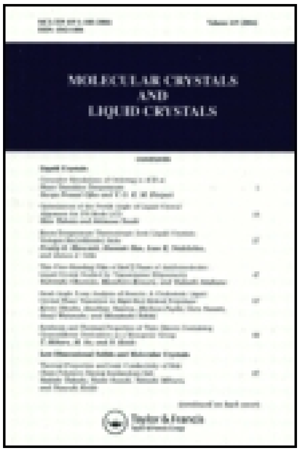

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The "Blue" Phase of Cholesteryl Proprionate

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THE "BLUE" PHASE OF CHOLESTERYL PROPRIONATE

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ABSTRACT

The claim that the cholesteric "blue" phase (BP) of cholesteryl proprionate (CP) is not the same as any of those of cholesteryl nonanoate (CN) was tested by studying the phase relations in the CP-CN system. The lowest-temperature BP (BPI) was continuous across the whole diagram, while the BPII dissappeared at between 76 and 90wt. % CP. It is therefore deduced that the BP of CP is the same phase as the BPI of CN.

I. INTRODUCTION

The "blue" phases (BP) of the higher ($n>7$) cholesteryl alkanoates have been investigated many times[1-3]. Most investigators find two three-dimensionally periodic ("crystalline") phases of either body-centered (bcc) or simple (sc) cubic symmetry. The structures of the two phases in some compounds have been deduced, with the result that the phase occurring at higher temperatures (BPII) is sc, while the other (BPI) is bcc[4]. However, there is a tacit assumption in much of the work that all BPI's are the same phase, and the same for BPII's. This presumption has been challenged recently by Nicastro, et. al., on structural grounds[5]. They argue on the basis of observed Bragg reflections that the single phase observed in the lower ($n=3,4$) cholesteryl alkanoates is not isostructural with either of the long-chain compound's BP's. To settle this question, I have done a phase-diagram study of the cholesteryl proprionate (CP) - cholesteryl nonanoate (CN) system. If the BP of CP is distinct from either of those in CN, then there should be three phases in the diagram, with limited or no miscibility between them. If there are less than three distinct phases, then either one of the CN BP's is the same as the CP phase, or there is a critical or tricritical point beyond which the CN BP's merge into one. Both situations are distinguishable from each other and from the presence of three different phases.

II. SAMPLE PREPARATION

The bulk mixtures were made by melting together CN and CP from Van Schuppen. The CN was recrystallized 4x in ethanol; the CP was used as recieved. The mixtures were stirred to insure compositional uniformity. The samples were made by loading 200μ thick flat capillaries with the isotropic mixtures. Their transition temperatures were spatially uniform over the observation area.

The transition temperatures were obtained by thermal microscopy using a Mettler hotstage. Scan rates of $<.01°/\text{min}$. were used and the results of upward and downward scanning were averaged. The samples were never allowed to enter the cholesteric state while in use. Thus, there are no data on the BP-cholesteric transition temperatures.

III. RESULTS

The BP-isotropic transition temperature varied smoothly from 115.0° for pure CP to 93.3° for pure CN. There may be a constant error of up to a degree due to the use of an extension cord on the hotstage which added to the resistance of its Pt thermometer. Also, the "fog" (BPIII, or "gray" phase)[3] was not reliably seen, and was counted as isotropic. This missing phase should not affect the result of this paper. Also, the inevitable two-phase regions were <.02° across and thus not visible.

Since the width of BPII was <.3° but the transition temperatures varied by 22°, I subtracted a quadratic function of the weight fraction of CN from all temperatures in order to display the topology of the phase diagram:

$$T_{smooth} = 115.79 - 38.74x + 16.2957x^2 \qquad 1$$

where x is the weight fraction of CN. The resulting phase diagram is shown in Fig. 1.

Note that the "BPI" region is continuous across the diagram. The color and general appearence of the lower-temperature phase changed continuously on moving from pure CN to pure CP:

green(CN)→yellow→orange→red&black→red&blue→multicolor

when the sample is viewed in transmission with crossed polarizers. I thus conclude that the BP of CP is BPI. Likewise, the BPII's appearence changed continuously in its existence region ($x \in [x_{min}, 1]$ with x_{min} between 10 and 24%). The 10% CN mixture showed a metastable BPII, which turned into BPI on cooling and did not return on heating. On cooling from the isotropic, this mixture produced platelets of BPI or BPII or both, possibly depending on cooling rate. However, BPI was always the stabler phase; BPII turned into BPI, but never the reverse.

Meiboom[6] has done optical spectra on unoriented samples of CP, cholesteryl butyrate, and cholesteryl pentanoate. He finds that the BP of CP, the low-temperature BP's of the other compounds mentioned above, and the BPI of CN all have similar selective-reflection patterns. This observation helps confirm my identification of the BP of CP with BPI.

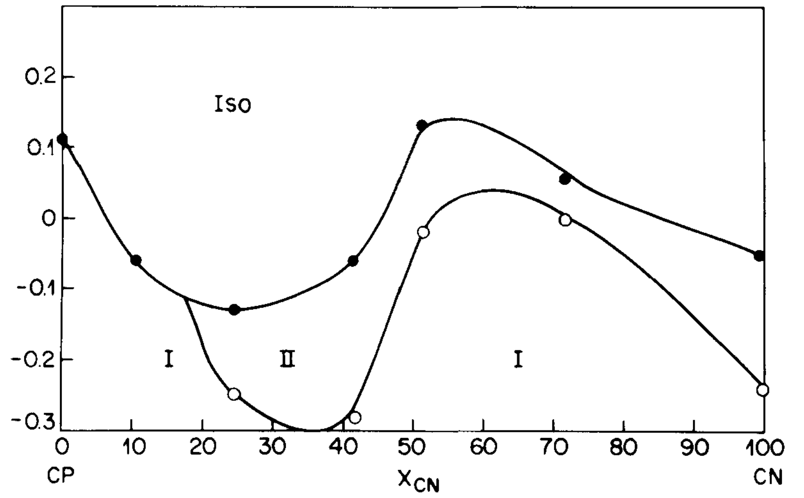

Fig. 1. Phase diagram for CP-CN system. See text for explanation of temperature scale.

CONCLUSIONS

This phase-diagram study showed that the BP of cholesteryl proprionate is identical to the BPI of cholesteryl nonanoate. The difference in appearance between the BP's is presumably due to a difference in lattice parameter. The observed color progression is:
green(CN)→yellow→orange→red&black→red&blue→multicolor(CP)
when the sample is observed in transmission between crossed polars. This progression is consistent with a steady increase of lattice parameter with CP content, and thus lends support to the identification of the blue phase of cholesteryl proprionate with the BPI of cholesteryl nonanoate.

REFERENCES

[1]M. A. Marcus, J. Phys. (Paris) **42**, 61 (1981)
[2]H. Onusseit, H. Stegemeyer, Z. Naturforsch **36a**, 1083 (1981)
[3]S. Meiboom, M. Sammon, Phys. Rev. **A24**, 469 (1981)
[4]M. A. Marcus, Phys. Rev. **A25**, 2272 (1982)
[5]A. J. Nicastro, P. H. Keyes, Phys. Rev. **A27**, 431 (1983)
[6]S. Meiboom, unpublished