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Designing new lyotropic amphiphilic mesogens to optimize the stability of nematic phases

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The factors which govern the stability of lyotropic amphiphilic nematic phases are delineated and then used to design mesogens which give rise to stable N_C and N_D phases on dissolution in water. The synthesis and phase behaviour of novel discoid amphiphiles, designed to form N_C phases, are described.

1. Introduction

The nematic phase has played a seminal role in the experimental and theoretical investigation of thermotropic liquid crystals and in their practical exploitation [1]. This is because only this phase can be macroscopically aligned and manipulated by electric, magnetic and surface interactions. Nematic phases have only fairly recently been known to exist in mixtures of lyotropic amphiphilic mesogens (conventionally, soaps, synthetic surfactants and biological surfactants) and water. Their absence, until now, has undoubtedly retarded the development of both our understanding and creative exploitation of lyotropic amphiphilic liquid crystals.

Lyotropic amphiphilic nematic phases were first discovered in 1967 [2]. They have been shown to be solutions of orientationally ordered discoid (N_D) or columnar (rod-shaped) (N_C) micelles [3–7]. These phases are generally believed to be stable only over very restricted concentration intervals in complex mixtures of an ionic surfactant, water, a co-surfactant and/or a simple inorganic salt [8, 9]. The view has been held that only ionic surfactants form nematic phases and that the role of the salt is to destabilize lamellar or hexagonal phases and thereby to promote the formation of nematic phases [5, 10]. It has also recently been argued [11] that the role of the co-surfactant (a long chain alcohol) is to stabilize small discoid micelles in N_D phases by "slowing down the growth of the aggregate with increasing concentration". This argument was advanced because current models [12] for the aggregation behaviour of amphiphiles in solution predict that small finite bilayer micelles are unstable. It is more likely, however, that the effect of the addition of salt or alcohol is simply to modify the smectic (columnar or lamellar) phase behaviour in such a manner as to bring the smectic to isotropic transition line into the temperature-composition domain where nematic phases are stable.

The picture which is beginning to emerge indicates that nematic phases occur intermediate to an isotropic micellar solution at higher temperatures/lower concentrations and a smectic phase at lower temperature/higher concentration. They appear to be stable within the concentration internal 0·1 to 0·5 volume fraction of amphiphile and below about 350 K. Conventional amphiphiles generally exhibit complex aggregation and phase behaviour (figure 1). This imposes severe restrictions on the extent of any nematic phase. To obtain nematic phases which are stable over a wide

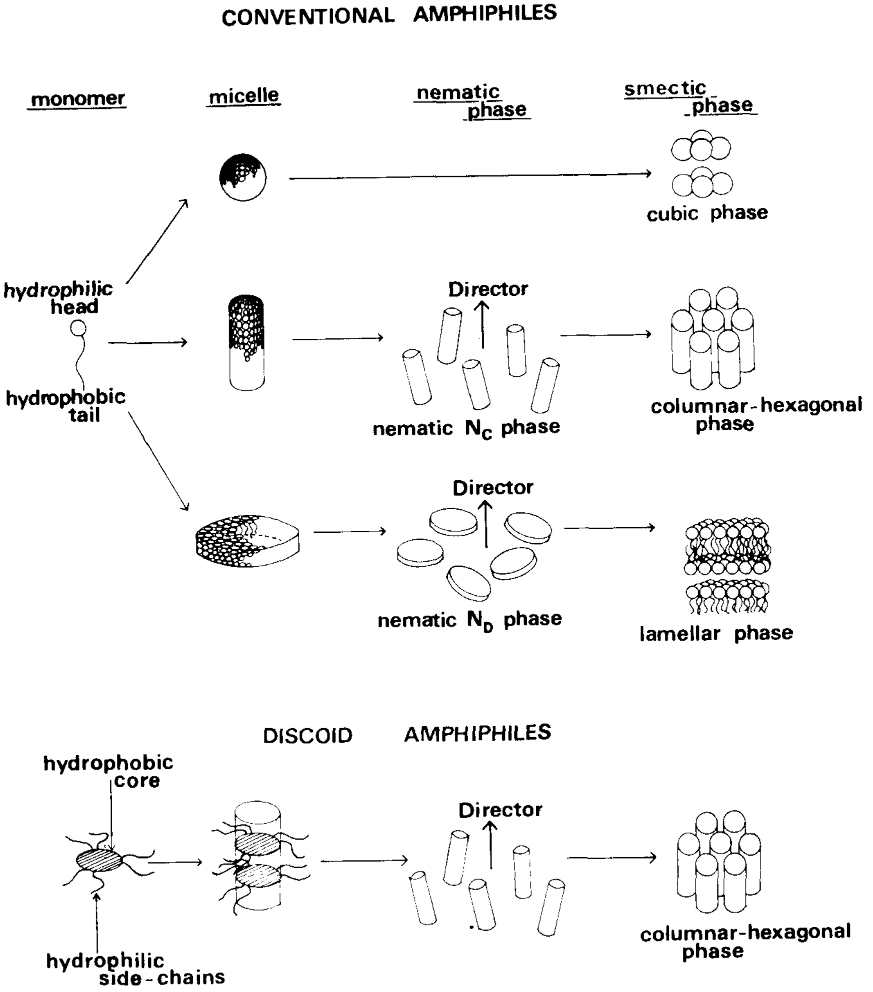


Figure 1. Schematic representation of possible structures of aggregates formed by conventional and discoid amphiphiles of the TP6EO2M type in water and their arrangements in mesophases. The concentration of amphiphile should be read as increasing from left-to-right and top-to-bottom.

concentration range it is necessary to constrain the structure of the aggregate to a single kind across, at least, this concentration window.

The structure of the aggregate depends upon both the chemical structure of the amphiphile and the inter-aggregate interaction. The influence of the latter on the shape of the aggregate, though not necessarily its size, can be suppressed by designing amphiphiles which can only form aggregates of a particular structure. For example, to obtain N_C phases it is necessary to choose an amphiphile which can only assemble into columnar aggregates. This requires a discoid amphiphile consisting of a hydrophobic core which is laterally surrounded by hydrophilic groups. An example of such a discoid amphiphile is 2,3,6,7,10,11-hexa-(1,4,7-trioxa-octyl)-triphenylene (**1d**, in figure 2) henceforth abbreviated TP6EO2M. In water this amphiphile forms a N_C phase over wide concentration (0·14 to 0·51 volume fraction of amphiphile) and temperature intervals [13, 14]. It occurs intermediate to an isotropic micellar solution at higher temperatures and a columnar hexagonal phase at lower temperatures. This is the first example of a non-ionic amphiphile which forms a nematic micellar solution in water.

