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The chromonic phases of dyes

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The chromonic phases of dyes

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It has been shown that the lyotropic liquid-crystalline phases formed by certain dyes are structurally analogous to the chromonic N and M liquid-crystalline phases previously thought to be unique to certain anti-asthmatic/anti-allergic drugs. We suspect that these two groups of compounds will prove to be representatives of a large new class of mesogenic materials.

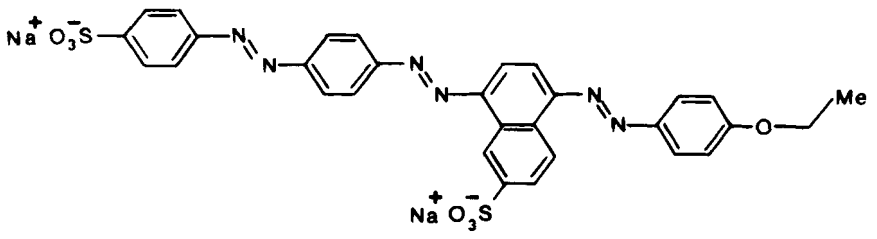
1. Introduction

It has been known for some years that certain dyes form liquid-crystalline or gel-like phases rather than isotropic solutions [1–4]. The earliest observations appear to be those of Jelley, in 1937, who described how an isotropic solution of 1 : 1′ diethylcyanine chloride 'ages' to produce a phase containing birefringent 'nematic threads' [1]. Although his paper does not include a micrograph of this texture, from the description given it is clear that the threads are actual structures rather than lines of disclination within a single-phase nematic region.

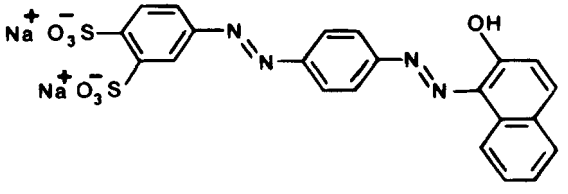
More recently, following a preliminary survey using polarization microscopy, each of the two azo dyes, Sirius Supra Brown RLL and Acid Red (cf. figure 1), was shown to form a single lyotropic mesophase at room temperature [5, 6]. The latter system in particular was studied in some detail and, on the basis of its optical texture, the mesophase formed was characterized as nematic. Moreover, on heating and cooling this phase, a rich variety of optical textures was exhibited and the overall form of the phase diagram therefore appeared to be complex.

These dye molecules are not of the conventional lyotropic mesogen form, with hydrophilic heads and long flexible hydrophobic tails; they are salts of planar polyaromatic acids and are therefore perhaps more readily identifiable with the anti-asthmatic/anti-allergic drugs which have previously been found to be mesogenic [7–9]. The first such mesogenic drug to be recognized was disodium cromoglycate (SCG) and the generic term 'chromonic' was subsequently coined to describe this type of mesophase formation. In general, two chromonic phases are encountered for each system: a fairly concentrated M phase, which is a hexagonal array of molecular stacks of some kind, and a more dilute N phase, which is a nematic array of probably the same stacks but separated by so much water that, although the parallelism is retained, the hexagonal ordering is lost.

In view of this apparent correspondence of molecular structure and the frequent reference to mesophase formation among such systems, there was clearly some likelihood that the dye mesophases which had previously been characterized as



Sirius Supra Brown RLL



"Acid Red"

Figure 1. The molecular structures of the two mesogenic dyes described in this paper, Sirius Supra Brown RLL, 4-[4-[4-(4-ethoxyphenylazo)]-7-sulphonaphthalenylazo]-phenylazo-benzene sulphonic acid disodium salt, 'Acid Red', 4-[[4-[(2-hydroxy-1-naphthalenyl)azo]-phenyl]azo]-1,2-benzenedisulphonic acid disodium salt.

nematic could be identified with the chromonic N phase. Furthermore, those instances where birefringent thread-like textures had been observed [1, 5, 6] were strongly suggestive of the presence of the chromonic M phase. We therefore set out to test the hypothesis that the mesophases of these two dyes were of the same structural types as the chromonic drug mesophases by seeking answers to the following questions:

(1) Do the dye systems give two mesophases with optical textures comparable with those of the chromonic drug N and M phases?

