimetric studies were carried out using Perkin Elmer Differential Scanning Calorimeter model DSC IB. About 5 mg of the sample was crimped in an aluminum sample pan with a cover. The sample chamber was continuously flushed with nitrogen. Different heating and cooling rates ranging from 1°C/min to 32°C/min were employed to investigate the effect of heat treatment. It was noticed that the heat treatment affected considerably the intermolecular interaction as reflected by the C—N stretching mode frequency, the DSC trace and the microstructure of the sample in the solid crystalline phase with negligible effects in the mesogenic and isotropic liquid phases.

After having obtained evidence of the SC polymorphism, X-ray diffraction studies were carried out to establish the three SC phases. X-ray powder diffraction photographs were taken using Cu K α radiation. Corresponding textural studies were carried out using Leitz polarizing microscope and a hot stage.

RESULTS AND DISCUSSIONS

The infrared spectrum of a virgin sample of M-24 at room temperature (Solid phase) is shown in Figure 1. One can discern easily the C—N stretching band in the vicinity of 2230 cm⁻¹, C—H stretching band in the vicinity of 2900 cm⁻¹, C—C stretching band in the neighborhood of 1600 cm⁻¹ and other bands. The C—N stretching band shows a doublet centered at 2228 cm⁻¹ and 2236 cm⁻¹. We have chosen the C—N stretching band to study the solid crystalline polymorphism in M-24 because this is a pure isolated vibrational mode without any other bands (fundamental) in this region. The observation of C—N stretching doublet is similar to the observation of a similar C—N stretching doublet in the Raman spectra of solid crystalline form of 5 CB (cyano biphenyl) reported by Gray and Mosley.¹ We will discuss the origin of this doublet a little later.

To identify the various phase transitions, the differential scanning calorimetry of the sample was carried out. Figure 2 shows the DSC trace of a virgin sample. The trace shows three prominent endothermic peaks showing transitions at 51°C, 54.5°C and 80°C in addition to a slight increase in the base line (hump) at 67°C. Observing the sample

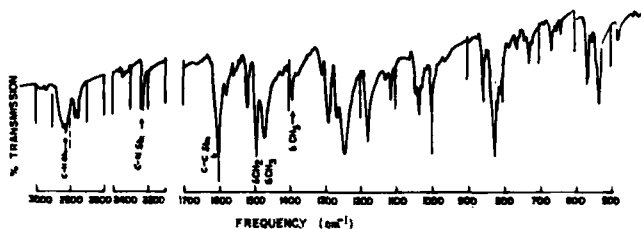


FIGURE 1 Infrared spectrum of the virgin sample (M-24) at room temperature, in KBr pellet in the region 4000 to 400 cm^{-1} .

under a polarizing microscope, it is easy to establish that the 54.5° corresponds to solid crystalline-smecticA phase transition. Similarly it is equally easy to allocate the 67°C and 80°C phase transitions to smectic A-nematic and nematic-isotropic liquid phase transitions. These transition temperatures agree closely with those reported earlier.⁸

It is, however, not easy to identify the 51°C phase transition. In order to elucidate this endothermic transition at 51°C , we carried detailed infrared studies on the sample.

Figure 3 shows the infrared spectra of the virgin sample in the C—N stretching region as it is slowly heated. It is seen that at room temperature (Figure 3, $T = 30^\circ\text{C}$), one observes a doublet centered at 2228 cm^{-1} , and 2236 cm^{-1} . The nature of the spectrum remains unchanged until 45°C . However, on further increase in temperature, one observes (Figure 3b) that the 2228 cm^{-1} peak decreases in intensity with a slight asymmetry developing on the high wave number side of the 2236 cm^{-1} peak. This process proceeds progressively and at 49°C , one clearly observes (Figure 3c) a doublet in the region of 2236 cm^{-1} with a shoulder

