



Molecular Crystals and Liquid Crystals

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Version of record first published: 20 Apr 2011.

To cite this article: S. C. Jain, S. A. Agnihotry, S. Chandra & V. G. Bhide (1984): Solid Crystalline Polymorphism in M-21, *Molecular Crystals and Liquid Crystals*, 104:1-2, 161-171

To link to this article: <http://dx.doi.org/10.1080/00268948408070407>

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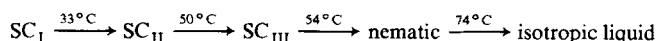
Solid Crystalline Polymorphism in M-21†

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(Received December 8, 1982; in final form May 28, 1983)

This paper reports on the different solid crystalline (SC) forms of 4-cyano-4'-heptyloxy biphenyl (M-21) as revealed through differential scanning calorimetric, polarizing microscopic and infrared spectroscopic investigations. There are three solid crystalline modifications, namely SC_I, SC_{II}, SC_{III} with the thermal phase diagram.



The appearance and preponderance of the SC forms depend critically on the manner in which the liquid crystalline melt solidifies. Each SC phase has its CN stretching band split into two components because of Davydov or correlation splitting. The position, separation and relative intensities of the two components characterize each SC phase. The systematic study of the variations in these three features with temperature leads to interesting information about the intermolecular ordering forces and the spatial arrangement of the molecules in the unit cell. It is shown that the intermolecular interactions of the dipolar nature play a dominant role in the SC phases but contribute negligibly in stabilizing the nematic phase. The angle between the correlated molecules in the unit cell changes in the order SC_I > SC_{II} > SC_{III} > nematic = 0, resulting in parallel arrangement of molecules in the nematic phase.

Liquid crystalline polymorphism i.e. the ability of a compound to exist in more than one form in liquid crystalline state is well known. It was Bernal and Crowfoot¹ who in 1939 proved the presence of Solid Crystalline (SC) polymorphism in a number of mesogenic materials. Over the last few years a large number of compounds exhibiting

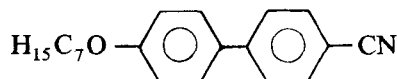
†Presented at the Ninth International Liquid Crystal Conf., Bangalore, 1982.

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different mesogenic phases such as nematic, smectic and cholesteric have been reported to exist in more than one solid crystalline form.²⁻¹⁷ SC polymorphism has been interpreted in many ways by different workers. On the basis of thermal and spectroscopic studies, Ogorodnik¹¹ suggested that SC polymorphism should be a necessary condition for a material to exhibit liquid crystalline properties.

In our previous publications,^{15,18} existence of SC polymorphism was established in 4-*n*-cyano-4'-*n*'-octyloxybiphenyl (M-24) through DSC, IR and optical studies. It was shown that SC polymorphism was due to conformational changes, each polymorph having a well defined three dimensional order. The present paper reports on the different SC forms of (M-21). All the three SC phases show a doublet in the CN stretching region with characteristic separation, intensity ratio and positions for the two components. These components arising because of "Davydov or correlation splitting" reveal information about the spatial arrangement of the molecules in the unit cell and also about the intermolecular ordering forces in various SC, mesogenic and isotropic liquid phases.

The liquid crystalline sample M-21, schematically represented by



was purchased from M/s BDH, England and was used as such without further purification. The material exhibits nematic phase between 54°–74°C. The experimental details have been described earlier.¹⁵

RESULTS AND DISCUSSION

DSC studies

Figure 1(a) is a typical DSC trace of virgin sample M-21 during heating (heating rate 4°C/min). The trace shows two endothermic peaks at 54°C and 74°C corresponding to solid–nematic and nematic–isotropic phase transitions. These transition temperatures agree very well with those reported earlier.¹⁹ However, detailed DSC investigations of the sample subjected to a variety of thermal treatments revealed interesting results.

Figure 1(b) shows the DSC trace during heating of the solid sample obtained by rapid cooling of the isotropic melt (cooling rate