(2) Do the temperature/composition phase diagrams of the dye systems have the same qualitative form as those of the drug systems?

(3) Do the dye mesophases give X-ray diffraction patterns with the same features as those of the chromonic drug phases?

2. Experimental

Two commercial dyes with mesogenic properties were studied. Both a commercial sample of Sirius Supra Brown RLL (Farbenfabriken Bayer AG) and a sample of this dye purified by paper chromatography were examined. The Acid Red, which is similar in structure to CI Acid Red 151 (CI 26900) [10], but which contains an additional terminal sulphonate group, was synthesized by conventional diazotization and coupling and salting out. This dye was then purified by recrystallization using the procedure described by Hall and Perkins to remove inorganic salt [11]. We estimate

that the residual level of electrolyte impurity of the purified dyes does not exceed 0·05 per cent.

Microscopic studies were carried out with a Vickers polarizing microscope fitted with a Mettler FP52 heating stage and a FP5 control unit. The micrographs shown were obtained using a Zeiss Ultraphot. The X-ray diffraction patterns were obtained with a camera originally constructed in the Astbury Department of Biophysics for use with biological fibres. This camera has a double pinhole collimator giving a parallel beam of 250 μm diameter. The specimen to film distance was 60 mm and the diffraction pattern was recorded on a flat circular film. Samples were contained in 0·2 mm Lindemann glass tubes. Nickel filtered CuK_α radiation was used. Exposure times were typically of the order of 2 days. Prior to exposure, samples were characterized by means of their optical textures, and, following each diffraction run, the capillaries were examined to see whether they had retained the same optical texture. To ensure that no loss of water had occurred during exposure, the samples were then heated to check that the transition temperatures had also remained the same.

3. Results

Both of the dye/water systems investigated were found to give two mesophases at room temperature. The optical textures of both commercial and purified samples (in the range $\approx$ 5–12 wt %) were schlieren patterns indistinguishable from those of the drug N phases (cf. figure 2). The more concentrated phases of the dyes, formed by peripheral evaporation of the nematic phase, adopted an ill-defined, grainy texture, as illustrated on the left-hand side of figure 2. However, we were not able to demonstrate the characteristic herring-bone texture and, since we had encountered this texture for all of the drug M phases, we initially felt that this threw some doubt on the complete identity of the two series of mesophases.

Heating and cooling samples of various concentrations gave sequences of phase and texture changes which were familiar from our studies of chromonic drug systems. These gave an unequivocal indication of the overall peritectic form of the temperature/composition phase diagrams as depicted in figure 3. For example, at room temperature a 16 per cent solution of Sirius Brown dye exists in the M phase and has a texture like that shown on the left-hand side of figure 2. On heating, the sample passes into the two phase M + N region prior to becoming entirely nematic, as indicated by the formation of the schlieren texture. At higher temperatures, as the sample enters the N + I region the distinctive reticulated texture, shown in figure 4 (*a*), is developed with islands of isotropic solution held within a continuous network of N phase. The sample then passes briefly through the M + I region, where the overall appearance of the phase remains the same but the lattice develops a more grainy appearance as the N phase changes to M. The whole sample then reverts to the isotropic liquid. On cooling, the sequence of phase changes is reversed, but the phases are often characterized by different textures. In particular, the reticulated M + I texture does not occur, as the M phase emerges from the isotropic liquid as well-developed birefringent ribbons (as shown in figure 4 (*b*)).

The X-ray diffraction pattern of the more dilute mesophases ($\sim$ 8 wt %) of both dyes contained the same features as those of the chromonic drug N phases: a strong, fairly sharp 3·4 Å axial reflection and a diffuse inner equatorial reflection corresponding to spacings in the 40–60 Å range. The diffraction pattern of the more concentrated mesophase (24 wt %) of Acid Red was similar to those of the drug M phases. In

Figure 2. Optical textures of the two mesophases of the dye Sirius Supra Brown RLL (× 300 between crossed polars). This micrograph shows the boundary between the N and M mesophases as formed by peripheral evaporation of a 10 wt % sample of the N phase at room temperature. Note that although the N phase has a well-formed schlieren texture, the M phase has a confused grainy texture not readily identifiable with the herring-bone texture exhibited by chromonic drug M phases. (See figure 6 (*a*).)

