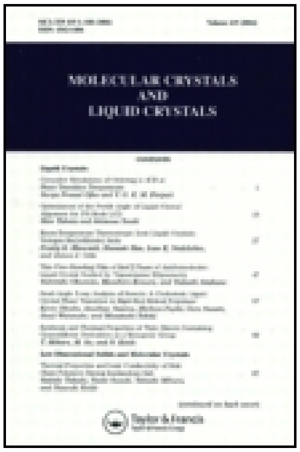

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Depolarized Light Intensity and Optical Microscopy of some Mesophase-forming Materials

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Abstract—Eight mesophase-forming compounds were studied by the technique of depolarized light analysis. The temperatures at which anisotropy changes occurred were compared with results from differential thermal analysis. Although anisotropy change and uptake of heat are usually synchronous, in some cases thermal uptake is almost complete prior to a significant change in the anisotropic behavior of the compound. The observations made explain many of the discrepancies between mesophase transition temperatures observed by differential thermal analysis and optical methods. Photomicrographs of the various mesophase types examined are presented.

The polarizing optical microscope equipped with a heated stage has been used for a number of years for the detection and determination of mesophase or liquid crystal transitions. Until recently, most of the large compilations of transition temperatures have been based on hot stage measurements.[1,2,3] Now, the techniques of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and classical adiabatic calorimetry are being applied to liquid crystal studies. Although these instrumental methods are measuring the same phenomena as the earlier extensive optical observations, some differences and lack of correlation of transition temperatures are to be expected due to different sensitivities to the various steps in the mesophase transition. Earlier work from this laboratory on cholesteryl myristate has indicated that the technique of depolarized light

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intensity (DLI) analysis is an excellent instrumental method for correlating earlier optical data with more recent thermodynamic examinations.[4,5] The present study reports the extension of this work to other nematic, smectic, and cholesteric mesophase-forming materials, and in particular compares the DLI results with our previous DTA data.

Experimental

The DLI apparatus used in this study has been described previously.[5] Briefly, it consists of a polarizing microscope, a hot stage controlled by a slope proportional heater control, a thermocouple system, photocell system, and x–y recorder. The samples were mounted between dust-free, 1-cm round cover slips 0.14 mm thick. The sample was melted into a layer 0.15 mm thick using a cover slip with a hole in the center as spacer. The sample was quickly cooled to room temperature and then heated at 8 °C/min. Photographs were made on tungsten Kodacolor-X 120 roll film with a Zeiss Ultraphot II microscope. The modification of the hot stage has been described elsewhere.[5]

The materials used in this study were obtained commercially as follows: Cholesteryl benzoate, anisoate, crotonate, cinnamate, dicholesteryl sebacate, and adipate were obtained from Eastman Organic Chemicals, Distillation Products, Rochester, New York; and *p*-(4-cyanobenzal-amino)-cinnamic acid active amyl ester and N-(*p*-cyanobenzal)-*p*-anisidine were obtained from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. All materials were recrystallized three times from hot ethanol.

Results

The DLI traces of the eight materials studied are shown in Figs. 1 to 8. The heating and cooling operations were carried out on the same preparations. The drawings presented are actual photographs of experimental curves with sufficient drafting applied to distinguish the heating from cooling cycles.

p-(4-Cyanobenzal-Amino)-Cinnamic Acid Active Amyl Ester

This material exhibits very sharp transitions from the solid to the mesophase and the mesophase to the isotropic liquid. See Fig. 1. Repeated runs indicated that, unlike many liquid crystal materials, the mesophase to solid transition supercools only a few degrees. Previous workers have stated that the mesophase is cholesteric.[3] This is supported by the photograph obtained in this study of the mesophases formed on heating the solid and cooling the melt. See Fig. 9. The texture is unmistakably cholesteric and the same as that formed on heating cholesteryl cinnamate or benzoate as reported by other workers.[6,7] The

