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The Crystalline State and the Mesophases of Cholesteryl Oleyl Carbonate

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The preparation of pure crystalline cholsteryl oleyl carbonate is described. The melting point, the mesophase transition temperatures, and the enthalpy of the melting process are recorded, and a method of maintaining cholesteryl oleyl carbonate in a pure state over extended periods of time is suggested.

INTRODUCTION

Cholesteryl oleyl carbonate (COC) is one of the main sterol derivatives exhibiting cholesteric liquid crystal properties which is used in commercial applications relying on a change in colour of the phase to relay information, e.g., thermal mapping and digital thermometry.

Two papers[1,2] have been published claiming the preparation of pure cholesteryl oleyl carbonate. In these papers, however, different transition temperatures (smectic-cholesteric and cholesteric-isotropic liquid) are quoted, and in no instance is it claimed that the crystalline solid of cholesteryl oleyl carbonate has been *isolated*. Therefore no melting point or enthalpy value is known for the compound. It has in fact been generally assumed that cholesteryl oleyl carbonate has a melting point below 0°C. Indeed, the widespread use of the ester in thermochromic mixtures stems from the fact that the melting range of a mixture is depressed, but the colour reflecting properties are maintained, by incorporation of cholesteryl oleyl carbonate. However, without an available enthalpy value, eutectic compositions are not readily evaluated, and many commercial mixtures incorporating the ester are non-eutectic. As a consequence, segregation of any excess of a material above the eutectic amount is always liable to occur.

Summary of earlier work on cholesteryl oleyl carbonate

It is of value to summarise here the work already carried out on cholesteryl oleyl carbonate, particularly that published by Maidachenko[1] in 1970 and Elser, Pohlmann, and Boyd[2] in 1976.

Maidachenko[1] synthesised cholesteryl oleyl carbonate from oleyl chlorocarbonate (obtained from the reaction of phosgene and oleyl alcohol) and cholesterol. The reaction was carried out at the boiling point, using dry benzene as solvent and a molar amount of pyridine. Pyridine hydrochloride was filtered off, the benzene was distilled off, and the impurities were "extracted into acetone." The cholesteryl oleyl carbonate (an oil) was "separated from the acetone, and the excess of acetone eliminated in a drying chamber at 30°C."

Cholesteryl oleyl carbonate prepared in this way gave a reversible cholesteric-isotropic liquid (Ch-I) transition at 39°C, and the cholesteric film apparently still persisted at 0°C. The colour play from violet to red was said to take place in the range from 23°C to 0°C. No smectic phase was reported, and no crystalline phase or melting point was mentioned.

In the paper by Elser, Pohlmann, and Boyd[2] and also in the book "Flüssige Kristalle in Tabellen" by Demus, Demus, and Zaschke,[3] Maidachenko is however accredited with observing the smectic to cholesteric (S-Ch) transition at 17°C and the Ch-I transition at 34°C.

Elser, Pohlmann, and Boyd[3] prepared cholesteryl oleyl carbonate from oleyl alcohol (synthesised from natural olive oil *via* methyl oleate) and cholesteryl chloroformate which had been crystallised twice from ethyl acetate. The reaction was again carried out using as solvent absolute benzene containing a molar amount of pyridine to combine with the hydrogen chloride produced. The reaction temperature was 0°C, and a nitrogen atmosphere and dark conditions were maintained.

Pyridine hydrochloride was filtered off, the benzene removed by evaporation, and the crude product purified by column chromatography. Certain impurities were first eluted from a silica gel column with pure hexane, but as the product progressed down the column, the composition of the eluant was changed by adding benzene until a mixture of hexane/benzene (70%/30%) was used. The fractions containing pure cholesteryl oleyl carbonate were combined and evaporated to dryness under vacuum at 30°C.

An analytical sample of cholesteryl oleyl carbonate was obtained by crystallisation from acetone at −35°C, when small flakes were said to have been formed. It is not clear whether these flakes were separated as solid from the solvent, as no melting point is quoted for the compound.

The physical constants for cholesteryl oleyl carbonate prepared in this way were:-

S-Ch	16.3°C	Ch-I	28°C	(heating)
Ch-S	10.8°C	I-Ch	24.3°C	(cooling)

A thin film of this cholesteryl oleyl carbonate in the Grandjean plane texture reflected visible light on heating from 20.3–21.1°C.