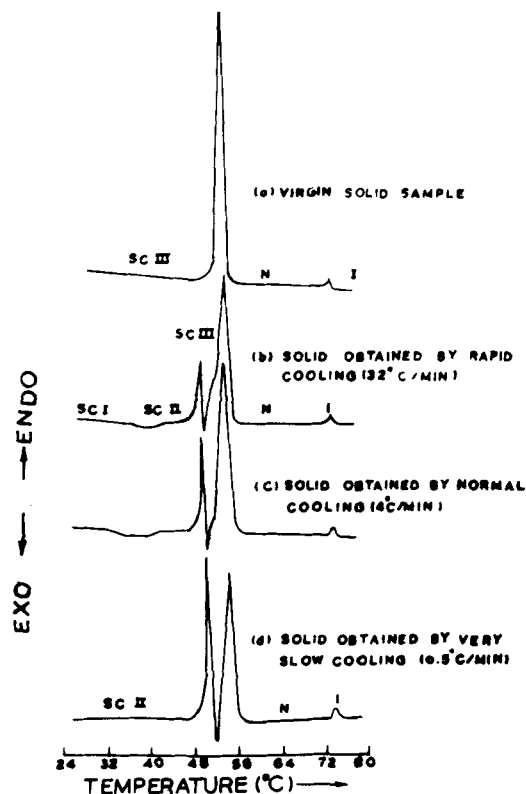


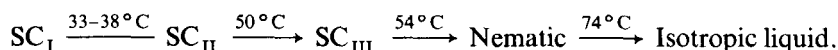
FIGURE 1 DSC traces of solid M-21 prepared under different cooling conditions.

32°C/min). Along with the two endothermic peaks at 54°C and 74°C, a new endothermic peak at 50°C and a broad exothermic dip between 33–38°C, are also observed.

Figure 1(c) shows the DSC trace during heating of the solid sample obtained by slow cooling (cooling rate 4°C/min) of the isotropic melt. It is qualitatively very similar to the DSC trace of the rapidly cooled sample in Figure 1(b). However, the intensity of the 50°C peak is much larger and it is accompanied by a small exothermic dip.

Figure 1(d) shows the DSC trace during heating of the solid sample, obtained by very slow cooling (cooling rate 0.5°C/min). This trace is very similar to the above two traces, except for the fact that the broad exothermic dip extending from 33°C to 37°C is completely missing. Secondly the height of the 50°C peak is even greater than that of 54°C.

Above observations clearly show that M-21 exists in three different solid crystalline forms. In the order of increasing temperature these can be called SC_I, SC_{II}, SC_{III}. Thus SC_{III} corresponds to the virgin M-21 sample which transforms into nematic phase at 54°C and further into isotropic liquid phase at 74°C. SC_I is another solid phase, obtained by fast cooling of the isotropic melt and transforms on heating to SC_{II} at 33°C. This is an exothermic transition. SC_{II} on further heating melts and crystallizes into SC_{III} at 50°C. The three distinct solid phases as revealed by DSC studies and their transformations are as follows:



These solid forms have been further investigated and established through infrared and polarizing microscopic studies.

Infrared studies

Infrared studies, particularly in the CN stretching region (2200–2300 cm⁻¹) bring out clearly the characteristics and differences of the various solid forms of M-21. The CN stretching band is selected, as it is isolated from all other fundamentals and not overlapped by other overtone or combination modes. Each solid phase, nematic and isotropic liquid phase gives CN stretching band characteristic in shape, position and intensity. Information about the three solid phases and the intermolecular ordering forces in the vicinity of the CN group, is contained in the features such as shape, intensity, position and width of this band. Of particular importance is their variation with temperature. The CN stretching band for all the three solid phases is observed to split into two components, their separation, relative intensities and positions being different in different phases. By contrast, the nematic and the isotropic liquid phases have their CN stretching band as a singlet, identical both in frequency and shape. Table I shows these details and Figure 2 shows the CN stretching band of various phases of M-21.

The appearance of a doublet in the spectra of various solid phases of M-21 is explained to arise because of interaction of translationally inequivalent molecules, known as Davydov, correlation or factor group splitting. For the two components having necessarily orthogonal transition moments, Davydov's theory predicts splitting of a band into two

TABLE I

Position and the nature of the CN stretching band for different phases of M-21

Phase	Position of the band maxima in cm^{-1}		Mean freq. cm^{-1}	Nature of the CN stretching band		
				Shape	Separation of the components (cm^{-1})	Intensity ratio
SC _I	2243	2232	2237.5	doublet	11	1
SC _{II}	2239.5	2231	2235.25	doublet	8.5	0.7
SC _{III}	2237.5	2230.5	2233.5	singlet with a shoulder	7.5	0.4
Nematic	2233		—	single sharp band	—	—
Isotropic liquid	2233		—	single sharp band	—	—

components, shifted symmetrically up and down from the original position; the shape, structure being preserved in this splitting. The number of fundamental components observed in the crystal spectra depends on the number of molecules per unit cell, the site and the unit cell geometry. A pair of molecules in a unit cell gives rise to two components, if their motions are coupled to each other but not to lattice. The doublets observed for all the three solid phases have the following characteristics.

The position of the components of the doublet and also their mean value shift to lower wavenumber in going from SC_I → SC_{II} → SC_{III} phase. The two components of the doublet in the phase SC_{III} collapse to a central maximum at the phase transition SC_{III} → nematic.

It is evident from Table I that the separation between the two components of the CN stretching band shows a systematic variation. It is the largest for SC_I and decreases in going to SC_{II} to SC_{III}. Further in the nematic and the isotropic liquid phase there is a single band and thus the separation reduces to zero.