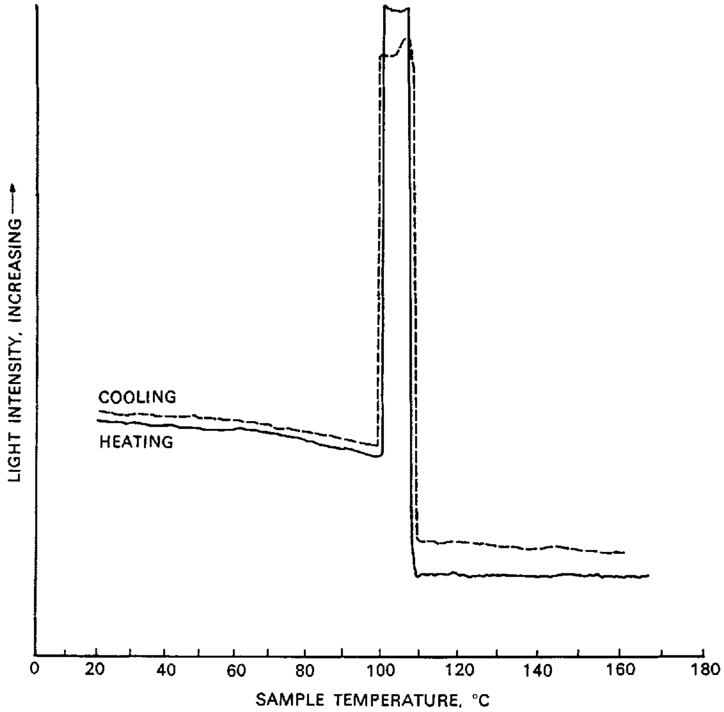


Figure 1. *p*-(4-CyanoBenzalamino)-Cinnamic acid active amyl ester. 8 °C/min heating rate.

nematic mesophase is usually characterized by a relatively featureless bright field in the absence of shear. Earlier work with the DLI apparatus used in this study has indicated good correlation between the DLI temperature scale and the DTA instrument used to obtain the data shown in Table 1.[5] However, the agreement between DLI and DTA transition temperatures is not very good for this compound. Much better agreement exists between DLI and other optical methods. Since DLI and DTA have agreed well in the past for simple first-order transitions,[5] it is plausible to assume that absorption of heat, as measured by DTA, is not exactly synchronous with the change in anisotropy. This is a real effect and not an instrumental artifact. From Table 1 it is evident that the thermal absorption for the solid→ mesophase transition is largely completed prior to a significant change in the anisotropic behavior of the compound. This is evidence of a pretransition thermal event which has been reported for other liquid crystal-forming materials. The mesophase→ isotropic liquid transformation is well synchronized with the absorption of heat by the liquid crystal structure. Persistence of some order at higher temperatures, requiring only a few hundredths of a calorie per gram for dissolution, has been postulated in the past.[8] This order is detectable in Fig. 1. The hump at 106 °C in the cooling curve is also a real optical effect easily verified by direct observation although previously undetected by thermal analysis. This hump is the " flash " which has been described by earlier workers using other mesophase-forming materials.[3]

N-(*p*-Cyanobenzal)-*p*-Anisidine

This material exhibits a complex set of solid→mesophase transitions, the details of which are not detectable by reasonably sensitive DTA. The major absorption of heat from 111 °C to 119 °C lies approximately in the middle of the mesophase change as detected by DLI.[9] See Fig. 2. The transformation range from 103 °C to 126 °C is illustrated in the photographs given in Fig. 10.

Compound	DLI transitions		DTA transitions Melting (10)[a]			Chemical source, °C	ICT (1), °C	Other, °C
	Heating, °C	Cooling, °C	T_b, °C	T_m, °C	T_e, °C			
p-(4-Cyanobenzal-Amino)-Cinnamic Acid Active Amyl Ester	101	100–98	75.2	90.0	93.9	96	95	92 (3)
	106–110	110–108	100.4	105.7	108.4	106	107	105 (3)
N-(*p*-Cyanobenzal) *p*-Anisidine	103–113	108	111.4	117.1	119.4	114	115	
	113–116	127	122.6	124.2	125.5	125	125	
	118							
	126.5–128							
Cholesteryl Benzoate	127–139	120–116	142.7	145.8	149.5	150	146 ± 1	149–150 (14), 145 (6, 13) 152 (6)
	142–144	127						
	181–185	181–179.9	179.2	180.7	182.6	178	178.5 ± 3	178 (14), 179 (6, 13)
Cholesteryl Anisoate	174–182		174.5	179.2	184.0	179		
	216–224							
	237–268	155–152						
	268–272	278–269	263.4	264.9	265.8	268		
Cholesteryl Crotonate	106	64–47	107.5	112.8	116.7	103		
	162–164	157–154	160.7	162.0	163.1	125		
Dicholesteryl Adipate	198–208	202–196	184.0	195.5	197.0	194		
	237–241	239–235	223.0	225.5	226.5	230		
Cholesteryl Cinnamate	163–170	136–123	160.5	162.6	167.3	161		156, 160, 162, 197, 199, 200 (6)
	206–227	225–214	214.3	215.2	217.0	214		
Dicholesteryl Sebacate	171–188	149–147	172.8	180.4	182.0	180		
		181	176.2‡	175.8‡	173.7‡	185		