Similarly, to prepare stable N_D phases it is necessary to choose an amphiphile which will only form discoid micelles and bilayer aggregates. An amphiphile consisting of a fairly rigid lath-shaped or rod-shaped hydrophobic moiety attached to a hydrophilic group which does not have a strongly hydrated counterion is required. The amphiphile caesium pentadecafluoroctanoate (CsPFO) satisfies these requirements. The CsPFO/water (^2H_2O) system has been shown [15] to exhibit an N_D phase over wide concentration (0·11 to 0·43 volume fraction of CsPFO) and temperature (284 to 350 K) ranges. This occurs between an isotropic micellar solution to higher temperature and a lamellar phase to lower temperature. Only aggregates with a bilayer structure are formed over the whole concentration range. This is a consequence of the rigidity and hydrophobicity of the fluorocarbon chain which combined with the low hydration energy of the caesium ion promotes the stability of bilayer aggregates as opposed to cylindrical ones. The LiPFO/water system exhibits the formation of a hexagonal phase [16] as a consequence of the larger hydration energy of the lithium ion. Thus, the PFO^- anion can be arranged into columnar aggregates. Other amphiphiles which would only pack into bilayer aggregates could readily be designed.

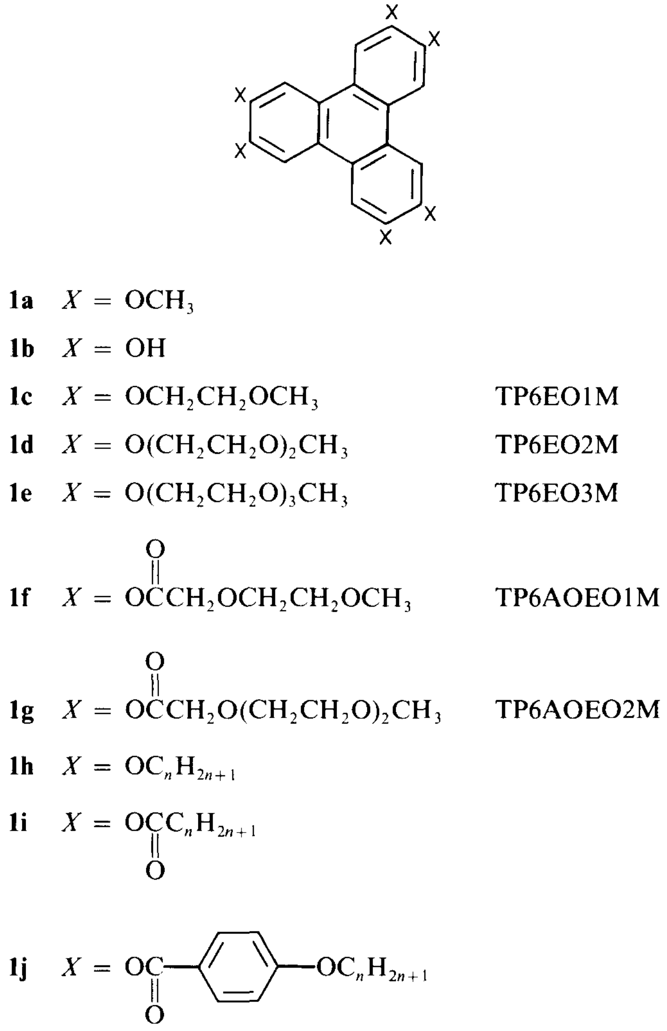
The phase behaviour of the TP6EO2M/water and the CsPFO/water systems show unequivocally that stable nematic phases can be formed in simple two component mixtures. There is clearly no need to add either salt or alcohol. The effect of addition of either of these components is to modify the underlying smectic phase behaviour in such a manner as to bring the smectic to isotropic transition line into the temperature-composition domain where nematic phases are stable.

By way of illustration of these principles we shall examine the relation between molecular structure and the mesophase behaviour of several novel discoid amphiphiles. In particular, we shall seek to specify those structural features of amphiphiles which promote the formation of N_C phases. First, we shall present a detailed description of the phase behaviour and aggregate structures of the TP6EO2M amphiphile in water as a model. The phase behaviour of the discoid amphiphiles **1c** to **1g** (figure 2) are then compared. Full details of the preparative methods and of the characterization of these compounds are contained in the section on synthesis. Finally, we review the structures and aggregation behaviour of molecules previously reported in the literature which possess the discoid amphiphile topology.

2. Synthesis of discoid amphiphiles

The amphiphiles **1c**–**1e** (figure 2) were obtained by treating the hexahydroxy compound **1b** with sodium hydride in dry dimethylsulphoxide followed by reaction with the appropriate alkyl halide. The corresponding esters **1f** and **1g** were obtained similarly by treating the hexahydroxy compound **1b** in pyridine with the appropriate acid chloride.

2,3,6,7,10,11-Hexa-(1,4-dioxapenyl)-, 2,3,6,7,10,11-hexa-(1,4,7-tri-oxaoctyl)-, and 2,3,6,7,10,11-hexa-(1,4,7,10-tetraoxaundecyl)-triphenylene (**1c**–**1e**). 2,3,6,7,10,11-Hexamethoxytriphenylene **1a** was prepared by treatment of veratrole with chloranil in 70 per cent v/v sulphuric acid [17] and purified by chromatography on sorbasil M60 (Crossfield) eluting with chloroform to give a light grey powder, m.p. > 300°C, δ_H ($CDCl_3$) 4·10 (18H, *s*, OCH_3) and 7·70 (6H, *s*, ArH). Demethylation could be achieved by treatment with borontribromide in methylene chloride, [13] but a higher yield of a purer product was obtained by using the hydrogen bromide/acetic acid method of Piattelli *et al.* [18]. 2,3,6,7,10,11-Hexahydroxytriphenylene **1b** was obtained as a light grey powder which was dried *in vacuo* over phosphorus pentoxide and which darkened on storage, δ_H (d_6-acetone) 7·85 (6H, *s*, ArH) and 8·10 (6H, *s*, exchanged by D_2O, OH).