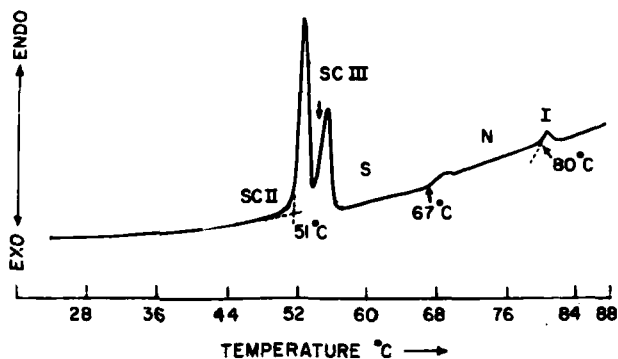


FIGURE 2 DSC trace of the virgin sample ($8^\circ\text{C}/\text{min.}$)

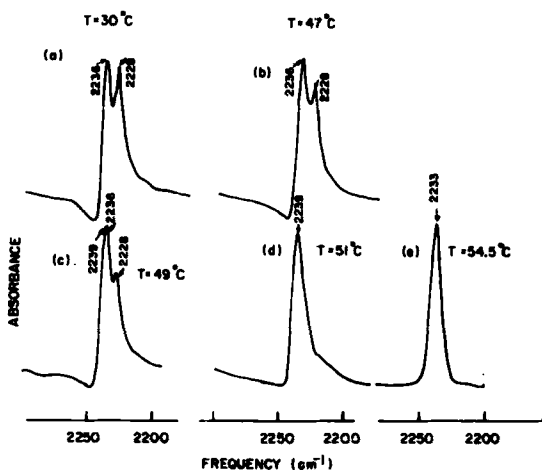


FIGURE 3 Infrared spectra of virgin sample in KBr pellet in the region 2200–2300 cm^{-1} at different temperatures; (a) 30°C, (b) 47°C, (c) 49°C, (d) 51°C, (e) 54.5°C.

at 2228 cm^{-1} . On detailed analysis, it is seen that this spectrum is made up of a peak at 2239 cm^{-1} and an original doublet at 2236 and 2228 cm^{-1} (with reduced intensity). In fact, asymmetry on the higher wave number side of the 2236 cm^{-1} peak in Figure 3b is essentially due to the appearance of a new peak at 2239 cm^{-1} . On further increase in temperature, one finds (Figure 3d) only one peak at 2239 cm^{-1} with a long tail on the lower wave number side at 51°C. The spectrum remains practically unchanged until 54.5°C. At and above 54.5°C, one observes a symmetrical singlet, peaked at 2233 cm^{-1} . It may be pointed out that the peak, at 2233 cm^{-1} just above 54.5°C, near the transition SCIII to smectic A phase is slightly broader than the peaks observed in the solid crystalline phases. However, in the smectic A phase or in the nematic phase, this peak no more remains broad. On the other hand it is a sharp peak throughout. It is only in the vicinity of the transition temp. (SCIII to Smectic A) that the broadening is observed. The spectrum does not change in terms of the location of the C—N stretching mode even though the substance phases through the nematic and isotropic liquid phases. It is thus seen that there are three distinct structures (1) a doublet centered at 2228 and 2236 cm^{-1} observed below 51°C (2) a singlet at 2239 cm^{-1} with a long tail on the low wavenumber side, between 51 and 54°C and (3) a symmetrical broad singlet at 2233 cm^{-1} above 54.5°C. We can thus ascribe the 51°C endothermic transition to a transformation from a solid crystalline structure (which we call SCII phase) giving a doublet to another solid crystalline structure (which we