‡ Cooling

[a] T_b = Temperature at onset of endotherm. T_m = Temperature at endothermal minimum. T_e = Temperature at end of endotherm.

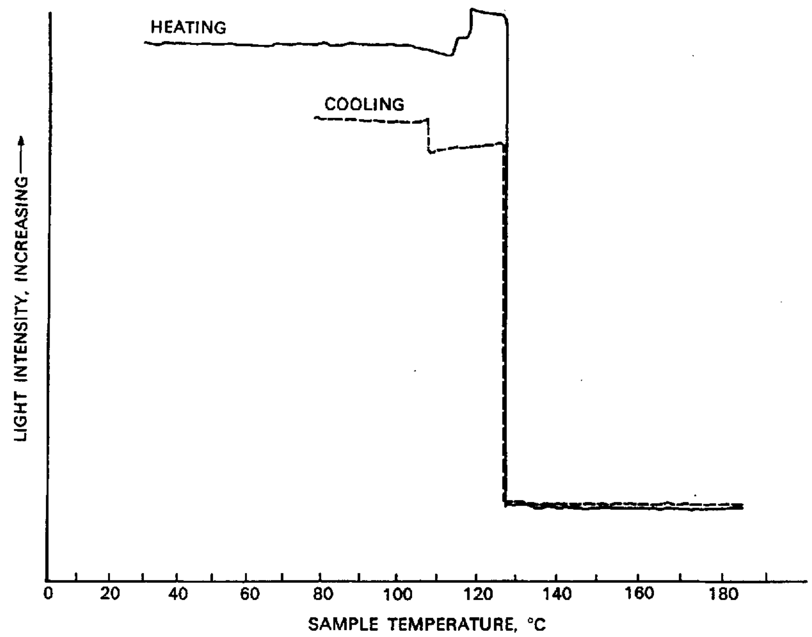


Figure 2. N-(*p*-Cyanobenzal)-*p*-Anisidine. 8 °C/min heating rate.

The solid structure below 103 °C is shown in *A*. This structure darkens in the interval 103 °C to 113 °C. At 113 °C the mesophase forms. This mesophase has the featureless light areas characteristic of the nematic but at the same time has some leaf-like structures characteristic of the smectic mesophase. A typical nematic phase forms at 118 °C and persists to 126.5 °C. The last trace of rotated polarized light vanishes at 128 °C. Cooling the isotropic liquid reproduces the nematic mesophase with little supercooling. The solid phase forms sharply at 108 °C with no indication of the intermediate mesophase seen on heating.

Cholesteryl Benzoate

This material furnishes an excellent example of mesophase interpenetration. The smectic and cholesteric mesophases exist in equilibrium from 127 °C to 120 °C on cooling. Figure 11 illustrates this case. The characteristic smectic plates and granular cholesteric texture formed at the same time from the solid phase and were stable at 140 °C for 10 hours. Above 144 °C only the cholesteric texture persists. The smectic mesophase is easily distinguished from the solid phase on the basis of optical signs and anisotropic brightness. The DLI curve in Fig. 3, although somewhat irreproducible, shows a portion of the sample converting from the smectic to the cholesteric phase at 142 °C to 144 °C. Previous DTA studies[6,10] have not separated the smectic from the cholesteric mesophases although Chistyakov has published a DTA curve with a very broad 145 °C endotherm. The transition from the solid to the mesophase is the large thermal event, 5.30 kcal/mole,[10] which could mask a small nearby mesophase→mesophase transition (usually less than 0.5 kcal/mole). On cooling, the isotropic liquid→cholesteric mesophase transition is not significantly supercooled. The mesophase→solid transitions are somewhat supercooled. This behavior has been noted for many other liquid crystal-forming materials.[3,9,11,12] In addition to mesophase changes, the DLI curve in Fig. 3 also shows a baseline