1a $X = OCH_3$

1b $X = OH$

1c $X = OCH_2CH_2OCH_3$ TP6EO1M

1d $X = O(CH_2CH_2O)_2CH_3$ TP6EO2M

1e $X = O(CH_2CH_2O)_3CH_3$ TP6EO3M

1f $X = O\overset{O}{\overset{\parallel}{C}}CH_2OCH_2CH_2OCH_3$ TP6AOEO1M

1g $X = O\overset{O}{\overset{\parallel}{C}}CH_2O(CH_2CH_2O)_2CH_3$ TP6AOEO2M

1h $X = OC_nH_{2n+1}$

1i $X = O\underset{O}{\underset{\parallel}{C}}C_nH_{2n+1}$

1j $X = O\underset{O}{\underset{\parallel}{C}}-\quad-OC_nH_{2n+1}$

Figure 2. Structures of derivatives of triphenylene.

2,3,6,7,10,11-Hexahydroxytriphenylene **1b** (325 mg) in dry dimethylsulphoxide under an atmosphere of dry nitrogen was treated with sodium hydride (240 mg, 60 per cent w/w suspension in paraffin). After stirring the mixture for 45 min 2-methoxybromoethane (3-oxabromobutane) (840 mg) in dry dimethylsulphoxide was added dropwise over 5 min. The stirred mixture was heated slowly (over 1 hour) to 90°C. Effervescence was noted at *c.* 45°C. The essentially clear solution was cooled, diluted with water, acidified (dilute hydrochloric acid), and extracted with chloroform. The chloroform extracts were washed with water, dried with magnesium sulphate, filtered and evaporated under reduced pressure. Trituration of the product with methanol gave the crude 2,3,6,7,10,11-hexa-(1,4-dioxapentyl)-triphenylene **1c** as a yellow solid (365 mg, 54 per cent). This was purified by short column chromatography on Kieselgel [19] eluting with chloroform and by recrystallization from benzene to give the triphenylene **1c** as white crystals m.p. 161 to 167°C (found: C, 64·4 per cent; H, 7·3 per cent. $C_{36}H_{48}O_{12}$ requires C, 64·3 per cent; H, 7·2 per cent) δ_H 3·51 (18H, *s*, CH_3O), 3·89, 4·39 (each 12H, approximate *t*, $J = 6$ Hz, OCH_2CH_2O), and 7·87 (6H, *s*, ArH), *m/e* 672 (M^+, 23 per cent) and 59 ($CH_3OCH_2CH_2^+$, 100 per cent).

In a similar manner, reaction of 2′-methoxy-2-ethoxybromoethane (3,6-dioxabromoheptane) [20] (8·55 g, 46 mmol) with 2,3,6,7,10,11-hexahydroxytriphenylene **1b** (2·19 g, 6·75 mmol) and sodium hydride (1·85 g, 60 per cent w/w. 46 mmol) gave 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)-triphenylene **1d** (0·962 g after purification, 15 per cent) as off-white needles, m.p. 51 to 53°C (found: C, 61·4 per cent; H, 7·8 per cent. $C_{48}H_{72}O_{18}$ requires C, 61·5 per cent; H, 7·7 per cent) δ_H ($CDCl_3$) 3·40 (18H, *s*, CH_3O), 3·60, 3·80 (each 12H, *m*, $-OCH_2CH_2O-$), 4·0, 4·40 (each 12H, approximate *t*, $-OCH_2CH_2O-$), and 7·88 (6H, *s*, ArH). Rigorous purification of this material required repeated short column chromatography [19] on Kieselgel G_F (Merck) eluting with 2 to 4 per cent ethanol in dichloromethane to free it from an oily impurity which had very similar chromatographic behaviour. Higher yields (up to 22 per cent after purification) could be obtained on a smaller scale but the yield was generally found to fall on increasing the scale employed.

In a similar manner reaction of 2″-methoxy-2′-ethoxy-2-ethoxybromoethane (3,6,9-trioxabromodecane, from 3,6,9-trioxadecanol and phosphorus tribromide [21]) with 2,3,6,7,10,11-hexahydroxytriphenylene **1b** gave 2,3,6,7,10,11-hexa-(1,4,7,10-tetraoxaundecanyl)-triphenylene **1e** as a colourless viscous oil. δ_H ($CDCl_3$) 3·40 (18H, *s*, CH_3O-), 3·5 to 4·0 (48H, *m*, 2 × $-OCH_2CH_2-$), 4·05, 4·47 (each 12H, approximate *t*, $-OCH_2CH_2O-$), and 7·98 (6H, *s*, ArH).

Aqueous solutions of TP6EO2M and related compounds (i.e. compounds **1c**–**1e** were subject to slow air oxidation and darkened on storage. Solutions must, therefore, be handled under an atmosphere of nitrogen or under vacuum.

3,6-Dioxaheptanoate and 3,6,9-trioxadecanoate esters of 2,3,6,7,10,11-hexahydroxytriphenylene (**1f** *and* **1g**). 3,6,9-Trioxadecanoyl chloride (from the reaction of 3·7 g 3,6,9-trioxadecanoic acid [22] and thionyl chloride) was added dropwise over 15 min to a stirred solution of 2,3,6,7,10,11-hexa-hydroxytriphenylene **1b** (972 mg) in pyridine under an atmosphere of nitrogen. A mildly exothermic reaction occurred and a white precipitate formed. The stirred mixture was heated at 90°C for 15 min. The brown solution was cooled and dilute hydrochloric acid added. It was extracted with chloroform, the chloroform extracts were washed with dilute hydrochloric acid and aqueous potassium carbonate, dried, filtered, and evaporated under reduced pressure to give the crude ester which was purified by short column chromatography on Kieselgel eluting with chloroform. 2,3,6,7,10,11-Hexahydroxytriphenylene hexa-3,6,9-trioxadecanoate **1g** was obtained as a colourless oil (700 mg, 18 per cent), δ_H ($CDCl_3$) 3·42 (18H, *s*, CH_3O-), 3·5 to 4·0 (48H, *m*, 2 × $-OCH_2CH_2O-$). 4·54 (12H, *s*, $-OCH_2CO-$) and 8·03 (6H, *s*, ArH).

In a similar manner reaction with the acid chloride of 3,6-dioxaheptanoic acid [22] gave 2,3,6,7,10,11-hexahydroxytriphenylene hexa-3,6-dioxaheptanoate **1f** as a white crystalline solid, δ_H ($CDCl_3$) 3·48 (18H, *s*, CH_3O-), 3·70, 3·93 (each 12H, *m*, $-OCH_2CH_2O-$), 4·57 (12H, *s*, $-OCH_2CO-$), and 8·01 (6H, *s*, ArH).