RESULTS AND DISCUSSION

In the process of our work, pure cholesteryl oleyl carbonate (COC) was required. However, the commercial COC that was available was found by thin layer chromatography (t.l.c.) to be impure and to degenerate on storage. We therefore decided to synthesise and purify COC following essentially the method of Elser, Pohlmann, and Boyd.[2]

The product of the reaction gave three spots by t.l.c. on silica gel (eluant = benzene:hexane, 1 : 1). After the column chromatography, one of these spots was completely removed and the other impurity was almost totally eliminated. Further chromatography on silica gel using chloroform alone as eluant was found to give a complete separation of the product from the small amount of impurity. The fractions containing the pure COC were combined and evaporated to dryness. The product existed as a cholesteric phase at 0°C and had a Ch-I transition at 10°C. On leaving a sample of this material in a flask open to the atmosphere it was observed after several weeks that the isotropic liquid had turned to a cholesteric phase at room temperature (*ca.* 20°C), the bulk of the fluid had diminished, and long needles had begun to separate on the sides of the flask.

The low constants for the supposedly "pure" COC were attributed to the presence of chloroform, and this was confirmed by differential thermal analysis (DTA) which gave a peak corresponding to evaporation of chloroform at about 61°C. The chloroform was however impossible to remove completely from the COC, even after prolonged storage under vacuum; this was confirmed by futher DTA runs.

Since Elser, Pohlmann, and Boyd[2] had prepared their analytical sample by crystallisation from acetone, this method was now tried. The first attempt gave crystals in the acetone, but when an effort was made to filter these off, the crystals appeared to melt in the pre-cooled filter funnel. The material was however isolated and submitted to prolonged evacuation to remove acetone. Despite this treatment, DTA showed a peak corresponding to the vapourisation of acetone.

On cooling and re-heating a sample of this material in the DTA apparatus, the transition temperatures of the sample progressively rose to give the S-Ch transition at 20°C and the Ch-I transition at 34°C. On cooling one of the samples contained in the DTA pan at 0°C in a desiccator for over eight hours, and then reheating in the DTA apparatus, a third peak was observed between the other two. This was attributed to a melting process due to the occurrence of a slight degree of crystallisation on prolonged cooling. The transition did not occur on a cooling cycle or on a subsequent reheating cycle. The third peak did however reappear after further prolonged cooling at 0°C. Since this partial melting process occurred above 20°C, there was therefore no reason for the platelets formed in the acetone crystallisation to have melted, unless the acetone was strongly depressing the crystal-mesophase transition temperature of the sample.

Another sample was therefore crystallised from acetone, but this was filtered very quickly through a cooled filter, thoroughly sucked dry, and placed in a cooled sample tube. This material was then stored in a cooled desiccator over P_2O_5 and kept at 0°C for one day. The sample was then allowed to warm up to ambient temperature while it was evacuated in the desiccator for one day; a rotary oil pump giving a reduced pressure of 1 mm Hg was used. The crystals could now be maintained as such for indefinite periods at room temperature (20°C).

The transition temperatures for this analytical sample (see Experimental Section), as determined by optical microscopy, were:-

C-Ch	26.7°C	
Ch-I	34°C	
S-Ch	20°C	(monotropic)

On cooling the isotropic liquid, the "blue phase" is formed at approximately 34°C; it can be seen by eye as a faint blueness in the clear COC film. The focal-conic cholesteric texture is generated at a lower temperature, depending on the rate of cooling of the sample.

After melting, the crystals do not regenerate at room temperature (20°C) or just below this temperature; only the smectic phase is formed at 20°C, and

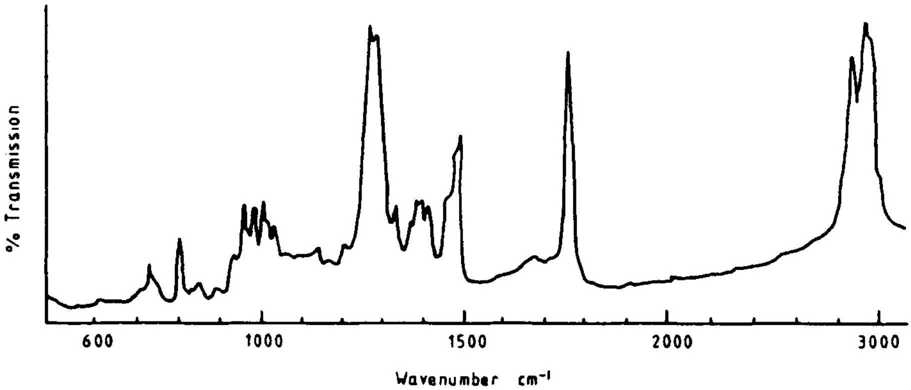

FIGURE 1 Infra-red Spectrum of Cholesteryl Oleyl Carbonate.