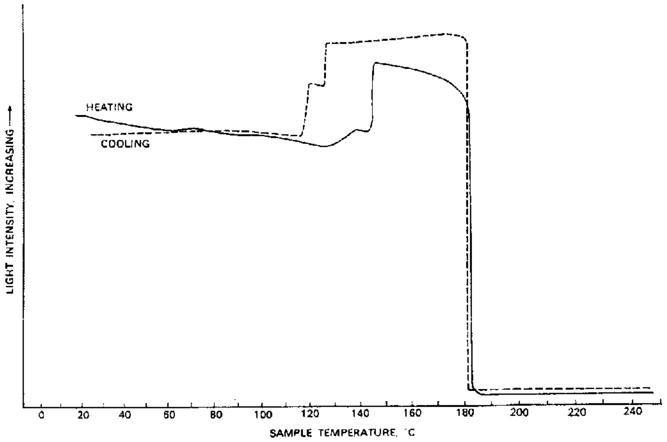


Figure 3. Cholesteryl Benzoate. 8 °C/min heating rate.

departure around 127 °C. This can be interpreted as a pretransition volume change. On optical inspection, the solid crystals show cracks forming at this temperature.

Cholesteryl Anisoate

The DLI curve of this ester, Fig. 4, shows only a single mesophase transition forming the cholesteric texture. The formation is synchronized with the uptake of heat by the transitions as shown by DTA.[10] The interval between 182 °C and 268 °C is one of increasing anisotropy on heating. The hump at 216 °C marks the onset of streaming in the cholesteric texture of the mesophase. This could mark a second-order transition which is not detected by DTA. The onset of the formation of the cholesteric mesophase on cooling is not appreciably supercooled. The steps in the DLI curve between 278 °C and 260 °C are due to the formation of progressive layers of the cholesteric texture between the cover slips. The formation of the solid phase is supercooled appreciably.

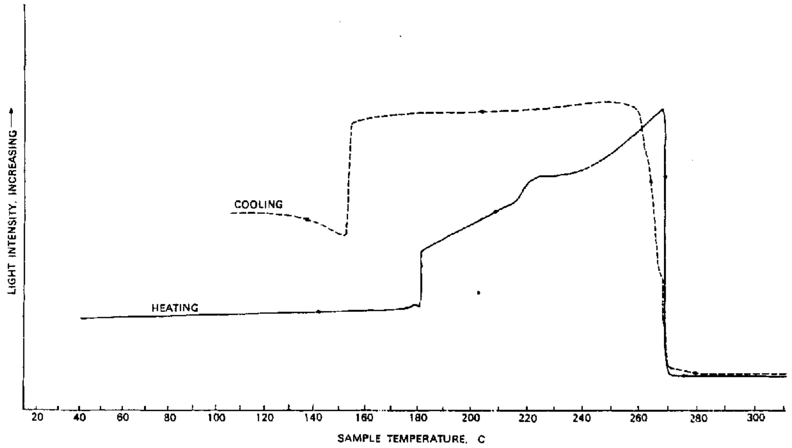


Figure 4. Cholesteryl Anisoate. 8 °C/min heating rate.

Cholesteryl Crotonate

This ester exhibits a DLI curve similar in most features to those previously discussed. The transitions are synchronized within the limit of temperature error with the uptake of heat as measured by DTA. The small cusps on the DLI curve in Fig. 5 are due to " flashing ".

