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Blue phases of cholesteryl nonanoate

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The transformation on heating of an ordinary (helical) cholesteric liquid crystal (CHOL) into the isotropic phase (ISO) often occurs via a number of intermediate "blue" phases. We find the following scheme of phase transitions in cholesteryl nonanoate: $\text{CHOL}\underset{91.35}{\rightleftarrows}\text{BPI}\underset{91.76}{\rightleftarrows}\text{BPII}\underset{91.84}{\rightleftarrows}\text{BPIII}\underset{91.93}{\rightleftarrows}\text{ISO}$. Here BPI, BPII, and BPIII indicate three distinct, thermodynamically stable phases; transition temperatures are in °C. From observations of supercooling and coexistence, we conclude that all these transformations are first order, except possibly the BPIII→ISO, the character of which remains in doubt. A similar behavior is found in cholesteryl myristate and in a mixture of cholesteryl nonanoate and cholesteryl chloride. A few observations having a bearing on the structure of the blue phases are reported.

INTRODUCTION

The occurrence in cholesteric liquid crystals of an intermediate "blue phase", stable in a narrow temperature range between the regular (helical) cholesteric phase and the isotropic liquid, was first reported nearly a century ago.[1] Recently there has been a renewed interest in the investigation of the blue phase, in its experimental[2-11] as well as its theoretical[12-15] aspects.

A major question is, of course, the nature and structure of the blue phase. It now seems probable that it has a large-scale cubic symmetry[12, 8] (but for a different model see Ref. 6). However, details of the structure are as yet unclear. The situation is complicated by the observation by Bergmann and Stegemeyer,[6] that a succession of two stable blue phases occurs, which they have denoted as blue phase I (BPI) and blue phase II (BPII), in the order of increasing temperature. Marcus[10] has described a third texture, which, from its appearance under the microscope, he called a "fog." It appears in a very narrow temperature range between the BPII and the isotropic liquid. In the following we shall refer to it as BPIII.

In the present paper, we report observations of the temperature ranges in which these various blue phases occur, and their relative thermodynamic stability. The technique used to identify the phases is their characteristic transmission spectrum in the visible and near ultraviolet, which is mainly determined by Bragg scattering (at the wavelengths used absorption is negligible). The technique is the same as that used in Ref. 8, the main change being greatly improved temperature control and homogeneity. This results in improved spectral resolution and detail, as can be seen by comparing spectra of the present paper with those reproduced in Ref. 8. All in all, the conclusions of Ref. 8 stand up well. However, in the present paper we shall not attempt to narrow down the structure of the blue phases—we still have insufficient detail and confirmation to feel confident about presenting more specific structures.

We determine the stability of the various blue phases by observing the transitions between them, at increasing as well as decreasing temperature, and draw conclusions as to the character of the phase transitions from the occurrence of supercooling and/or the coexistence of the phases. The results reported here apply to cholesteryl nonanoate and mixtures of that compound with cholesteryl chloride (which have a longer cholesteric pitch). Very similar results, not reported here in detail, were obtained for cholesteryl myristate. We believe that some, though probably not all, of the observations apply in a qualitative way to many other cholesteric compounds, including cholesterics which are not cholesterol derivatives. This is suggested by the observations reported in Refs. 2, 10, and 11, which cover a variety of compounds. The only point we want to make here is that the occurrence of one or more blue phases is not a quirk of a specific compound, but seems to be an inherent property of many cholesteric materials.

Our conclusions can be summarized as follows: In the compounds studied, there are indeed three thermodynamically stable blue phases. With increasing temperature the cholesteric-isotropic transformation takes place according to the succession: Regular (helical) cholesteric → Blue Phase I → Blue Phase II → Blue Phase III → Isotropic.

It is remarkable that the above transformations take place in an overall temperature range of about 1 °C. All the transformations, with the possible exception of BPIII → isotropic, are first order, as concluded from the occurrence of supercooling or phase coexistence. Supercooling or coexistence has not been observed for the BPIII → isotropic transition, and its character has not been determined.

EXPERIMENTAL

A simplified diagram of the spectrophotometer is given in Fig. 1. The sample cell is made up of two fused silica disks and a glass spacer. Sample thicknesses most commonly used were about 0.25 or 0.50 mm and transverse size was roughly 5×10 mm^2. The sample cell was enclosed in a double oven, with windows kept as small as compatible with light beam size. The outer oven was equipped with a thermistor and was regulated to within about 0.1 °C. The inner oven had a platinum thermometer in an ac bridge, and proportional, differential, and integral feedback. It kept temperature to within 0.001 °C of the setting.