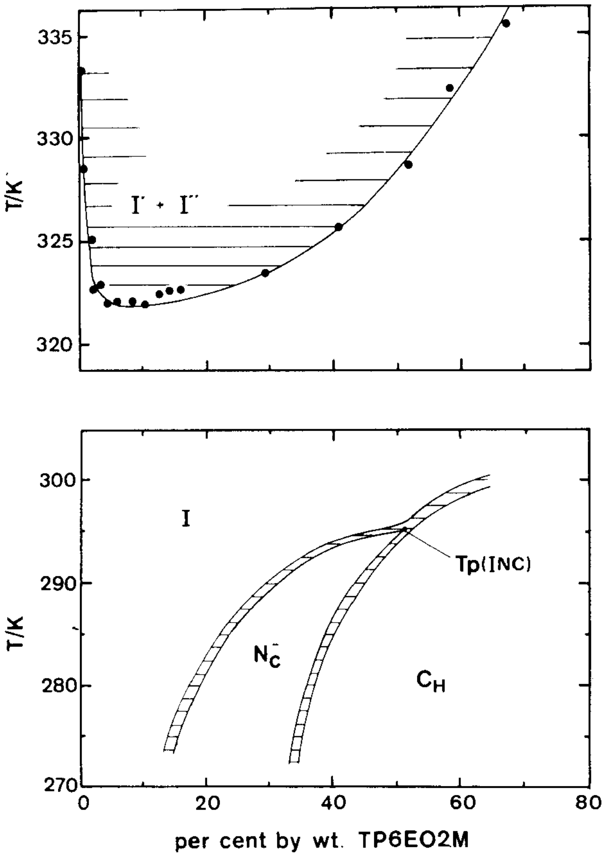


Figure 3. A portion of the phase diagram of the TP6EO2M/water (^2H_2O) system showing isotropic micellar solution (I), nematic phase with negative diamagnetic anisotropy and columnar shaped micelles (N_C^-), columnar phase with hexagonal arrangement of aggregates (C_H), the isotropic–nematic–columnar triple point T_p (INC) (51·2 ± 0·4 per cent by weight TP6EO2M, 295·4 ± 0·2 K), and the coexistence of the two isotropic phases I′ and I″.

3. Phase behaviour of the TP6EO2M/water system

The phase diagram of TP6EO2M in water (^2H_2O) is shown in figure 3. The unshaded areas represent homogeneous states and the shaded areas regions of phase separation. The nematic phase is seen to extend from 14 to 51 per cent by weight of TP6EO2M (with a roughly corresponding extent on a volume fraction scale). The lower temperature boundary below 273 K has not yet been determined. The phase boundaries were mapped by deuterium N.M.R. spectroscopy. This technique also established the anisotropy of the diamagnetic susceptibility ($\Delta\chi = \chi_\parallel - \chi_\perp$) of the nematic and hexagonal phases as negative, i.e. the nematic phase is of type N_C^- [7]. In the N.M.R. experiments the temperature of the sample was controlled to within ± 5 mK and measured to a precision of ± 10 mK; the phase boundaries may therefore be regarded to have a precision of ± 50 mK. The consolution (cloud point) curve was determined by direct observation and is considered to have a precision of ± 1 K. Above this curve the system separates into two isotropic micellar solutions I′ and I″.

There are a number of features of the phase diagram to which we wish to draw attention. First, it demonstrates how the phase behaviour of an amphiphile/water mixture is greatly simplified when the amphiphile can only assemble into aggregates of a particular structure, irrespective of concentration. Secondly, it shows that nematic phases of the type N_C can be stable over wide concentration ranges in simple two component mixtures. Thirdly, both the hexagonal to nematic and nematic to isotropic transitions are first order as predicted by molecular field theories for the analogous thermotropic transitions [23]. Fourthly, the phase behaviour is similar in form to that already established for the CsPFO/water system which shows a corresponding lamellar–nematic (N_D) isotropic sequence of phases [15].

4. Structures of mesophases

The structures of the various phases have been studied by X-ray diffraction. The X-ray scattering patterns observed on cooling a sample containing 40 per cent by weight of TP6EO2M in water (^2H_2O) are shown in figure 4. In the isotropic phase at 301 K the low angle X-ray pattern exhibits a characteristic single broad isotropic reflection. From the maxima of the scattering curve, using Bragg's Law, we calculate $d_0 = 2{\cdot}61$ nm. If we assume the X-rays are scattered from the (1 1 1) planes of a face centred cubic lattice [24] with separation d_0, a value for the volume of the micelle can be calculated from $V_m = \frac{3}{4}\sqrt{3}\phi_A d_0^3$ where ϕ_A is the volume fraction of amphiphile (0·409). This gives $9{\cdot}45 \times 10^{-27}\,m^3$ for V_m and an aggregation number of 6·5 ($V_{mol} \approx 1{\cdot}46 \times 10^{-27}\,m^3$). The inter planar separation of the molecules in the columnar micelle is 0·352 nm (see later) which gives a value of 2·36 nm for the length of the aromatic core of the micelle. The centre-to-centre separation of the micelles, $s = \sqrt{\frac{3}{2}}\,d_0$, is 3·2 nm.

The low angle X-ray scattering pattern (figure 4 (*b*)) of the aligned nematic phase at 298 K is anisotropic and indicative of columnar micelles with their symmetry axes aligned along the direction of the nematic director (z axis). The intense reflection in the *equatorial* plane arises from the side-by-side separation $d_\perp$ of the micelles in the plane perpendicular to the director. The weak reflection in the *meridional* plane most likely arises from unaligned mesophase rather than from the end-to-end separation of the micelles. (Stable, single domain samples are difficult to prepare in Lindemann capillaries because of the strong interaction of the mesophase with the walls.) The absence of any information about this separation means we have a very limited picture of the packing of micelles in this phase. To obtain a rough estimate of the density of micelles we have assumed the micelles are arranged on a face centred cubic packed lattice, as in the isotropic phase, with the nematic director aligned perpendicular to the (1 1 1) planes. From $d_\perp$ (2·95 nm) we obtain $d_0 = \frac{1}{3}(2)^{3/2}d_\perp$ which gives a value of $11{\cdot}4 \times 10^{-27}\,m^2$ for V_m. The aggregation number of the micelle is 7·8 molecules, the length of the aromatic core is 2·75 nm and its centre-to-centre separation is 3·4 nm. These values are quite acceptable when compared with the corresponding ones in the isotropic phase at 301 K. The micelles are a little longer and their lateral separation a little greater.