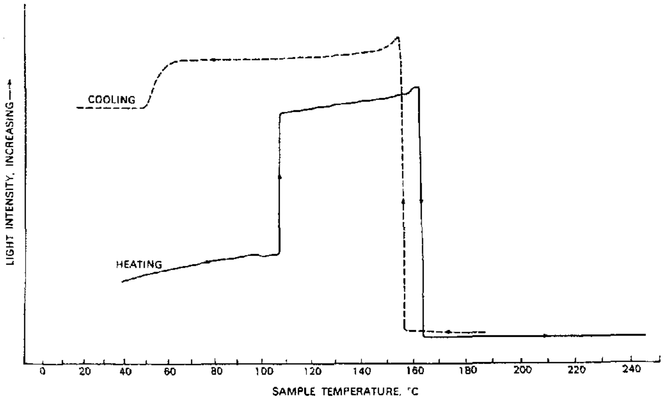


Figure 5. Cholesteryl Crotonate 8 °C/min heating rate.

Dicholesteryl Adipate

This ester exhibits several unique features in the DLI curve shown in Fig. 6. The cholesteric mesophase is reproducibly less

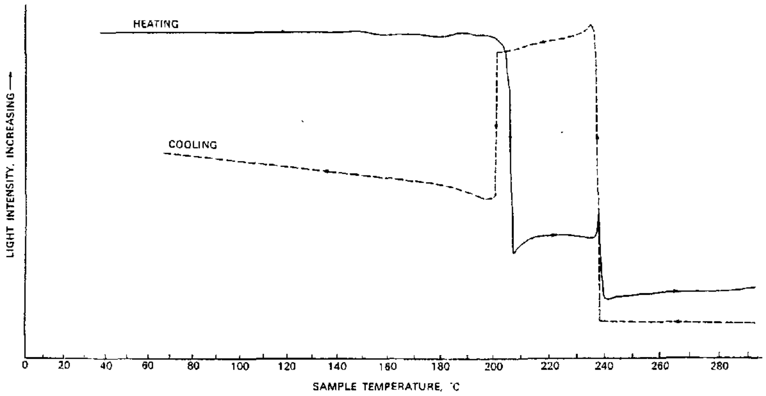


Figure 6. Dicholesteryl Adipate 8 °C/min heating rate.

bright on heating than either the solid phase or the cholesteric mesophase formed on cooling. This indicates a lower light rotating ability. The solid phase appears to almost totally convert to the isotropic liquid at 208 °C (dark field), and then the characteristic cholesteric mesophase forms. The DLI curve is poorly synchronized with the DTA curves at this point. The major heat absorption is complete prior to the large change in field brightness. The cholesteric mesophase converts to the isotropic liquid with flashing and streaming. Cooling the isotropic liquid produces the cholesteric mosaic texture with little supercooling. The mosaic texture is significantly brighter than the net texture formed on heating.

Cholesteryl Cinnamate

Chistyakov has discussed the thermal behavior of this ester.[6] The transition temperatures presented in this paper are lower than those observed by the present authors either by DTA or DLI. See Fig. 7. This is probably due to differences in purity. The open net cholesteric structure pictured by Chistyakov forms from 163 °C to 170 °C. This mesophase persists to 206 °C. The threads in the mesophase begin to darken and vanish at 227° C. These

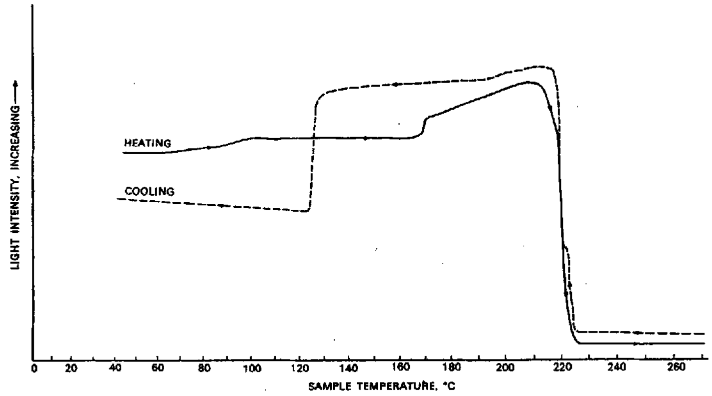


Figure 7. Cholesteryl Cinnamate 8° C/min heating rate.

events are reasonably well synchronized with the absorption of heat as detected by DTA.[10] On cooling, a faint cloud forms at 225 °C which does not develop into the well-defined cholesteric texture until 221 °C. This phase is fully formed by 214 °C.