The illuminated area of the sample was about 1×5 mm^2, and was a rough image of the exit slit of the monochromator. The incident light beam was always normal to the faces of the sample cell, and apertures were such that the maximum ray deviation from the normal direction was about 1 degree.

Most of the data processing is done in the PDP8 minicomputer. The outputs of the main photomultiplier tube (PMT A) and of the reference (PMT B) are digitized, and the difference of the intensities with the chopper open and closed is computed, so as to eliminate background. Next, the ratio of these corrected A and B outputs is computed to produce a transmission spectrum independent of light source intensity. The computer also controls the wavelength scan of the spectrometer, and stores the spectra in memory. One more processing step is involved in producing the spectra reproduced here. For every new sample we first run a spectrum in the isotropic phase, generally one to two degrees above the clearing point. This is kept in computer memory as the reference spectrum. Subsequent spectra are always plotted as the ratio of the measured intensity (processed as described above) to the corresponding intensity in the reference spectrum. This procedure of plotting ratio spectra compensates for the unavoidable differences in the spectral responses of the two photomultiplier tubes, as well as for any wavelength dependence of the beam splitter. In the isotropic phase, light scattering in the sample is very small, and the ratio spectrum is thus by definition a horizontal line at unity ordinate.[16] On lowering the temperature, transition to the liquid crystalline phase is accompanied by greatly increased scattering, and thus is indicated by a drop of the spectrum below the unity ordinate. In short, in the spectra presented, the distance of the spectral trace below unity is a direct measure of the total intensity scattered by the sample.

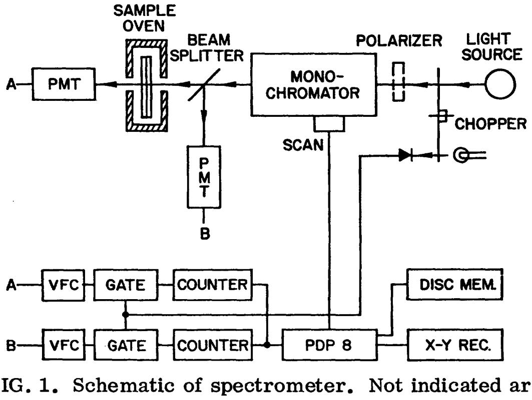

FIG. 1. Schematic of spectrometer. Not indicated are a number of mirrors which image the light source on the entrance slit of the monochromator and its exit slit on the sample. The light source is a combination of a halogen incandescent bulb and a deuterium uv lamp.

Some spectra were made with circularly polarized light. Because the polarizer was only occasionally used, it is indicated in broken lines in Fig. 1. It consisted of a combination nicol prism and quarter wave plate. No attempt was made to maintain accurate circular polarization over the wavelength scan, and results must therefore be considered as qualitative.

The cholesteryl nonanoate used was obtained from van Schuppen Chemicals, Veenendaal, Holland. Part of it was repeatedly recrystallized from petroleum ether till an unchanging clearing point of 92.0 °C was reached. There was no appreciable difference in the behavior of the original and the recrystallized material. The cholesteryl chloride used in the mixtures was obtained from Eastman, and recrystallized in acetone.

RESULTS

We shall discuss our results with the help of Figs. 2 to 8, each of which gives a set of spectra. We want to stress that each set represents a single actual run, with no selection or combination of spectra from different runs. In a run the temperature is decreased (or increased as the case may be) in discrete steps, to values indicated in the figure and its caption. At each temperature a spectrum scan is taken. The time interval between successive scans was generally between two and three minutes.[17]