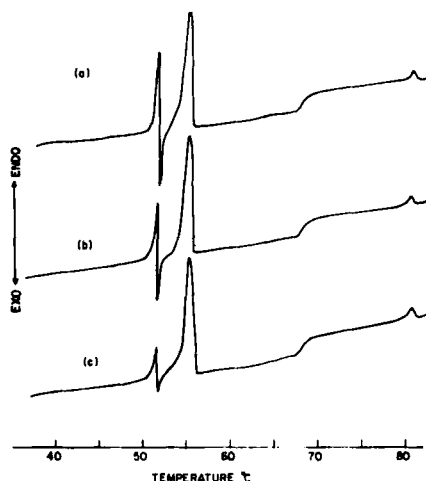


FIGURE 4 DSC traces of the virgin sample during heating: (a) heating rate $1^{\circ}\text{C}/\text{min}$, (b) annealed at 45°C for one hour and heated at $1^{\circ}\text{C}/\text{min}$, (c) annealed at 45°C for three hours and heated at $1^{\circ}\text{C}/\text{min}$.

call SCIII phase) giving a singlet at 2239 cm^{-1} with a long tail. Further, it appears that the 51°C phase transition is a sluggish phase transition. In order to understand this phase transition in little more detail, we carried out detailed DSC studies after giving the sample a variety of heat treatment. Figure 4a shows the DSC trace of a sample (virgin) when we heated at $1^{\circ}\text{C}/\text{min}$. We again see the two endothermic transitions at 51°C and 54.5°C . However, in this trace one can clearly see the peak due to recrystallization at 51°C . This trace brings out vividly that at 51°C , the SCII phase melts and then recrystallizes into SCIII phase. Figures 4b and c show the DSC traces of the same sample after annealing it at 45°C for 1 to 3 hours respectively. These traces are qualitatively similar to the trace in Figure 4a. They also exhibit two endothermic transitions at 51 and 54.5°C but on looking carefully one can make out that though the intensity of the 54.5°C peak remains the same, the intensity of the 51°C peak and the crystallization dip decreases as the annealing time increases. These observations lead us to believe that normally just below 51°C , there is a coexistence of SCII and SCIII phases; their proportions being dependant on the annealing time. The SCII phase transforms completely through a melting process into the SCIII phase at 51°C .

In another series of experiments, we studied the effect on the SC structure and the corresponding phase transitions, of cooling the material from the smectic melt and the isotropic liquid melt at different

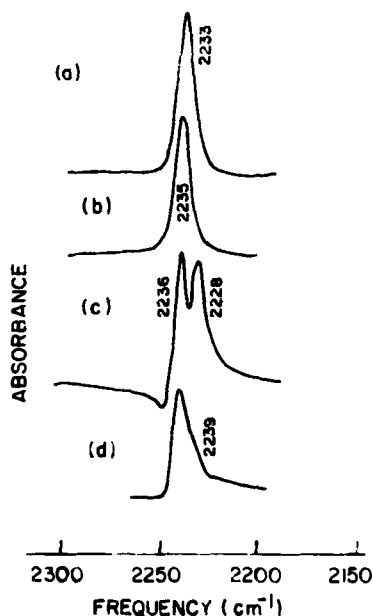


FIGURE 5 Infrared spectra of solid M-24 in the region 2200–2300 cm^{-1} , prepared under different cooling conditions; (a) in the smectic phase at 57°C, (b) on very slow cooling (0.5°C/min)-at 25°C, (c) on cooling at the rate 1°C/min-at 25°C, (d) on rapid cooling at 25°C.

rates. Figure 5a shows the infrared spectrum in the C—N stretching region (a singlet at 2233 cm^{-1}) of the sample in the smectic A phase at 57°C. When this smectic melt was cooled very slowly (0.5°C/min), it got crystallized at 30°C and gave the spectrum shown in Figure 5b. This is a symmetrical singlet centered at 2235 cm^{-1} . However, when the smectic melt was cooled at a faster rate (1°C/min.) the crystallization commenced at a lower temperature and the sample thus solidified when examined in the infrared spectro-photometer (Figure 5c), gave a doublet centered at 2228 cm^{-1} and 2236 cm^{-1} , a phase which we have identified earlier as SCII. In contrast, if the isotropic liquid melt is rapidly cooled, the spectrum of the solid thus obtained is quite different as is shown in Figure 5d. This is a singlet, peaked at 2239 cm^{-1} with a long tail on the lower wave-number side. This we have seen earlier is due to solid crystalline phase SCIII. Although we could easily identify the spectra in Figure 5c and 5d and to be due to SCII and SCIII phases respectively, one could not identify the spectrum in Figure 5b peaked at 2235 cm^{-1} . In order to understand this solid phase, we subjected it, to a detailed infrared study in the increasing temperature cycle.