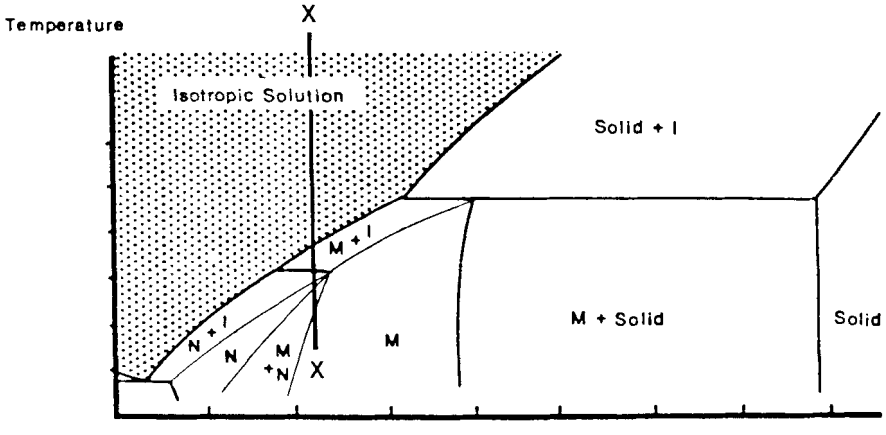
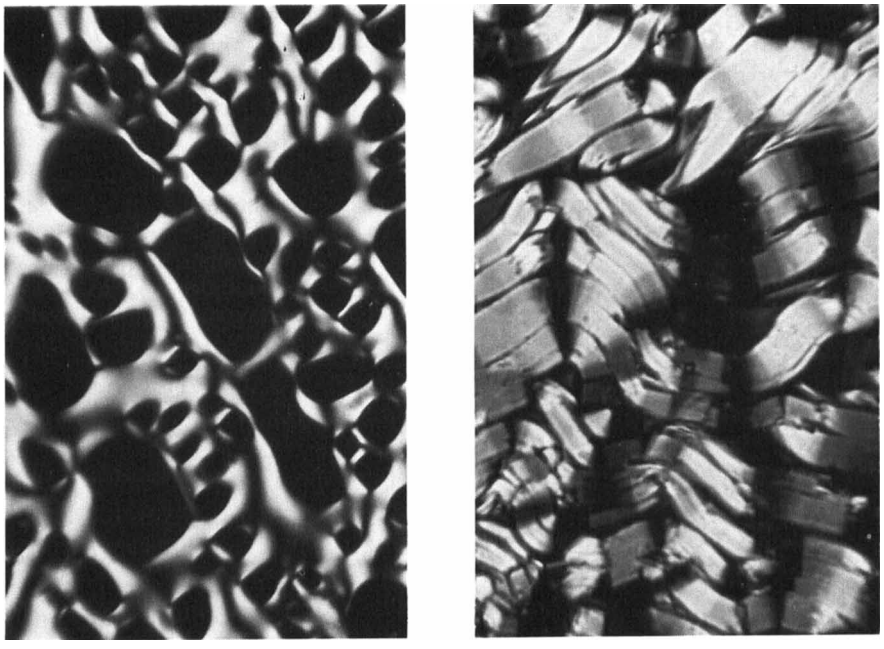
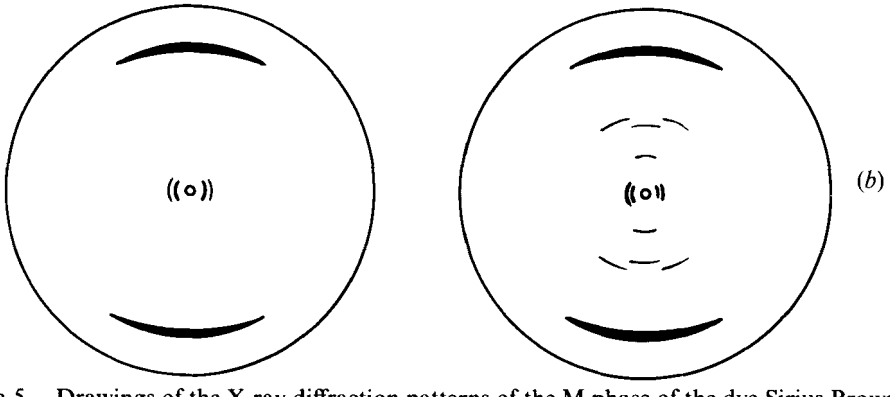