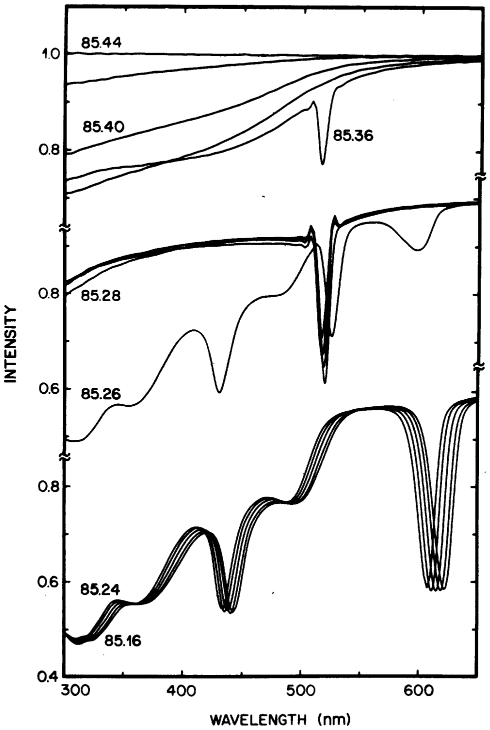

FIG. 2. Transmission spectra of a mixture of 85% cholesteryl nonanoate and 15% cholesteryl chloride. The sample cell was 0.5-mm thick and the inside surface was treated with polyvinyl alcohol as a surfactant. The crystallites (platelets) are highly oriented. Spectra were recorded at intervals of 0.02 °C, in order of decreasing temperature, starting in the isotropic phase. To avoid excessive overlap, spectra have been shifted vertically, as indicated by the numbers on the intensity axis. These are "ratio" spectra, as explained in the experimental section.

All the spectra discussed here are largely determined by Bragg scattering, but their appearance may vary. Two extreme cases are exemplified by Figs. 2 and 4. The only difference between these cases is in the preparation of the surfaces of the sample cell. For Fig. 4 the fused silica surfaces of the sample cell were cleaned by exposure to oxygen gas in a high-frequency plasma cleaner. This treatment produces a surface that presents no preferred orientation for the blue phase crystallites, which are randomly oriented as a "powder." Figure 4 gives spectra characteristic of such a powder sample. They exhibit a number of stepwise decreases in intensity, each step occurring at a wavelength at which an additional Bragg reflection becomes possible, i.e., at wavelengths given by[8] $\lambda_{hkl} \leq 2n(\lambda)d_{hkl}$, where λ_{hkl} is the vacuum wavelength, $n(\lambda)$ the index of refraction of the sample, and d_{hkl} the spacing of the (hkl) crystallographic planes.

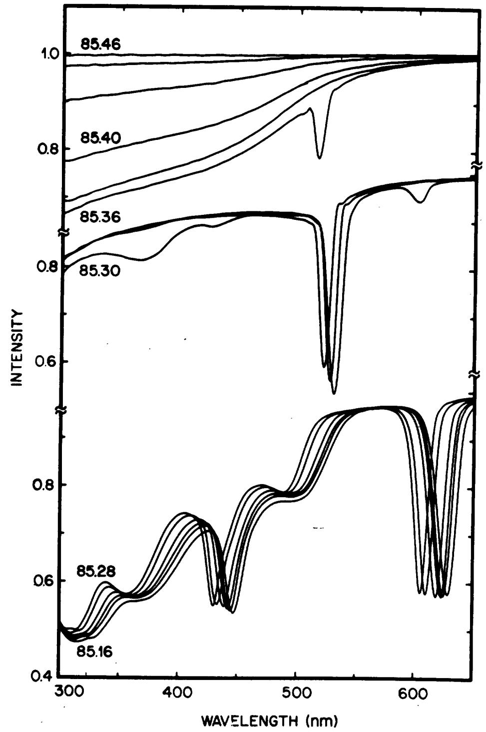

FIG. 3. As in Fig. 2, but recorded in order of increasing temperature. Figures 2 and 3 constitute the record of a single run, in which the temperature was first lowered and then raised back to the isotropic phase.

The other extreme in spectrum appearance is shown in Fig. 2. The only change in experimental conditions from those of Fig. 4 is that the cell surfaces are treated with a thin layer of polyvinyl alcohol as a surfactant and are subsequently rubbed with filter paper. This produces a sample in which the crystallites ("platelets") are preferentially oriented by the surface, and narrow reflections (dips in the transmission spectra) occur when the Bragg condition is met: $\lambda_{hkl} = 2n(\lambda)d_{hkl}\sin\phi$, where ϕ is the angle between the light rays and the hkl plane. Note that most of the dips in Fig. 2 correspond to steps in Fig. 4, indicating that for these reflections $\phi = 90°$. This is, however, not necessarily the case: There is no step corresponding to the dip at about 500 nm. We will return to this point in the next section.

Spectra intermediate to the ones described above are often observed: A given Bragg reflection may be expressed by a superposition of a step and a dip, or in a single trace one reflection may have a dip character, while another has a step character. It all depends whether and how the crystallites are oriented by the cell surfaces. As can be expected, that varies with surface treatment, history, and imponderables.