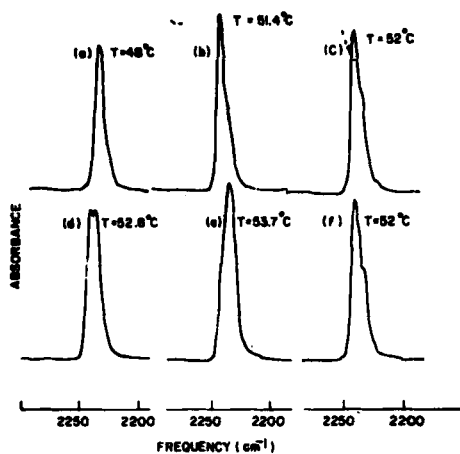


FIGURE 6 Infrared spectra of solid M-24 (obtained by slow cooling from the smectic melt) in the region 2200–2300 cm^{-1} , in the temperature range 48°C–52°C; (a) 48°C, (b) 51.4°C, (c) 52°C, (d) 52.8°C, (e) 53°C, (f) 52°C.

Figure 6a shows the spectrum of such a solid obtained from the smectic melt when cooled slowly. It is a symmetrical singlet, peaked at 2235 cm^{-1} . On increasing the temperature, one finds there is no change in the infrared spectra of this sample until 45°C. However, above 45°C, it seems to get transformed into a mixture of SCII and SCIII phases. This transformation is temperature reversible provided one does not exceed 54°C (Figure 6b, c, d, e, f). In order to understand this further, we studied the DSC traces of solid crystalline sample obtained after cooling the smectic and isotropic melts at different rates.

Figure 7a is the DSC trace of a slowly cooled sample from the isotropic melt (1°C/min). This trace is similar to that of a virgin sample (Figure 2) showing a 51°C phase transition from SCII to SCIII and 54.5°C phase transition from SCIII to smecticA phase. Figure 7b is the DSC trace of rapidly cooled isotropic melt (32°C/min). Surprisingly, it shows small endothermic peak showing transition at 46°C followed by crystallization dip and prominent endothermic transition at 54.5°C. The phase below 45°C which gives an infrared spectrum in the C—N stretching region at 2235 cm^{-1} transforms after melting at 45°C to the SCIII phase.

Figure 7c is the DSC trace of a solid obtained by cooling a smectic melt at rate less than 0.5°C/min (compare infrared spectra in Figure 5b giving a single peak at 2235 cm^{-1}) which transforms at and above 45°C into a mixture of SCII and SCIII. This trace is very revealing. It shows

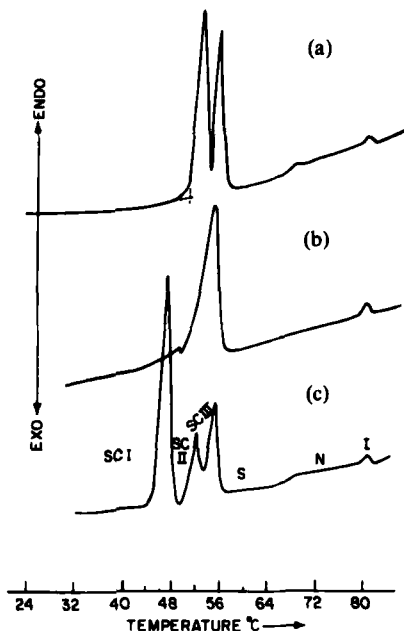
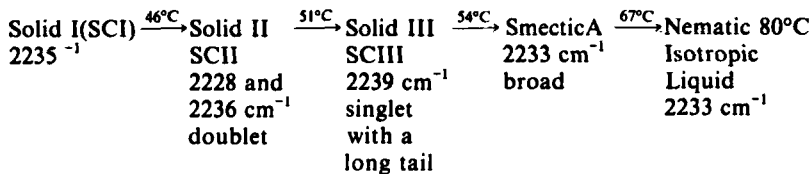