Dicholesteryl Sebacate

No liquid crystal phase is detectable on heating this material. The solid phase melts directly to the isotropic liquid. See Fig. 8.

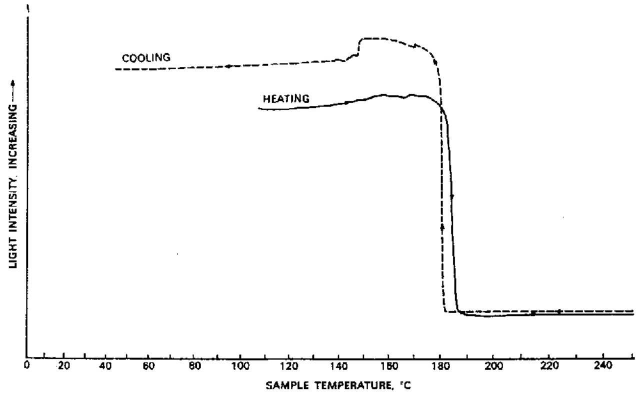
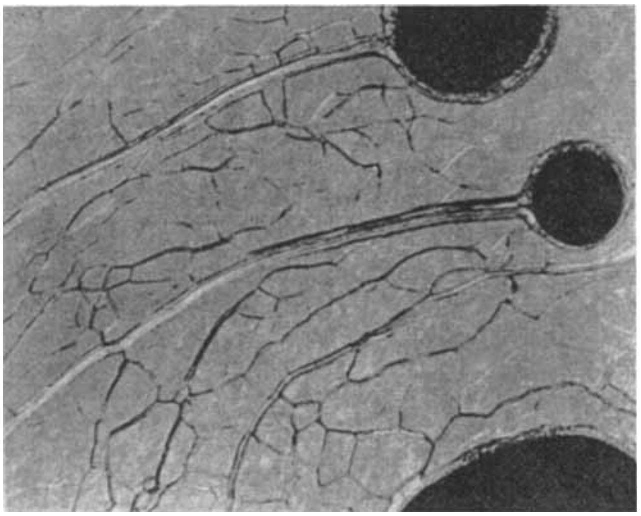


Figure 8. Dicholesteryl Sebacate. 8 °C/min heating rate.

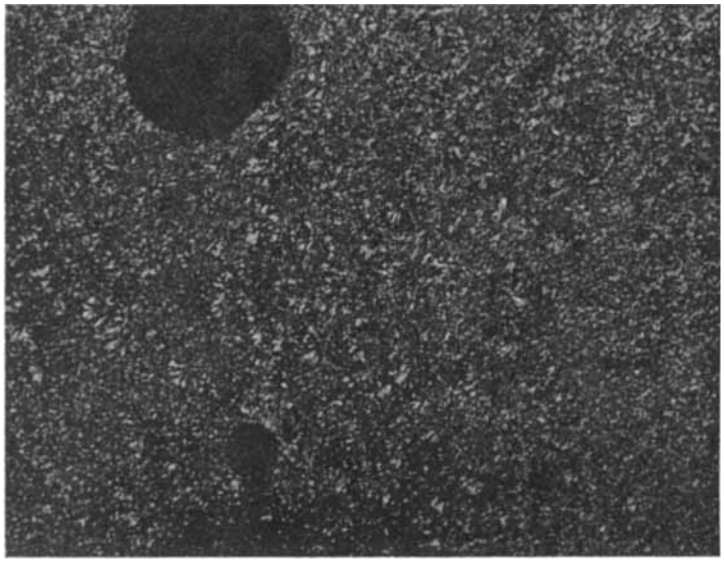
Similar results have been reported previously[2,11] and are common with the normal saturated acid cholesteryl esters. On cooling, a well-defined cholesteric texture appears at 181 °C. This converts sharply at 149 °C to the solid phase.