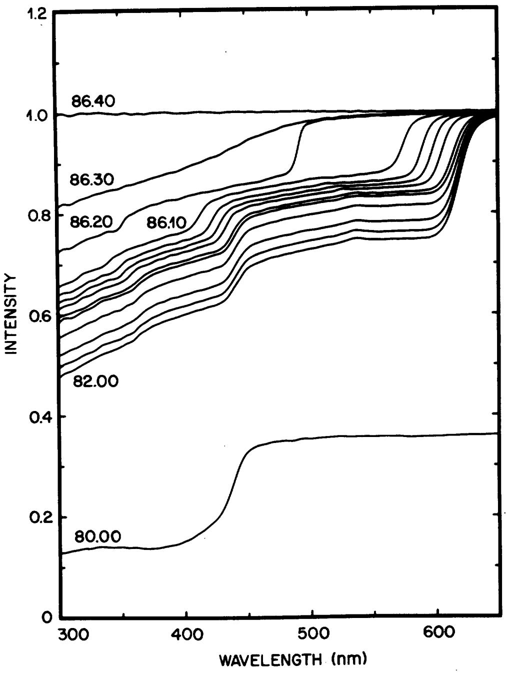

FIG. 4. Spectra of a sample of the same composition and thickness as in Fig. 2, but here the inner surface of the fused silica sample cell was cleaned by a plasma discharge in O_2. This produced a "powder" sample. Traces were recorded in order of decreasing temperature. Where not indicated in the figure, the temperatures from top to bottom are 86.00, 85.90, 85.80, 85.60, 85.50, 85.00, 84.00, 83.00.

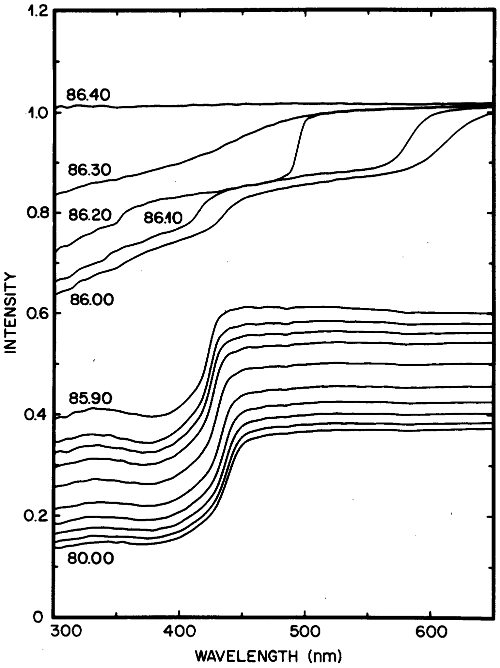

FIG. 5. Continuation of the run of Fig. 4, but now with increasing temperature. Where not indicated in the figure, the temperatures of the traces from bottom to top are 81.00, 82.00, 83.00, 84.00, 85.00, 85.50, 85.70, 85.80.

In Ref. 8 we have discussed the interpretation of the wavelengths of the Bragg reflections in terms of a cubic structure of the BPI. The conclusions reached there are in agreement with the present more detailed results, and will not be repeated. However, a few additional observations will be commented on in the next section.

The spectra of Figs. 2 and 3 are from one single experimental run, successive spectra being made at temperature intervals of 0.02 °C. Figure 2 gives the spectra for decreasing temperature, starting in the isotropic liquid, while Fig. 3 was made while going back up in temperature.

One aim in presenting Figs. 2 and 3 is to stress the sudden changes in spectral character as one phase changes into another. The isotropic phase is indicated by a horizontal line at unity intensity and is very nearly temperature independent.[16] Entrance into the BPIII is indicated by a drop in intensity at the shorter wavelengths, but the spectrum is essentially featureless (traces for 85.42, 85.40, and 85.38 °C). The appearance of the BPII is indicated by the sharp dip at 520 nm (note also that the scattering at the shorter wavelengths decreases on entering this phase). The BPII persists in the traces for 85.34, 85.32, 85.30, and 85.28 °C (these traces partially overlap). The BPI appears at 85.26 °C, and is shown fully developed in the 85.24 to 85.16 °C traces, the spectrum shifting to longer wavelengths as the temperature is lowered. As will be shown in subsequent figures, the BPI can, in fact, persist in a supercooled state to much lower temperatures, finally transforming into the regular helical cholesteric. However, in the present run, on reaching 85.16 °C the direction of the temperature scan was reversed and the sample was brought back into the isotropic phase. Figure 3 gives the spectra during this scan. The main conclusion we draw from Figs. 2 and 3 is that the same succession of phases appears with rising as with falling temperature. There is a small hysteresis of a few hundredths of a degree.