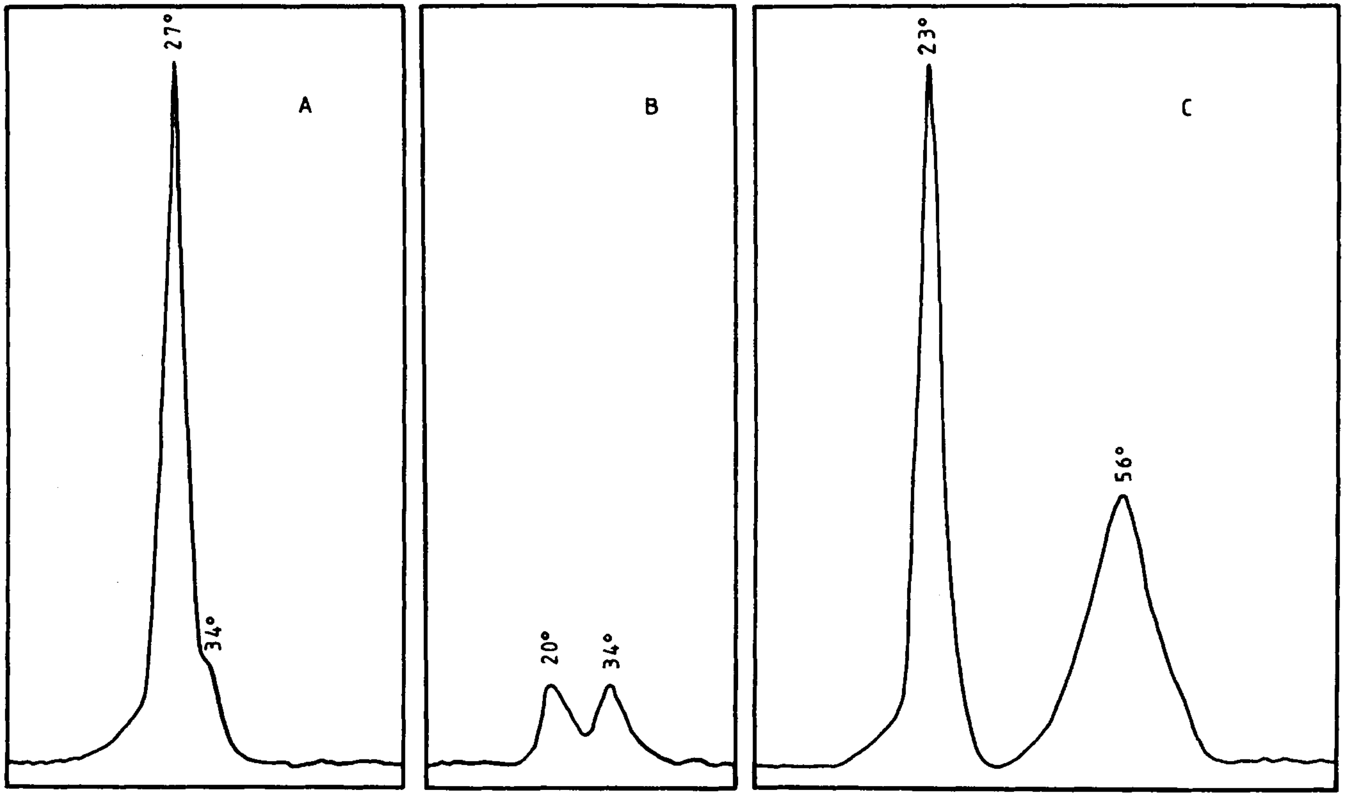

FIGURE 2 DTA traces for cholesteryl oleyl carbonate (COC) (A) Thermogram for pure, crystalline COC showing the melting (C-Ch) peak at 27° and the partly resolved shoulder associated with the Ch-I transition at 34°. (B) Thermogram obtained when the isotropic liquid produced in A is cooled to 0° and then reheated. This shows the peak for the monotropic S-Ch transition at 20°, and that for the Ch-I transition at 34°. (C) Thermogram for crystalline COC contaminated with acetone. The temperature of melting is depressed to 23°; the Ch-I transition suffers a greater depression, and the heating cycle no longer shows a shoulder for this transition. The broad peak at 56° corresponds to vapourisation of the acetone.

this appears to persist indefinitely at temperatures down to 0°C. DTA confirmed the above observations, and the enthalpy value for the transition of the crystals to the cholesteric phase was 6.53 kcal mol^{-1}.