FIGURE 7 DSC traces during heating ($8^{\circ}\text{C}/\text{min}$) for solid M-24 prepared under different cooling conditions; (a) cooled slowly from the isotropic melt ($1^{\circ}\text{C}/\text{min}$), (b) cooled rapidly from the isotropic melt ($32^{\circ}\text{C}/\text{min}$), (c) cooled from the smectic melt ($0.5^{\circ}\text{C}/\text{min}$).

three distinct endothermic transitions at 46°C , 51°C , and 54.5°C besides the other peaks at 67°C , 80°C . The phase sequence of this material is thus seen to be as follows.



The crystal structure of the three solid crystalline phases is reflected in the X-ray powder photographs (Figures 8a, b, c). The three structures are different and reveal a well defined three dimensional order for all three modifications. Efforts are in progress to determine the precise structure of the three solid phases.

Some of the phase changes as revealed by the infrared spectra and the differential scanning calorimetry are reflected clearly in the micrographs. Figure 9a, b, c and d show series of micrographs of virgin sample at 30°C , 52°C , 55°C , 70°C respectively. Micrograph at 48°C shows

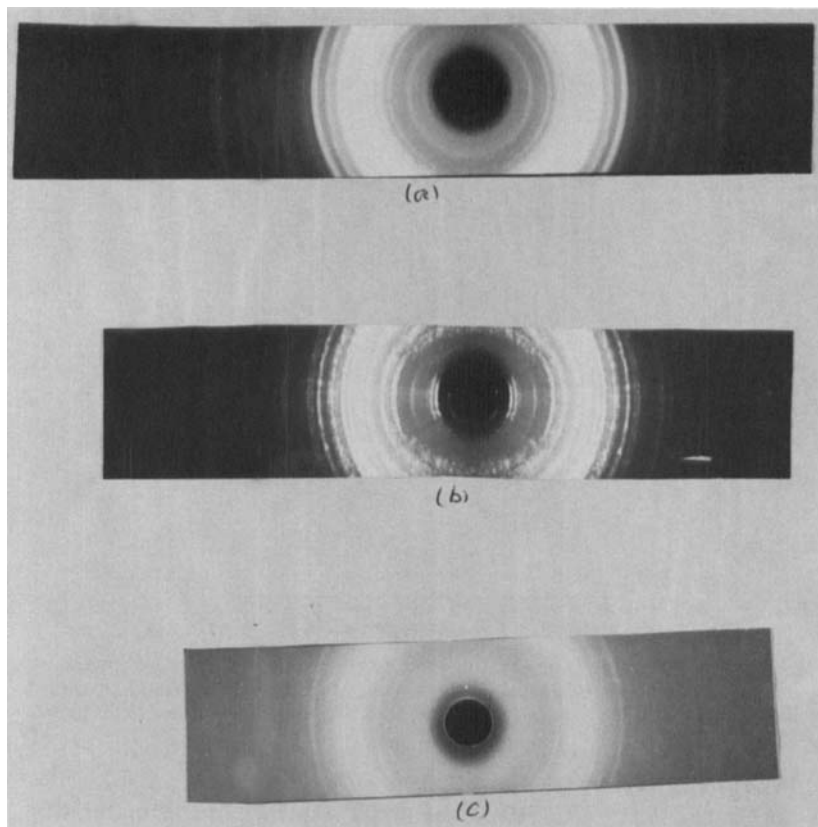


FIGURE 8 X-ray powder photographs of the three solid crystalline phases of M-24; (a) virgin sample, (b) slowly cooled ($0.5^{\circ}\text{C}/\text{min}$) sample, (c) rapidly cooled sample.