Another set of spectra for the same material is shown in Figs. 4 and 5, made at decreasing and increasing temperatures, respectively. These runs are with a cell cleaned with O_2 plasma discharge and no surfactant. The temperature intervals used here are larger than in Figs. 2 and 3, and as a result the BPII and BPIII are represented by only a single trace. However, the BPI supercools easily, to about 82 °C. It then transforms into the regular (helical) cholesteric, character-

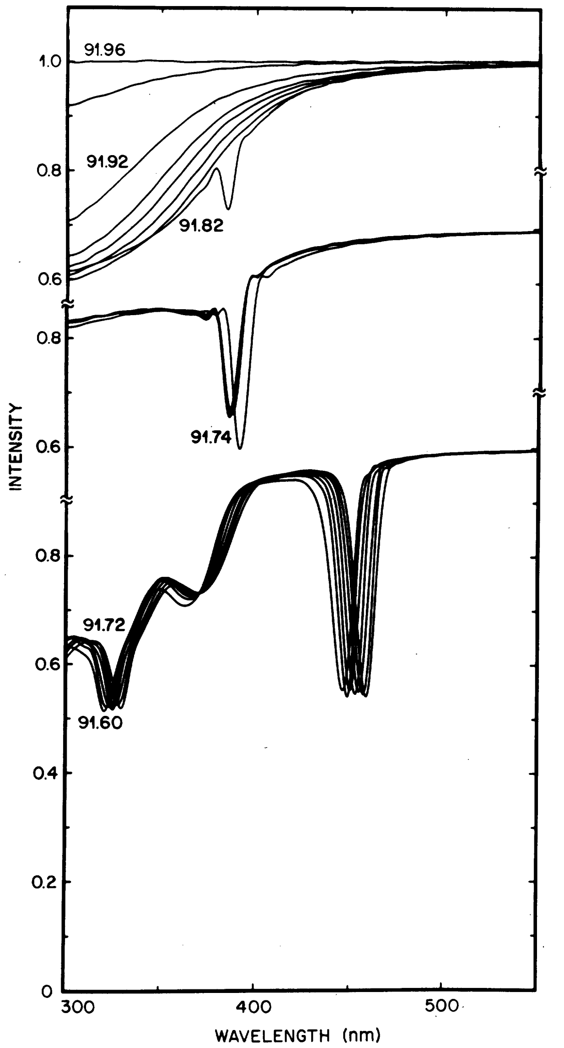

FIG. 6. Spectra for neat cholesteryl nonanoate. Other details same as in the caption of Fig. 2.

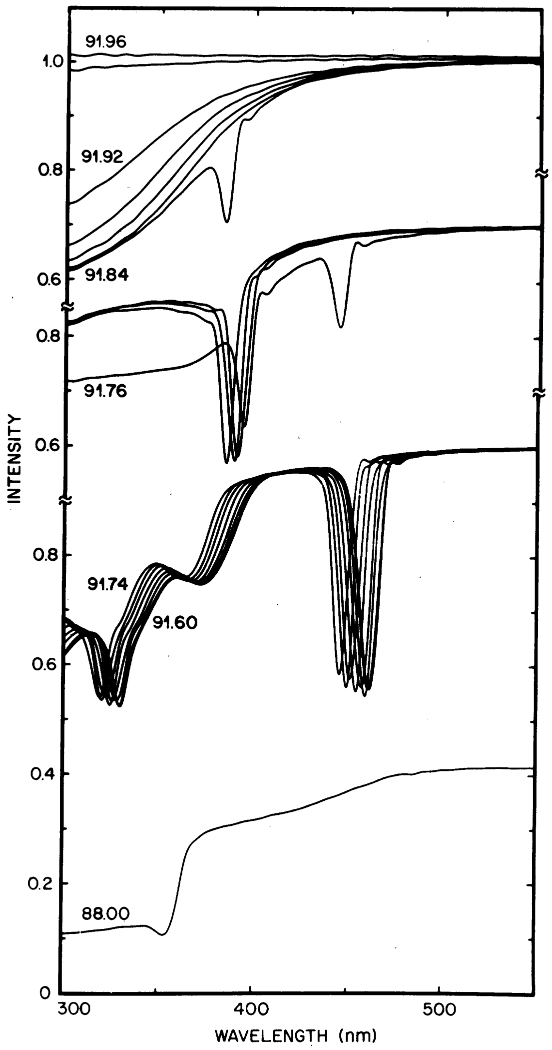

FIG. 7. Continuation of the run of Fig. 6, but now with increasing temperature. The trace at the bottom of the figure (88.00 °C) was made after completion of the run, and serves to indicate the wavelength of the Bragg reflection in the helical cholesteric phase.

ized by the bottom trace in Fig. 4.[18] The fact that this is indeed a case of supercooling is evident from Fig. 5, which shows the behavior of the same sample on reheating. The regular cholesteric persists to 85.9 °C. The sample then again goes through the succession BPI → BPII → BPIII → isotropic.