The low angle X-ray diffraction of an unaligned sample at 279 K in the hexagonal phase shows two distinct rings (figure 4 (*c*)) corresponding to spacings ($d_1 = 2{\cdot}68$ nm and $d_2 = 1{\cdot}57$ nm) in the ratio of $1 : 1/\sqrt{3}$ which is characteristic of a two-dimensional hexagonal lattice. (The outer ring is of low intensity and its position is indicated in the figure by the arrows.) The centre-to-centre separation of the aggregates can be

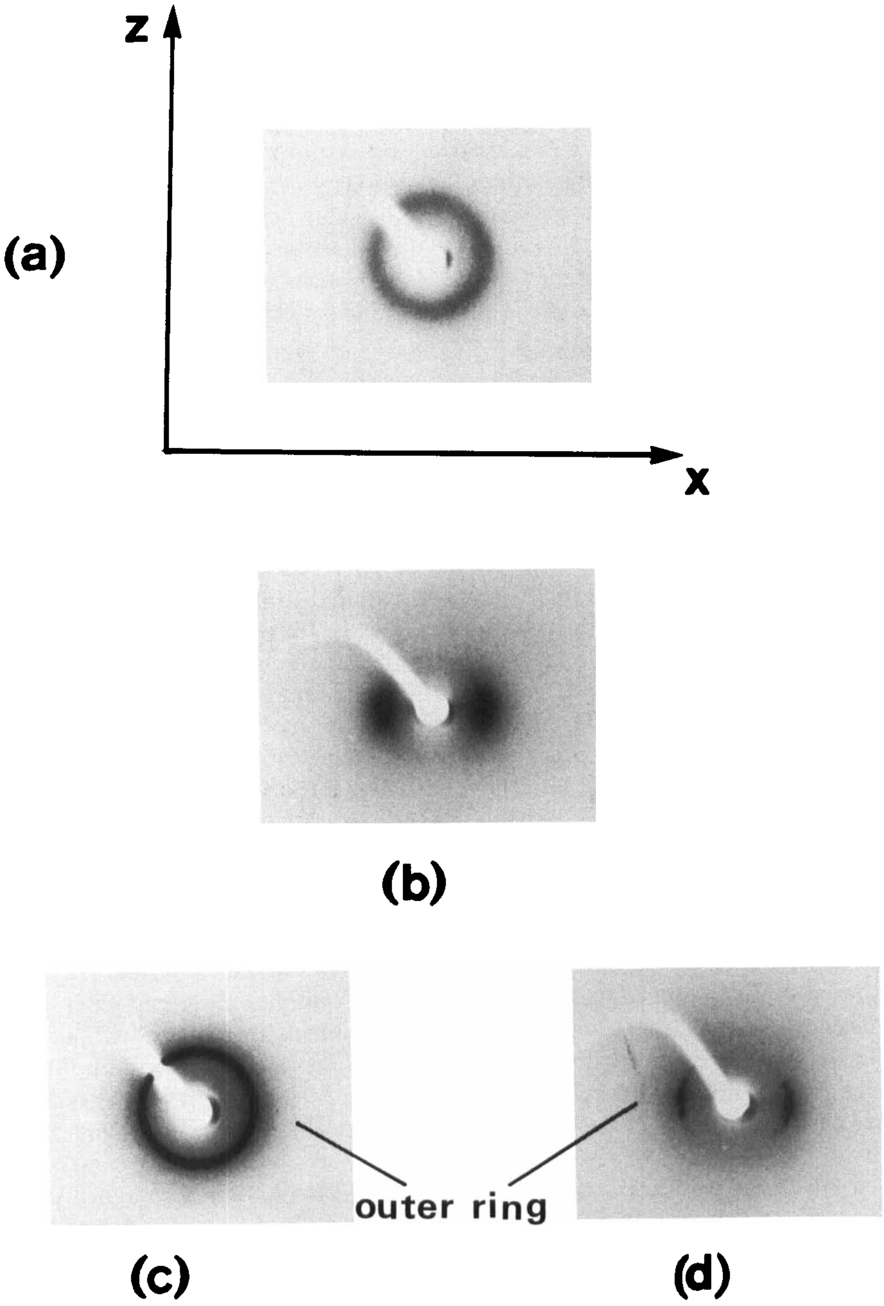


Figure 4. X-ray scattering patterns of TP6EO2M (40 per cent by weight)/$^{2}H_2O$ ((*a*) isotropic micellar solution at 301 K; (*b*) aligned nematic phase at 298 K; (*c*) unaligned hexagonal phase at 279 K; (*d*) as in (*c*) but with an aligned sample) observed with a pinhole camera, monochromatic Cu/K_α radiation of wavelength 0·154 nm, point collimation and Lindemann sample tube (0·5 mm i.d.) to flat plate distance of 117·5 mm. The nematic director was aligned parallel to the *z* axis (*meridian*) by rotation of the capillary tube about its long axis which is oriented perpendicular to a 0·4 T magnetic field. The direction of the magnetic field is parallel to the *x* axis (*equator*).

obtained from $d_1 = \frac{1}{2}\sqrt{3}s$ and has the value 3·10 nm. The scattering pattern of the aligned sample (figure 4 (*d*)) shows that the alignment is not perfect. It is impossible to tell whether or not the columnar micelles are of indefinite extent in the hexagonal phase. At larger angles a weak diffuse reflection (not shown in figure 4 (*c*)) occurs in the *meridional* plane. A similar reflection is also observed in the nematic phase. It arises from diffraction of X-rays by the aromatic planes regularly stacked perpendicular to the symmetry axis of the micelle. The interplanar separation is 0·352 nm and is very similar to the separation (0·359 nm) of the aromatic rings in the columns of the hexagonal phase of the analogous thermotropic mesogen 2,3,6,7,10,11-hexa-pentyloxytriphenylene [25].

A more refined X-ray study of the structures of both the nematic and hexagonal phases is undoubtedly required. However, the results of the present investigation show quite clearly that the amphiphiles are stacked in columns in a manner similar to that depicted in figure 1. This result enables us to understand why $\Delta\chi < 0$. It is because the lowest energy configuration of a triphenylene ring is when its plane lies in the direction of the magnetic field. The magnitude of $\Delta\chi$ is probably unusually large for a lyotropic nematic phase as indicated by the short magnetic relaxation time of the nematic director. Such a conclusion is consistent with the large diamagnetic susceptibility exhaltation found in polynuclear aromatic compounds [26].