The intensity ratio of the two components decreases in going over from SC_I to SC_{II} to SC_{III}.

The study of these features gives very interesting information about the two molecules in the unit cell of the three SC phases. The separation of the two components represents the measure of the coupling between the two molecules. The systematic decrease in the separation in the three SC phases suggests similar variation in their coupling. The intensity ratio of the two components represents a direct

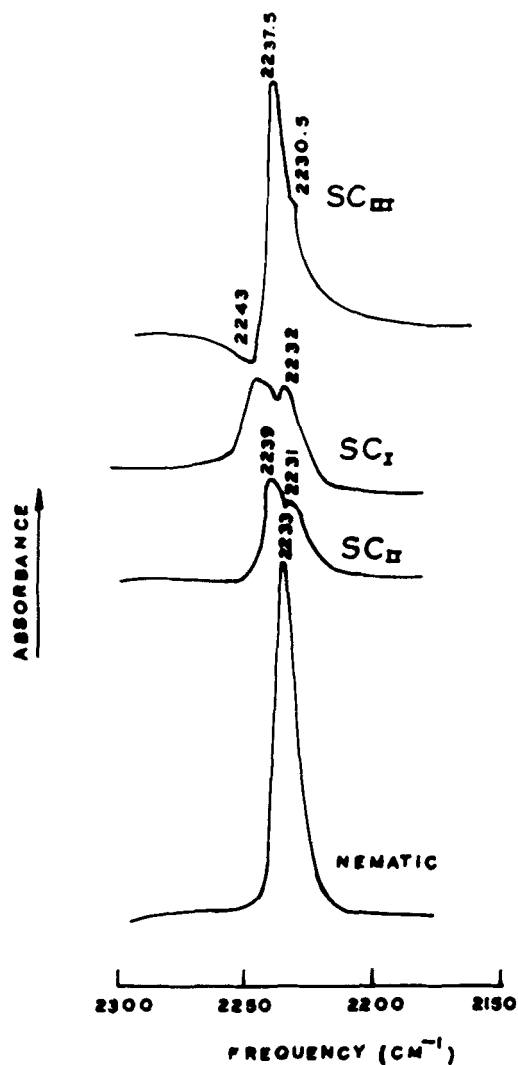
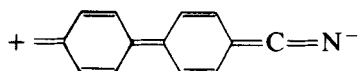


FIGURE 2 CN stretching band of different phases of M-21.

measure of the relative orientation of the two molecules in the unit cell. The above results suggest that the angle between the two molecules in the unit cell decreases, the two molecules becoming parallel to each other in the nematic phase.

The third feature, namely the position of the two components or their mean and their changes reflect on the variations in the degree of

conjugation from one solid phase to the other. The frequency of the nitrile group on conjugation, in aromatic compounds usually shifts to lower values, as is evident from extensive studies by Kitson and Griffith.²⁰ These changes in the degree of conjugation are being studied from other infrared bands and results of the analysis will be published separately. These variations can be thought of to arise from varying contribution of the polar structures such as



The CN stretching frequency thus depends on the nature and the amount of the double bond character of the CN bond. In other words the three SC polymorphs differ in the degree of conjugation. The detailed spectroscopic observations to confirm this, are underway.

These changes in the nitrile frequency attributed to changes in the molecular conformation give information of the type of the intermolecular forces playing important role in the SC phases. Of course in the experiments reported here, only one aspect of the intermolecular force is probed and that is in the vicinity of the CN group. The positions of the frequency maxima differ in the three SC polymorphs. By contrast, the CN stretching band of the nematic and the isotropic liquid phases are identical in frequency. Thus the phenomenon which causes the shift in the CN stretching frequency in the SC polymorphs is no more active in the liquid crystalline states. In other words after the transformation $\text{SC}_{\text{III}} \rightarrow \text{nematic}$, there seems to be no more increase in the degree of conjugation. Thus the contribution of the polar structures or intermolecular interactions of the dipolar nature, plays an important role in the SC polymorphs. However, their contribution is insignificant in the liquid crystalline and liquid state or they contribute negligibly in stabilizing the nematic phase. It is quite likely that at higher temperatures (after $\text{SC}_{\text{III}} \rightarrow \text{nematic}$) the increased thermal movements of the molecules hinder the mutual orientations of the two benzene rings, resulting in no further change in the degree of conjugation.