Figure 3. The temperature/composition phase diagram for chromonic systems. This peritectic form of phase diagram appears to be characteristic for chromonic systems—presumably because of the structural relationship between the N and M mesophases. This type of phase diagram is relatively easy to recognize from the sequence of phases formed on heating and cooling samples of various compositions. In particular, heating a sample with the composition represented by the line $\times - \times$ gives the sequence of phase changes; $M \rightarrow M + N \rightarrow N \rightarrow N + I \rightarrow M + I \rightarrow I$, where each one-phase or two-phase region has a very distinctive optical texture. On cooling, this sequence of phases is reversed, but with a different pattern of optical textures.



(*a*) (*b*)

Figure 4. Optical textures of two-phase regions of dye/water systems (× 300, between crossed polars). (*a*) The reticulated texture of the N + I region which occurs on heating the N phase. (*b*) The ribbon texture of the M + I region which occurs on cooling the isotropic solution. We have come to regard these two textures as being highly characteristic of chromonic systems, and these two samples are virtually indistinguishable from similar two-phase regions of chromonic drug/water systems.



(*a*) (*b*)

Figure 5. Drawings of the X-ray diffraction patterns of the M phase of the dye Sirius Brown RLL (18 per cent by wt) and of the M phase of the drug SCG (30 per cent by wt). The samples were contained in 0·2 mm diameter Lindemann glass capillary tubes. The axis of the tube corresponds to the vertical direction of the diffraction pattern. The samples aligned spontaneously on being drawn into the tubes and no magnetic alignment was required. The high-angle, axial arcs correspond to a spacing of 3·4 Å (the thickness of an aromatic molecule). The sharp, inner equatorial reflections correspond to the various repeat distances of the hexagonal lattice. (*a*) For Sirius Brown RLL, the two inner equatorial reflections correspond to spacings of 40 Å and 23 Å (i.e. in the ratio $1 : 1/\sqrt{3}$) and indicate a hexagonal lattice with column to column centre spacing of 46 Å. (*b*) For the SCG M phase the two equatorial spacings correspond to 31 Å and 18 Å (also in the ratio $1 : 1/\sqrt{3}$) and are the first two reflections from a hexagonal lattice with a 36 Å spacing.

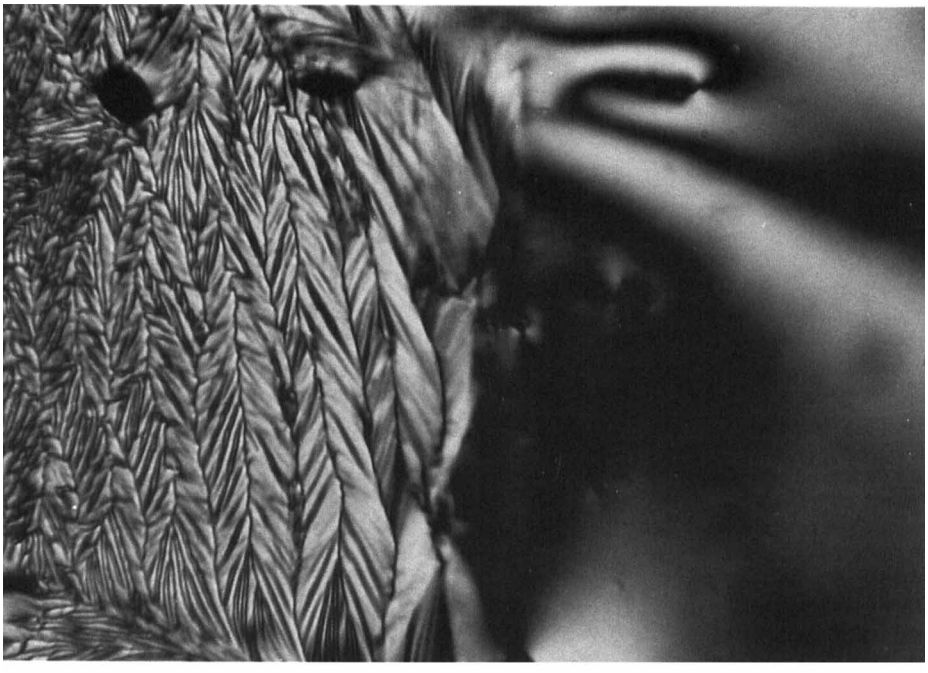
addition to the axial 3·4 Å reflections, there was a strong, sharp inner equatorial reflection at 46 Å and a weak, barely distinguishable reflection outside this. Finally, the diffraction pattern of the more concentrated phase (18 wt %) of Sirius Supra Brown RLL (cf. figure 5) also contained the same 3·4 Å arcs and a pair of sharp equatorial reflections with spacings of 40 Å and 23 Å, i.e. in the ratio $1:1/\sqrt{3}$, indicative of a hexagonal lattice.