For N_C phases formed by conventional amphiphiles, the axial ratio l/d is typically 2 to 4 [4]. In the case of TP6EO2M micelles it is not obvious as to what values to take for l and d. This is because the micelle consists of a fairly rigid aromatic core, of length roughly 2·4 to 2·8 nm and diameter 1·2 nm coated with a layer of ethyleneoxy chains which have a maximum extension of 1·15 nm. The actual thickness of this layer will probably be somewhat less depending upon the conformation of the ethyleneoxy chains. The normally preferred conformation of ethyleneoxy chains is a spiral *tgt* sequence [27]. Assuming the maximum possible extension of these chains gives an axial ratio in the range 1·33 to 1·44, whilst for the core itself the values are in the range 1·96 to 2·29. The latter values are more in line with the behaviour of nematic phases formed by conventional amphiphiles and we are tempted to conclude that the effective size of the micelle is governed by the hard core dimensions with the ethyleneoxy side-chains forming part of the fluid dispersing medium; but this is probably far too simple a notion.

The result that the length of the micelle (assuming the hard core dimensions) is of the order of the centre-to-centre separation has implications for the applicability, or, rather, the non-applicability, of the Onsager model [28]. This model has recently been used by Gelbart and co-workers [29] as the basis of statistical mechanical models for such systems. The Onsager model predicts an isotropic to nematic transition at a density $\varrho^* \approx 1/dl^2$ which is greater than that attained here. It could be argued that the Onsager model is quite inappropriate to the TP6EO2M/water system. It is, however, probably quite significant, too, that in the CsPFO/water system the diameter of the discoid micelle is of the order of the centre-to-centre separation across the entire concentration range of the nematic phase. The notion which is beginning to emerge is that the factors which control the size of micelles in concentrated solutions of amphiphiles in water are universal and not directly governed by the chemical structure of the hydrophilic group(s) of the amphiphile.

A referee has objected to the description of the aggregates formed by TP6EO2M in water as micelles. A detailed investigation of the aggregation behaviour and surface activity of this substance is in progress and the results will be published elsewhere when it is complete. It is, however, appropriate to refer briefly here to some preliminary results which confirm that we are indeed concerned, in the concentration interval of mesophase formation, with well defined aggregates which satisfy the description of micelles in the spirit of the original usage of McBain and Salmon [30]. First, using U.V. spectroscopy, it has been established that at 293 K the C.M.C. is approximately 10^{-5} mol dm^{-3} and the aggregation number is between four and five. Micellization will, as a consequence of this low aggregation number, occur over a wider concentration interval than it would for a conventional water soluble surfactant which forms micelles with aggregation number between 40 to 100 monomer molecules [31]. Secondly, using X-ray diffraction, it has been shown that at the same temperature the size of the micelle increases with concentration, reaches a maximum aggregation number of 15 molecules at approximately 0·4 mol dm^{-3} and thereafter decreases. Significantly, this behaviour is quite analogous to that exhibited by the caesium pentadecafluorooctanoate/water system, except that in this case the maximum size occurs at 1·0 mol dm^{-3}. Incidentally, the phase behaviour of this latter system is very similar to that of TP6EO2M, but with an N_D phase occurring intermediate to an isotropic micellar solution at high temperature and a lamellar phase at lower temperature; the aggregation number for what are believed to be discoid micelles in this system varies between 100 to 300. Returning to the TP6EO2M system, the micelles are found to increase in size with temperature on approaching the cloud point curve. For example, for a 40 per cent by weight TP6EO2M sample, the aggregation number is 34 at 320 K. It is important to recognize that each molecule of TP6EO2M has six side-chains and must, therefore, be considered as equivalent to six conventional amphiphiles when comparing aggregation numbers. If we accept this view it means that the micelles have equivalent aggregation numbers from 30 to 210 which is quite normal. Moreover, experiment also shows that in the micellar aggregates the triphenylene rings are close-packed one on top of the other. Thus, the micelles are quite clearly well defined aggregates and not ill-defined, loose associations of amphiphiles.

5. The nature of the phase-transitions

The D.S.C. thermogram recorded for a sample which contains 40 per cent by weight TP6EO2M is reproduced in figure 5. The lower temperature peak A is identified with the hexagonal to nematic transition and the higher temperature peak B with the nematic to isotropic transition. The widths of the peaks are somewhat greater than the widths of the corresponding transitions obtained from N.M.R. ($T_{\rm HN}$ = 284·50 K, $T_{\rm NH}$ = 286·38 K: $\Delta T_{\rm HN}$ = 1·88 K; $T_{\rm NI}$ = 293·70 K, $T_{\rm IN}$ = 294·25 K: $\Delta T_{\rm NI}$ = 0·55 K). The transition enthalpies $\Delta H_{\rm HN}$ = (0·87 ± 0·17) kJ mol^{-1} (of amphiphile), $\Delta H_{\rm NI}$ = (1·87 ± 0·19) kJ mol^{-1} and entropies $\Delta S_{\rm HN}$ = (0·37 ± 0·07) R and $\Delta S_{\rm NI}$ = (0·77 ± 0·07) R are in the inverse of the order one might have expected.

The value of $\Delta S_{\rm NI}$ is in the range usually encountered for thermotropic mesogens [1]. However, such comparisons are not significant because the nematogenic particles are discrete micelles whose structure does not change substantially at the nematic to isotropic transition; for a micelle containing seven amphiphilic molecules $\Delta S_{\rm NI} \approx 5{\cdot}39\,R$ (per mole of micelle), which is rather a large value. Studies of the concentration dependence of $\Delta S_{\rm NI}$ are currently in progress.