For reference purposes, the infra-red spectrum of the pure COC is recorded in Figure 1.

The following interesting observation was made on one sample of the material.

On leaving the pure COC in the desiccator over the same P_2O_5 that had been used to remove the acetone initially, it appears that atmospheric water vapour was slowly taken up by the P_2O_5 and the acetone was released back into the atmosphere over the COC. Apparently the acetone was again taken up by the COC, since DTA gave lower transition temperatures and a peak for vapourisation of the acetone at 56°C (see Figure 2). The S-Ch transition was depressed more than the melting temperature or the Ch-I transition. The purity of the sample was restored by evacuating the desiccator and using fresh P_2O_5.

These results show how tenaciously COC clings to acetone and chloroform, and how readily it adsorbs the vapours of acetone. Bearing these points in mind, it is recommended that once the pure, solid COC has been obtained, the material should simply be stored in a brown-glass, screw capped bottle at room temperature (*ca.* 20°C). Samples of pure crystalline COC stored in this way have remained pure (by t.l.c.) for several months, and it is therefore suggested that this is a much more effective way of storing COC than elaborate methods that have been suggested for maintaining the purity of COC when it is in the cholesteric phase.

CONCLUSION

It appears therefore that a pure sample of COC in the solid state has been obtained for the first time, and its melting point and enthalpy of fusion have been recorded. It is difficult to comment on the purity of the cholesteric phase used by Maidachenko,[1] but it seems possible that the material isolated by Elser, Pohlmann, and Boyd[2] contained acetone, as their recorded transition temperatures are low. Other workers have reported that they purified commercial COC by crystallisation;[4] no constants for any solid phase are however given, and the usual temperatures recorded are S-Ch, 17°C and Ch-I, 33°C. These transition temperatures suggest that a small amount of crystallisation solvent may have been present in these "pure" materials, as the S-Ch values are depressed more than the Ch-I values, and this corresponds with our observations made on samples containing small amounts of solvent.

EXPERIMENTAL

Preparation of cholesteryl oleyl carbonate

A solution of dry, distilled pyridine (1.5 ml, 0.0186 mol) in absolute benzene (9.25 ml) was added over a period of $1\frac{1}{2}$ hr to a stirred solution of cholesteryl chloroformate (8.35 g, 0.0186 mol) (supplied by Aldrich Limited, and crystallised twice from ethyl acetate) and oleyl alcohol-purity, 99%, supplied by Sigma London Chemical Co. Ltd.—(5 g, 0.0186 mol) in absolute benzene (37.5 ml) at 0°C. The reaction mixture was maintained in the dark under a nitrogen atmosphere during the addition and for 12 hr thereafter, during which time stirring was continued and the mixture allowed to reach room temperature (*ca.* 20°C). The reaction mixture was filtered and the solvent evaporated from the filtrate at 30°C under reduced pressure. The residue was dissolved in hexane (20 ml) and the solution introduced onto a chromatography column of silica gel.[2] After eluting with hexane, until two fast-running impurities had been eluted, the composition of the solvent was slowly changed to a mixture of hexane/benzene (70%/30%).

All fractions containing COC were combined and evaporated to dryness. Small portions of this material (2 g) were dissolved in chloroform and passed down a silica gel column. Using chloroform as eluant, the COC is eluted quickly and the impurity is retained on the column. The fractions containing pure COC were combined, evaporated to dryness and placed in an evacuated desiccator.

This pure COC was dissolved in the minimum volume of acetone at room temperature (*ca.* 20°C) and left to crystallise at 0°C. The crystals were filtered off rapidly using a pre-cooled filter, and quickly sucked dry. They were placed in a cooled sample tube which was left in a desiccator at 0°C over P_2O_5 for 24 hr. The desiccator was then evacuated at room temperature for 24 hr; a rotary oil pump was used to achieve a reduced pressure of 1 mm Hg. The total yield of crystalline cholesteryl oleyl carbonate (C-Ch, 26.7°C) was 6.2 g (49.2%) (Found: C, 81.2%; H, 12.1%. Calc for $C_{46}H_{80}O_3$: C, 81.1%; H, 11.8%).

Physical methods

Transition temperatures were measured by optical microscopy using a Nikon LKe polarising microscope in conjunction with a Mettler FP52 heating stage and temperature control unit or a Reichert cold stage (Optische Werke AG, Wien, Austria).

Differential thermal analysis was carried out using a Stanton Redcroft low temperature thermal analyser (Model No. 671B).

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