The above results were obtained with a mixture of cholesteryl nonanoate and cholesteryl chloride, and some skepticism as to their significance may be justified. We have therefore made similar measurements with neat cholesteryl nonanoate. The pitch in this material is smaller than in the mixtures, and accordingly, the spectrum is shifted toward the violet. However, enough of the spectra is observable to identify the phases without doubt. Figures 6 and 7 give the results of one run, at decreasing and increasing temperatures, respectively. The bottom trace in Fig. 7 gives the spectrum of the regular cholesteric, but was made separately and is not part of the down-up run. It is seen that the three blue phases, I, II, and III, appear as before, on decreasing as well as increasing temperature, with no or very little hysteresis. However, supercooling of the BPIII is occasionally observed; the most dramatic example is shown in Fig. 8, which was produced by a run in which the sample cell was cleaned with detergent.[19] Here the BPIII supercools into the stability range of the BPI, and the BPII is leapfrogged altogether. On reheating, this sample went through

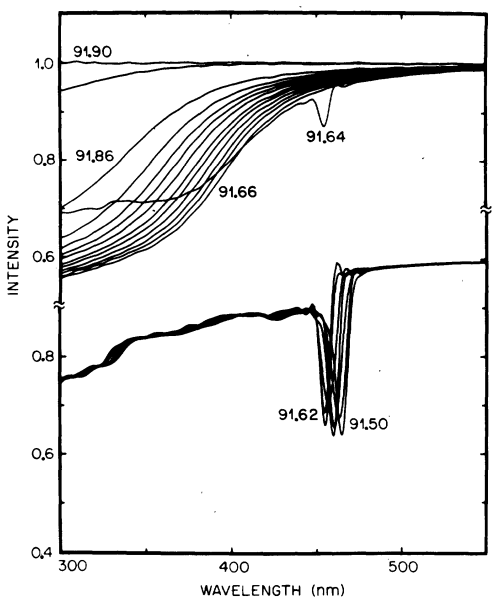

FIG. 8. Spectra for cholesteryl nonanoate made in order of decreasing temperature at intervals of 0.02 °C. The sample-cell surface was cleaned with detergent—see Ref. 19. This treatment produced supercooling of the BPIII.

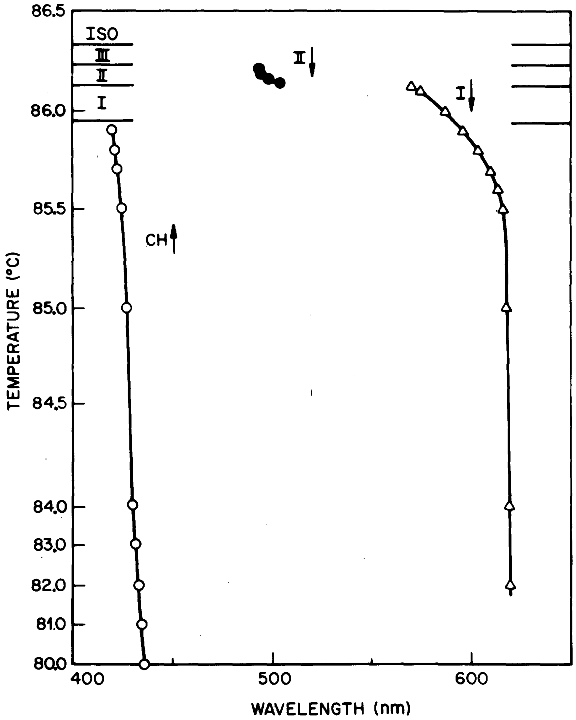

FIG. 9. Pretransition behavior of a mixture of 85% cholesteryl nonanoate and 15% cholesteryl chloride. Plotted is the wavelength of the first (longest wavelength) Bragg reflection as a function of temperature. The range of stability of the various blue phases is indicated in the left upper corner. The curve at the right of the figure is for BPI, made with decreasing temperature and continues into the supercooled range. The curve at the left is for the regular (helical) cholesteric, made with increasing temperature. The center, short curve is for BPII. Except for the supercooling, the curves are essentially reversible.

the normal I, II, and III sequence. We conclude that the BPII→BPIII transition is first order.