It is instructive to compare the variation with concentration of the hexagonal to nematic and nematic to isotropic transition temperatures with the predictions of the mean field theories developed for the analogous thermotropic mesophases [23]. The

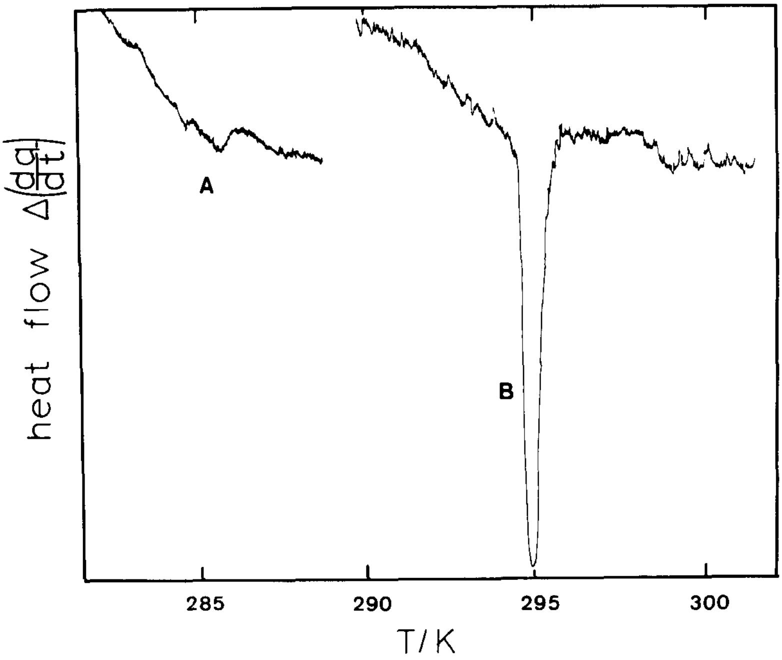


Figure 5. D.S.C. thermograms observed for a sample of TP6EO2M (40 per cent by wt)/^2H_2O using a DuPont 900 instrument.

theory predicts that the temperature of the hexagonal to nematic transition increases with increasing strength of the interaction driving the transition. For thermotropic mesogens this is believed to be the mutual attraction of the central aromatic cores. The transition temperature is, therefore, expected to increase with the length of the alkyl side-chains. In the case of the TP6EO2M/water system, T_{HN} is seen to increase roughly in proportion to the volume fraction of amphiphile ϕ_A. In the nematic phase the amphiphilic molecules are packed into small discrete micelles. However, it has not been established whether at the nematic to hexagonal transition these micelles retain their structure or form columns of indefinite size. The small entropy of transition implies that the former model cannot be excluded. Nevertheless, the transitions must be driven by the inter-micellar interactions. The entropic repulsive interaction between ethyleneoxy side-chains is probably the controlling factor. This interaction would be minimized by arranging the micelles on a two-dimensional hexagonal lattice; this arrangement maximizes the separation of the micelles. However, these arguments are at best speculative. A combined X-ray diffraction study of the structures and arrangement of the aggregates and a ^2H N.M.R. study of the ordering of the aromatic core and ethyleneoxy side-chains is required.

The nematic-isotropic transition temperature is seen to vary roughly in proportion to the volume fraction of micelles ϕ_m. This behaviour can be understood in terms of the molecular field theory of the nematic to isotropic transition in binary mixtures [32]. The potential of mean torque for a cylindrically symmetric micelle dispersed in water is given by

$$U(\beta) = -\varepsilon_{mm} V_m^{-1} \phi_m \bar{P}_2 P_2(\cos\beta), \tag{1}$$

where β is the angle between the symmetry axis of the particle and the nematic director and ε_{mm} is determined by the strength of the anisotropic interaction between the micelles of volume V_m. The corresponding nematic to isotropic transition temperature T_{NI} is then

$$\begin{aligned} kT_{NI} &= 0{\cdot}2202\varepsilon_{mm}V_m^{-1}\phi_m, \\ &= 0{\cdot}2202\varepsilon_{mm}\varrho_m, \end{aligned} \qquad (2)$$

where ϱ_m is the number density of micelles. Consequently, T_{NI} is predicted to increase with ϕ_m which is what is observed.

6. Comparison of the phase behaviour of discoid amphiphiles

It is instructive to compare the mesogenic behaviour of TP6EO2M with that of other discoid amphiphiles which we have made (figure 2, compounds **1c**–**1g**). We have found that, in designing these triphenylene derivatives, it is essential to maintain a balance between the hydrophobic and hydrophilic properties of the molecule. If the ethyleneoxy chains are too short the compounds are not water soluble. Presumably the enthalpy of solvation is insufficient to overcome the crystal lattice binding energy. If the chains are made too long, on the other hand, the compounds become very water soluble and no mesophases are observed. This may be because, in solution, the amphiphile exists as monomers over the whole concentration range, or because the micelles which are formed are insufficiently anisometric to give liquid crystals.

For example, on comparing TP6EO2M, **1d**, with the compound with one less ethyleneoxy unit in each chain TP6EO1M, **1c**, we find that in the latter case the reduction in hydrophilic character is so great as to render the compound almost insoluble in water. Conversely, the compound with one more ethyleneoxy unit in each chain, TP6EO3M, **1e**, has too much hydrophilic character. It is so water soluble that no nematic or hexagonal phase can be observed above the freezing point. Similar behaviour is found for the esters **1f** and **1g**; these have an acetoxy unit, $-OCOCH_2O-$, as the first element of the side-chain. The shorter chain ester TP6AOEO1M, **1f**, is only sparing soluble in water. The ester with the longer chain TP6AOEO2M is very water soluble, but it is found to yield mesophases at low temperatures. The occurrence of these phases is illustrated by the photomicrograph in figure 6 (*a*). It shows a thin film of solution as observed under a polarizing microscope at $-10°C$. A concentration gradient was established by allowing water to penetrate into neat TP6AOEO2M. A nematic phase (N_C) is seen to occur between what must be an isotropic micellar solution (I) and a columnar phase (C). The nematic phase is identified by its mobility and schlieren texture and the columnar phase by its mosaic texture. Similar photomicrographs are obtained at room temperature in the TP6EO2M/water system and figure 6 (*b*) shows the sequence of textures obtained by allowing water to evaporate from an isotropic solution. In our experiments we have concentrated on isomerically pure materials with a single side-chain length. This has advantages when making fundamental studies. In technical application, however, it would be advantageous to tailor the properties of these materials by using appropriate mixtures of chain lengths.