Conclusions

Depolarized light intensity measurements indicate that the maximum change in anisotropy of mesophase-forming materials does not in all cases coincide with the maximum heat consumption as determined by DTA. This is particularly true of mesophase

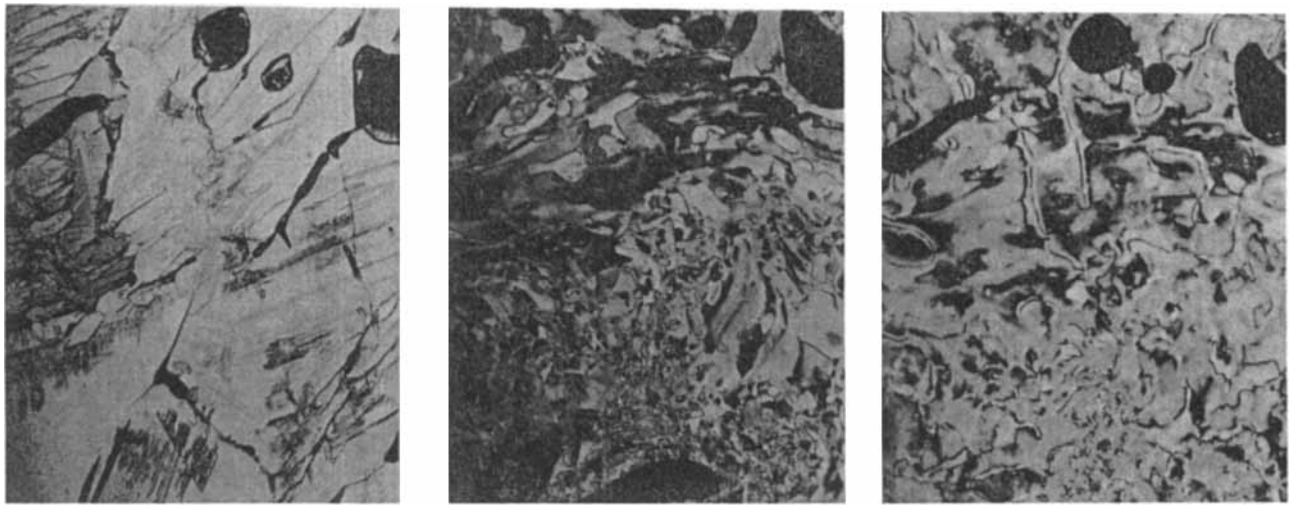


Formed at 101 °C on heating.



Formed at 110 °C on cooling.

Figure 9. The Cholesteric mesophase of *p*-(4-Cyanobenzalamino)-Cinnami acid active amyl ester.



Solid phase stable to 103 °C.

First mesophase
stable from 113 to 116 °C

Second mesophase
stable from 118 to 126.5 °C.

Figure 10. Phases of N-(*p*-Cyanobenzal) *p*-Anisidine.

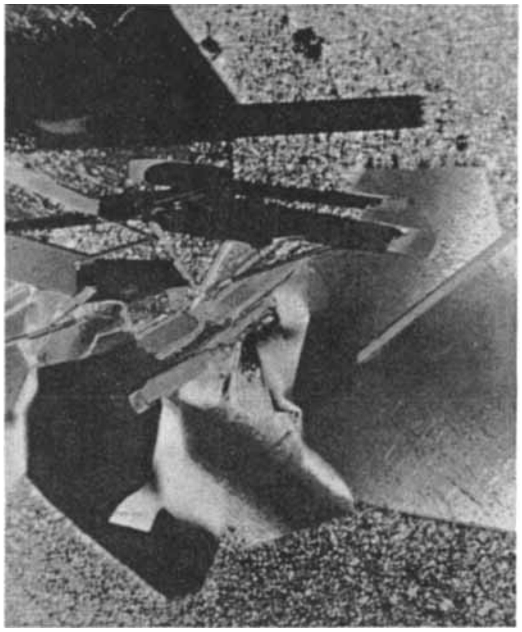


Figure 11. The Smectic and Cholesteric mesophases of Cholesteryl Benzoate at 140 °C.

transitions where the amount of heat involved for the whole transition is minor. The solid→mesophase transition, which is the thermally large event, can totally mask the existence of smectic or intermediate liquid crystal phase. By the use of DLI it is possible to reconcile much of the earlier work on mesophase-forming materials with the more recent DTA and calorimetric data.

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