What about the BPI→BPII transition? At no time did we observe an appreciable supercooling; the small hysteresis, of a few hundredths of a degree, observed occasionally may be instrumental. Also, this is the only transition in which pronounced pretransition effects appear. Specifically, the spectrum of BPI shifts to shorter wavelengths as the BPII is approached (see Figs. 2 and 4). From the other side of the transition, the BPII shows a spectrum shift to longer wavelengths as the transition is approached, but the effect is smaller than that for the BPI. On the other hand, we observe coexistence of the BPI and BPII phases—see the 85.26° C trace in Fig. 2 and the 91.76 °C trace in Fig. 7—and we have never seen a peak situated between the wavelengths of the coexistent peaks. It seems, therefore, that the transition is first order, but only weakly so, with pronounced pretransition effects. A plot of the pretransition behavior is given in Fig. 9.

Finally, what about the BPIII→isotropic transition? We have never observed any supercooling, and the featureless character of the BPIII spectrum makes the detection of coexistence impractical. We must therefore leave the character of this transition an open question. There could be some doubt whether the scattering in the BPIII range is due to a real phase change, rather than a pretransition effect in the isotropic phase. However, the magnitude and temperature dependence of the observed scattering do not fit such an explanation, as discussed in some detail in Ref. 16. Another observation relevant to this point is that the BPIII strongly scatters circularly polarized light of one sense, and to a much smaller degree light of the opposite sense. This is illustrated in Figs. 10 and 11. (This is, of course, also true for the other blue phases and the helical cholesteric.) This observation indicates that the BPIII has a correlation length of the pitch comparable to, or longer than the wavelength of light, i.e., long-range molecular ordering.

NOTES ON THE STRUCTURE OF THE BLUE PHASE

In this section we report some observations which may contribute to the elucidation of the

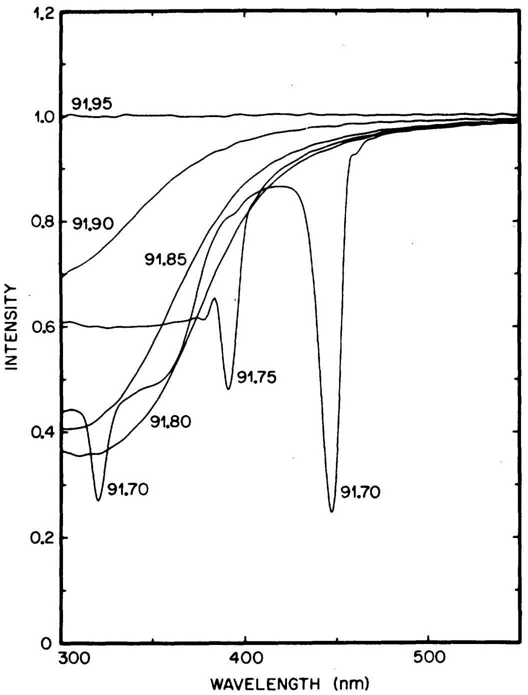

FIG. 10. Spectra for cholesteryl nonanoate, similar to those of Fig. 6, but made with circularly polarized light.

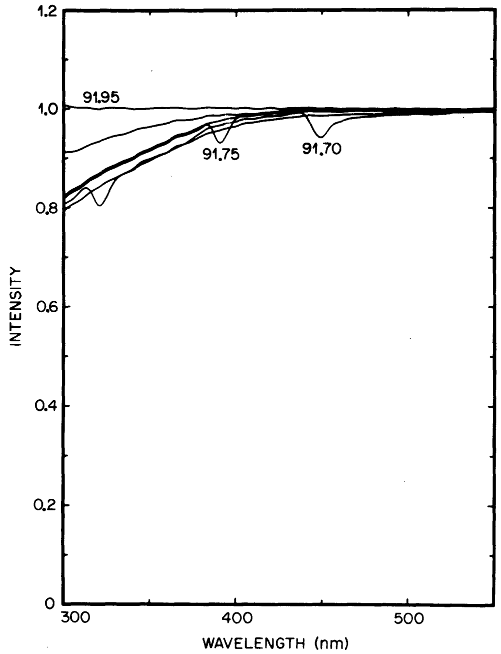

FIG. 11. As in Fig. 10, but with the opposite polarization sense.

structure of the various blue phases. They add to the results given in Ref. 8. We now observe a clear second Bragg reflection in the BPII—the step at about 350 nm in Figs. 4 and 5, and also in a number of other records not reproduced here. The wavelengths of the two observed reflections are in a ratio of $\sqrt{2}$ (with a small correction for refractive index[8]). We have made a rather intensive search for higher-order reflections in the BPII, but without success. We tentatively conclude that the BPII is cubic—see also Ref. 11.