clearly the coexistence of the two phases, one of which disappears in the micrograph at 52°C . The micrograph at 55°C is typically characteristic of a smectic A phase. It may be recalled that when the smectic melt is cooled very slowly at a rate less than $0.5^{\circ}\text{C}/\text{min}$, one gets the solid crystalline SCI phase. The microstructure of this SCI phase is shown in Figure 10a and reveals the spherulitic structure with Maltese crosses which rotate with the rotation of the polarizer and analyzer. In contrast if the specimen is cooled rapidly one gets a phase whose microstructure is shown in Figure 10b. This microstructure is distinctly different from the microstructure shown in Figure 10a.

We may now briefly comment on the perfection of these three solid crystalline phases. The infrared spectrum of the SCI phase shows a symmetrical singlet at 2235 cm^{-1} . This phase is obtained on very slow

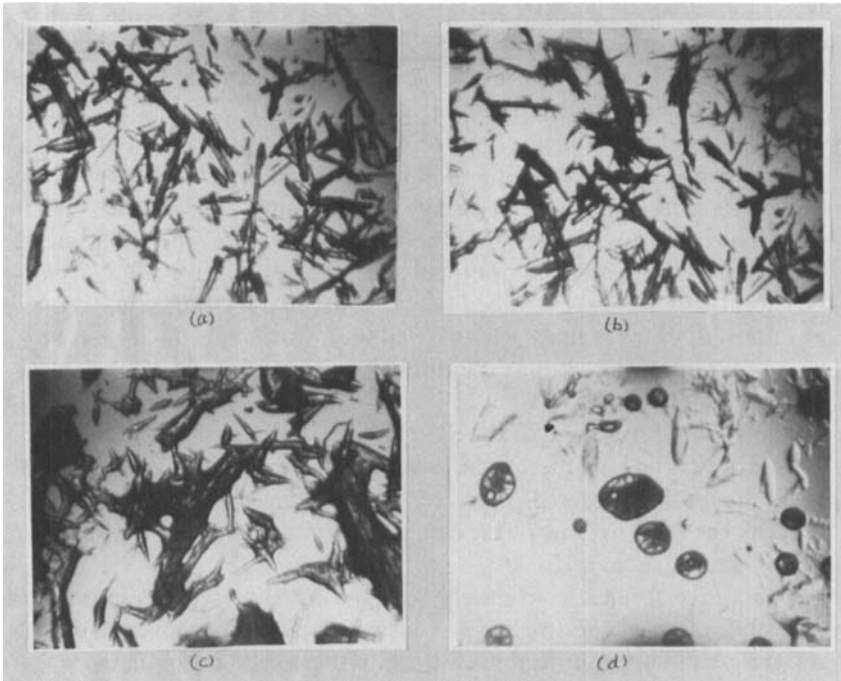


FIGURE 9 Micrographs of M-24 at different temperatures; (a) 30°C, (b) 52°C, (c) 55°C, (d) 70°C.

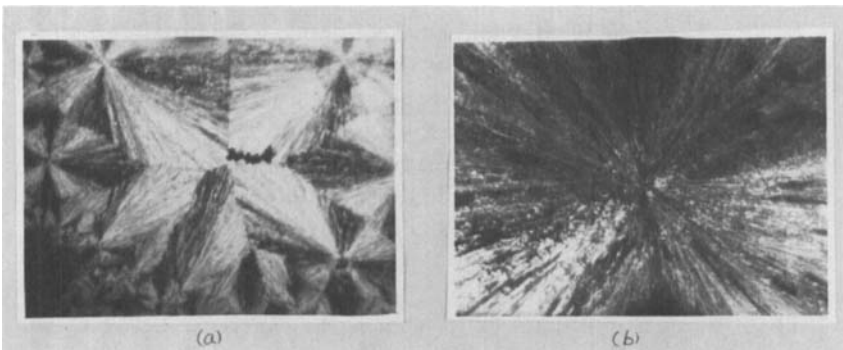


FIGURE 10 Micrographs of M-24 at room temperature under different cooling conditions; (a) very slowly cooled (0.5°C./min), (b) rapidly cooled (32°C/min).