The occurrence of the strong, sharp 3·4 Å axial reflections in all of the dye mesophase diffraction patterns implies that a feature inherent in the structures of these systems is an untilted stacking of molecules into extended columns, since this distance corresponds precisely to the thickness of an aromatic molecule. In the more dilute phases these columns stand off from each other by essentially random distances, while in the more concentrated phases a hexagonal array is adopted. Since all of these features are common to the diffraction patterns of the drug/water systems, we therefore regard this as convincing evidence for identifying the dye mesophases as structurally analogous to the chromonic drug N and M phases.

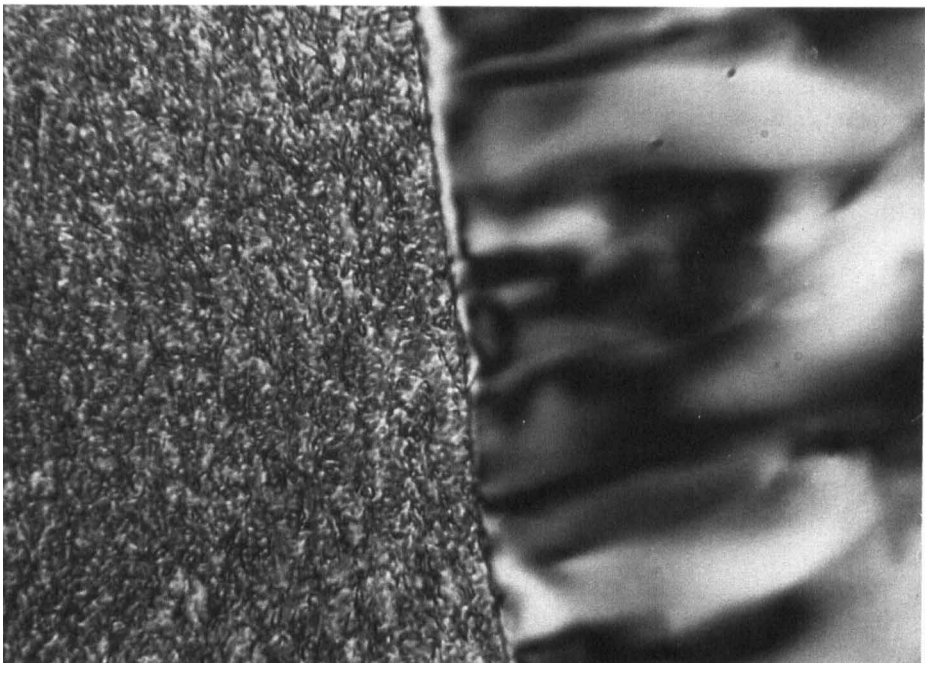
4. Discussion

A general correspondence between the optical textures, the X-ray diffraction patterns and the forms of the phase diagrams has been observed for the drug and dye mesophases. The only significant difference between the two families of mesogens appears to be in some of the optical textures and rheological properties of the M phases. While the drug M phases form a well-defined herring-bone texture and flow in a homogeneous manner when mechanically disturbed, the dye M phases from a poorly-developed, grainy texture and flow as distinct, fairly rigid domains. Such behaviour would appear to be suggestive of a phase tending towards a more gel-like state, with a greater degree of mechanical rigidity than an entirely homogeneous M phase. However, we feel that this need not be regarded as a fundamental distinction and may be due, in part, to the difference in dimensions of the two sets of mesogens, the dye molecules being, in general, two or three times as long as those of the chromogenic drugs. Indeed, the conditions for the formation of gels may not be very different from those required for the formation of chromonic M phases, and there may well be a smooth gradation of properties between these states. Two quite separate observations support this notion: firstly, we have found that an appreciable number of drugs and dyes, with molecular structures very closely related to those of chromonogenic species, form viscous gels rather than mesophases; and secondly, in contrast to the situation for conventional amphiphile mesophases, we have found that the addition of electrolyte impurities in mesophase samples tends to increase the viscosity of the M phase and causes it to assume a more gel-like nature; for example, the addition of 1 per cent of sodium chloride to the SCG/water system, whilst not noticeably affecting the schlieren texture of the N phase, does however inhibit the formation of the M phase herring-bone texture, giving a grainy appearance (cf. figure 6) virtually indistinguishable from that assumed by the dye M phases.