One striking new observation is a dip in the BPI spectrum at about 370 nm in cholesteryl nonanoate, Fig. 6 (and a similar dip at about 500 nm in the mixture, Fig. 2). It is noteworthy that we have never observed a corresponding step in the powder spectra. It is tempting to take these facts as indicating a bcc structure for the BPI: The dip would be due to (110) reflections from crystallites oriented with their (111) planes parallel to the cell surface. These reflections would occur at a wavelength $\sqrt{2/3}$ of that of the (110) dip, in accordance with observation. Also, for a bcc structure, the (111) reflection is absent, and no step in the powder spectrum is expected, again as observed. However, a simple cubic structure can still not be ruled out: In this structure (100) reflections in a (211) oriented crystallite would give the same observations. Although a (211) crystallite orientation seems less probable than a (111) orientation, one would like to have some corroborative evidence, which we have been unable to obtain.[20]

CONCLUSION

We have shown that in cholesteryl nonanoate the transformation of the cholesteric phase into the isotropic one takes place in no less than four discrete steps, according to the scheme[21]

$$\text{CHOL} \xrightarrow[91.35]{} \text{BPI} \xrightarrow[91.76]{} \text{BPII} \xrightarrow[91.84]{} \text{BPIII} \xrightarrow[91.95]{} \text{ISO}\ ,$$

where the transition temperatures are in °C. From observations of supercooling and coexistence, we conclude that all these transitions, with the possible exception of the BPIII → ISO, are of first order. The character of this transition is left open. We have made similar observations in cholesteryl myristate, with the following transition temperatures:

$$\text{CHOL} \xrightarrow[84.30]{} \text{BPI} \xrightarrow[84.78]{} \text{BPII} \xrightarrow[84.86]{} \text{BPIII} \xrightarrow[84.96]{} \text{ISO}\ .$$

For the mixture 85% cholesteryl nonanonate and 15% cholesteryl chloride (by weight), the transitions are

$$\text{CHOL} \xrightarrow[85.95]{} \text{BPI} \xrightarrow[86.34]{} \text{BPII} \xrightarrow[86.38]{} \text{BPIII} \xrightarrow[86.50]{} \text{ISO}\ .$$

ACKNOWLEDGMENTS

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[16] We neglect here critical fluctuation scattering in the isotropic phase, which can become very appreciable as the transition point is approached. [T. W. Stinson III, and J. D. Litster, Phys. Rev. Lett. 25, 503 (1970)]. In the thin samples of cholesterol derivatives used here, this effect is small, and can just be detected as a small drop in spectral intensity at shorter wavelengths, too small to be clearly seen on the scale used here for the figures. However, the effect can be quite pronounced for other compounds; for instance, we have observed a large scattering in a nematic cyanobiphenyl. The reason for this difference in magnitude is in the fact that the scattering intensity is proportional to the square of the anisotropy of the refractive index, and the latter is an order of magnitude larger in the cyanobiphenyls than in the cholesterol derivatives resulting in two orders of magnitude difference in the scattering. This is qualitatively what we observe.

[17] This time interval was sufficient to reach approximate thermal equilibrium, as can be ascertained by comparing the temperatures of corresponding traces in Figs. 2 and 3 (or 5 and 6), which were made at decreasing and increasing temperature settings, respectively. Because detection of supercooling was one of our aims, the time interval was chosen as small as possible, while still compatible with the requirement of thermal equilibrium.

[18] This phase is in the focal conic texture, which accounts for the strong scattering. The fact that the wavelength of the step in the spectrum indeed corresponds to the regular cholesteric pitch was checked by Grandjean rings—see Ref. 8.

[19] The detergent used is marketed under the trade name "Deconex 11". It is manufactured by Borer Chemie, Zurich, Switzerland, and is distributed by Atomergic Chemetals Corp., Plainview, New York. It seems probable that a monolayer of detergent adhered to the surface, but we have made no attempt at elucidating surface effects in a systematic way.

[20] It could be thought that the dip at about 360 nm in Fig. 2 is a similar feature. However, this reflection can be identified as the (211) for bcc [or (111) for simple cubic], as evidenced by the appearance of a corresponding step in the powder spectrum of Fig. 4.

[21] The transition temperatures are those of Fig. 7, except for the first one which is taken from other spectra not reproduced here.