Polarizing microscopic studies

Figures 3(a, b, c) show a typical set of micrographs of M-21 (a) the virgin sample, SC_{III} (b) solid obtained by rapid cooling of the isotropic melt, SC_{I} and (c) solid obtained by slow cooling of the nematic melt, SC_{II} respectively. It was seen that the virgin M-21 sample melted directly into the nematic phase at 54°C which on subsequent heating



(a)



(b)



(c)

FIGURE 3 A typical set of micrographs of different SC phases of M-21 (a) SC_{III} —the virgin sample; (b) SC_I —solid obtained by rapid cooling of the isotropic melt; (c) SC_{II} —solid obtained by slow cooling of the isotropic melt.

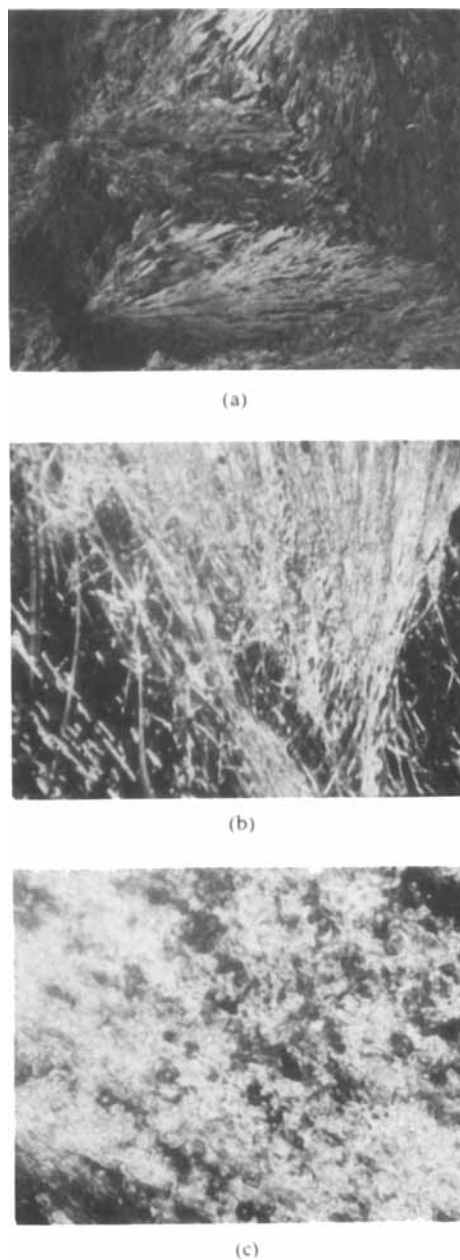
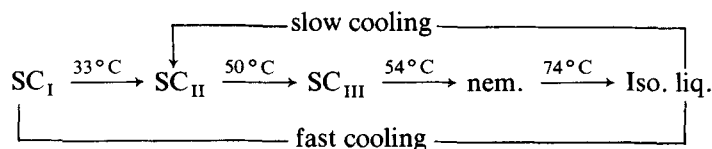


FIGURE 4 A typical set of micrographs of M-21 at different temperatures (a) $SC_I \rightarrow SC_{II}$ (36 °C); (b) $SC_{II} \rightarrow SC_{III}$ (49 °C); (c) $SC_{III} \rightarrow$ nematic (54 °C).

melted into isotropic phase at 74°C. Figures 4(a, b, c) show the micrographs of the sample during heating cycle around $SC_I \rightarrow SC_{II}$, $SC_{II} \rightarrow SC_{III}$ and $SC_{III} \rightarrow$ nematic phase transitions. It is seen from micrographs in Figures 3b & 4a that there are relatively very small structural changes in going over from SC_I to SC_{II} . DSC studies, Figure 1(b, c) also indicate only small transition energy for this transition. However, the structural changes in going over from SC_{II} to SC_{III} seem to be on a larger scale. Detailed X-ray and ultra-violet spectroscopic studies will bring out clearly the difference in these SC states and studies are underway to examine these differences.

CONCLUSION

DSC, infrared and microscopic investigations have clearly shown that there are three solid crystalline forms of M-21 namely SC_I , SC_{II} and SC_{III} . The appearance and preponderance of these SC forms depends critically on the manner in which the liquid crystalline melt solidifies. Each solid phase shows a characteristic infrared absorption spectrum in the CN stretching region. The doublet structure of the CN band arises because of Davydov splitting. The variation in the intensity ratio, separation and position of the components of the doublet yields information about the intermolecular interactions and about the spatial arrangement of molecules in the unit cell for the three SC phases. The intermolecular interactions of the dipolar nature play a dominant role in the SC phases but contribute negligibly in stabilizing the nematic phase. The angle between the correlated molecules in the unit cell changes in the order $SC_I > SC_{II} > SC_{III} > \text{nematic} = 0$, resulting in parallel arrangement of molecules in the nematic phase. The scheme of the various transitions is as follows:



Acknowledgments

The authors gratefully acknowledge Dr. P. C. Jain, Physics Department, Delhi University for his kind permission to obtain DSC data.

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