cooling of the smectic melt. This appears to be the most perfect phase. If however, the smectic melt is cooled a little rapidly one obtains SCII phase giving a doublet centered at 2228 cm^{-1} and 2236 cm^{-1} . Such a doublet structure can be obtained when the unit cell contains two molecules and has a screw axis—along the axis joining the center of the molecules. This splitting is called the correlation or the Devydov splitting. The other possibility is that these two peaks at 2228 and 2236 cm^{-1} are uncorrelated and arise out of two different structures. The second possibility does not seem to be likely because in the virgin sample, one obtains a doublet spectrum with equal intensities reproducibly. It appears more than likely that the doublet arises because of correlation splitting.

The infrared spectrum of the SCIII phase shows a singlet, peaked at 2239 cm^{-1} with a long tail on the lower wavenumber side. This appears to be the most disordered structure. This inference is further strengthened by the fact that this phase can be precipitated by very rapid cooling of the isotropic melt.

The above studies have clearly brought out that depending on the rate of cooling of the smectic and isotropic melt, one can precipitate different solid crystalline phases. Each of these solid crystalline phases have a well defined three dimensional order. Ogorodnik⁴ has observed for some liquid crystal materials, exhibiting solid crystalline polymorphism, broadening of the CN stretching band just above the transition temperature (solid \rightarrow mesogenic). This broadened band was shown to be a composite band of the bands, corresponding to the various solid crystalline phases. A similar observation of the broadened band near the transition temperature, would lead one to conclude that different solid crystalline phases are related to the short range order of the mesophase.

In such a case the band would have continued to be broad throughout the temperature range where the material is in the mesogenic phase. However, the band no more remains broad and shows typical "motional narrowing" associated with liquids and solutions. The broadness of the band can be thus explained as possibly due to the mixture of the solid crystalline and liquid crystalline phases. It is, therefore, apparent that the solid crystalline polymorphism is not due to frozen in short range order in the smectic-nematic phases of the mesogens.

Then the question arises as to what is the difference between the three solid crystalline polymorphs and how they are related to the structure of the mesophases.⁹ Comparative study of the other homologues of the same series and many other mesogenic compounds in their

solid crystalline and liquid crystalline states have led us to conclude⁹ that there is no basic difference between the phenomena of solid crystalline and liquid crystalline polymorphism. They appear to be a sequence of changes from the solid crystalline phase to an isotropic liquid phase, gradually liberating one degree of freedom after another. Solid crystalline polymorphism is essentially due to different molecular arrangements in the lattice network and the conformational changes in the central core of the molecule with or without conformational changes in the terminal tails.

The difference in the structure of the three solid crystalline polymorphs of M-24 is reflected in the Infrared and Raman spectra. Apart from the CN stretching band, as discussed above, several other bands indicating the conformational changes of the aromatic frame and of the alkyl chain show considerable variations in their intensity and frequency. These variations positively indicate the conformational changes in going over from one solid crystalline phase to another. The parent aromatic frame of Biphenyl itself shows such changes where the dihedral angle changes in going over from the crystalline solid to the vapor state via the liquid state.^{10,11} Some of the important bands sensitive to the dihedral angle changes, showing variations are (1) CH in plane bending vibrations at about 1285 cm^{-1} and (2) a band near 415 cm^{-1} which is a complex band arising out of the central C—C stretching and ring angle deformation. A detailed study of the observed changes in the infrared and Raman Spectra will be published separately.

Thus the solid crystalline polymorphism in M-24 is due to conformational changes, each polymorph having a well defined three dimensional order. The metastable states, in view of the X-ray studies, seem to exist which are formed with different probability for kinetic reasons.

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