These observations are entirely consistent with those of Yu and Saupe who studied the effects of the addition of sodium chloride to nematic SCG/water systems using deuteron magnetic resonance [12]. They found that the added electrolyte raised the temperature of the N to I transition and they explained this in terms of a decrease in the electrostatic repulsions between the charged aggregates. In a similar fashion, we visualize the presence of salt impurities reducing the repulsive forces between the



(*a*)



(*b*)

Figure 6. The effect of adding sodium chloride on the optical textures of chromonic drug mesophases. (× 300, between crossed polars). (*a*) The boundary between the N and M mesophases of the SCG/water system. Note the schlieren texture of the N phase on the right and the well-developed herring-bone texture of the M phase on the left. The specimen was prepared by peripheral evaporation of a 15 wt % sample of the N phase at room temperature. (*b*) The N/M boundary of a sample of the SCG/water system prepared as in (*a*) but with the addition of 1 per cent sodium chloride. Note the correspondence of the N phase textures but the deterioration of the M phase texture to a confused grainy state similar to that shown by the dye/water M phases (as in figure 2).

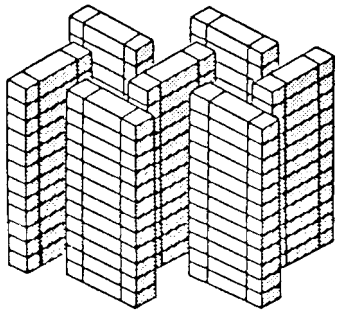


Figure 7. The new herring-bone model for the structure of the chromonic M phase. This sketch shows an instantaneous snapshot view of the proposed structure. Although the axes of the columns lie on a hexagonal lattice, this array has only orthorhombic symmetry, but rotational disorder gives rise to the hexagonal symmetry in a manner similar to that which operates in the thermotropic smectic B phase. (Reproduced with permission from [13].)

columns in the dye M phase causing the phase to contract and stiffen into a gel with a concomitant reduction in long range order resulting in a deterioration of the optical texture.

Recently we proposed a model for the structure of the chomonic M phase in which the molecules are stacked, as shown in figure 7, in an untilted fashion in columns that lie in a herring-bone array within a water continuum [13]. The hexagonal spacing of this model is equal to half the molecular length plus half the molecular width together with a layer of water and counter-ions. The lattice dimensions derived from our diffraction data and the dimensions of the molecules concerned are entirely compatible with this model and indicate that the water plus counter-ion layer is of the order of 10–20 Å. (A quantitative survey of a number of M phases will be given in a further paper.)

5. Conclusion

We conclude that the pairs of mesophases formed by the two sulphonated azo dyes, Sirius Supra Brown RLL and Acid Red, are structurally analogous to the chromonic N and M phases of anti-asthmatic/anti-allergic drugs. We suspect that other dye/water systems will also prove to be of this type and that chromonic phases therefore represent a large, well-defined new category of mesogens, embracing drugs, dyes and other similar hydrophilic aromatic species.

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