It is also instructive to compare the behaviour of TP6EO2M with that of molecules of a similar topology that have been made by other workers. To the best of our knowledge none of these give rise to nematic phases in water although several are known which have a discoid amphiphile topology and give micelles in water and one is known which apparently gives a columnar phase in water. The largest group of

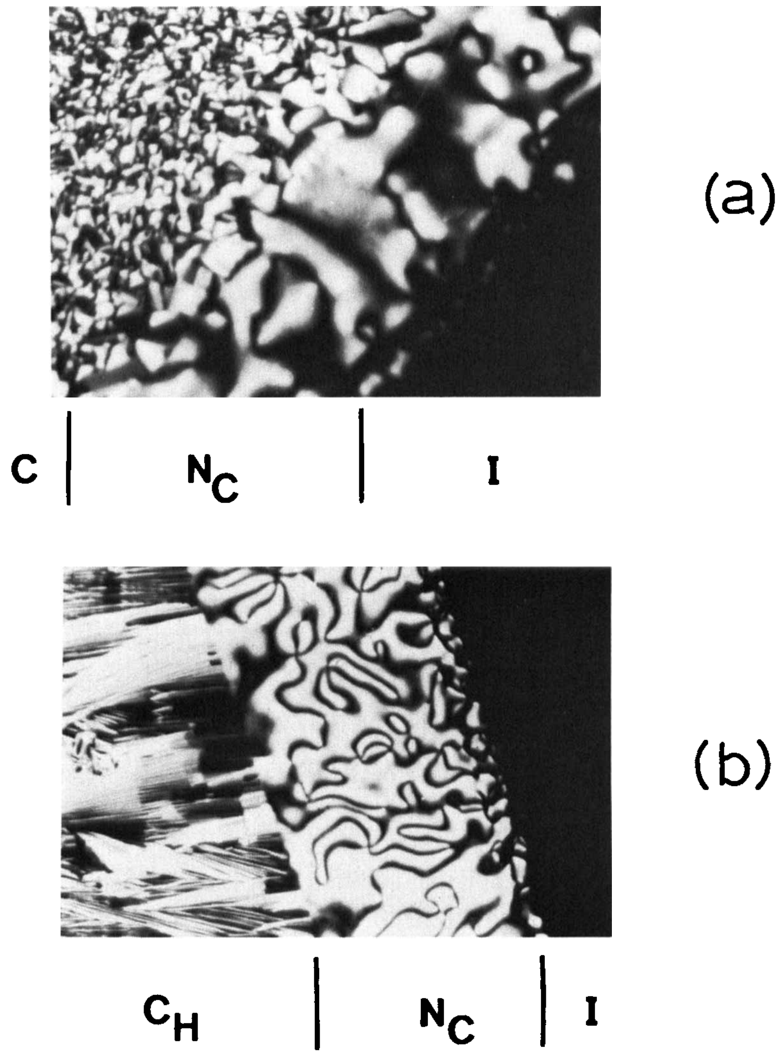
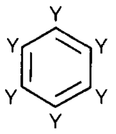
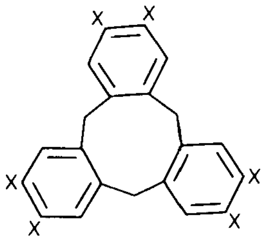


Figure 6. (*a*) Photomicrograph of textures observed for TP6AOEO2M-water mixtures at *c.* −10°C and with magnification × 100. A concentration gradient was established by allowing water to penetrate into the neat sample. (*b*) Similar experiment on TP6EO2M at room temperature. Magnification × 50. The concentration gradient was established by allowing water to evaporate out of the sample cell. Nomenclature; I, isotropic micellar solution; N, nematic phase; C, columnar phase of undetermined structure; C_H, columnar-hexagonal phase.

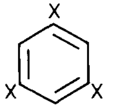
compounds with the same topology as TP6EO2M are the ionophoric polypodands prepared by Vögtle and co-workers [33]; a typical example is compound **2** [34]. The structural similarity to TP6EO2M is clear; the aromatic core is surrounded by polyethyleneoxy chains. The polypodands have been prepared as ion-complexing agents and unfortunately there seem to have been no investigations of their self-aggregation or liquid crystal properties. It is, however, interesting to speculate that like the polypodands the triphenylene derivatives which we have prepared should

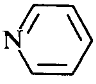


2, $Y = -CH_2S(CH_2CH_2O)_3C_4H_9$



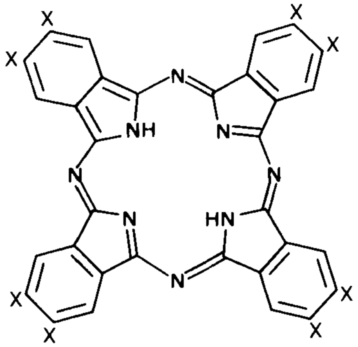
3a, $X = -O(CH_2)_{10}CO_2Na$
3b, $X = -(OCH_2CH_2)_3OC_2H_5$



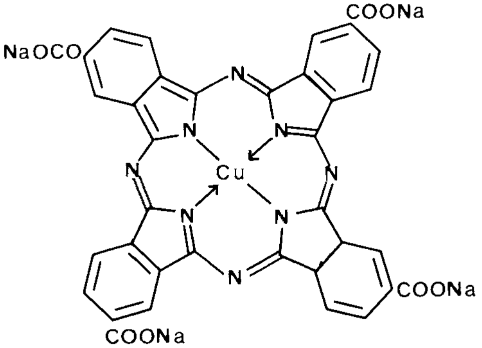
4, $X = -O(CH_2)_{11}^{+}N$ 

complex to Group I metal ions and that addition of salts of the metals should provide a useful mechanism for modulating their liquid crystal and phase behaviour. Two other molecules with the topology of discoid amphiphiles which also seem to have been prepared, principally as complexing agents, are the hexapus and trigapus compounds **3** [35, 36] and **4** [37]. Once again these contain an aromatic core surrounded by hydrophilic chains. For the hexapus compounds **3**, because of the conformational constraints imposed by the nine-membered ring, this core is dish-shaped rather than planar. The hexapus compound **3a** [36] is reported to be a weak surfactant and to form micelles of not dissimilar size (9 ± 1 at 4×10^{-4} to 1×10^{-2} mol/litre) to those of TP6EO2M (6 ± 1). Another system which has a similar topology to TP6EO2M and which seems to form micelles is the phthalocyanine derivative **5** recently reported by Piechocki and Simon [38]. The related phthalocyanine **6** has been studied by Gaspard *et al.* [39]. On the basis of polarizing microscope studies, it seems that this forms a columnar hexagonal phase in water but not a nematic phase. The analogy between the phthalocyanines **5** and **6** and TP6EO2M seems sound in so far as they are all disc-shaped molecules with hydrophilic substituents around the periphery. On the other hand the core of these phthalocyanines is not truly hydrophobic and phthalocyanines have a tendency to form columnar stacks quite independent of any hydrophilic/hydrophobic interaction.

It is also interesting to compare the phase behaviour of TP6EO2M in water with that exhibited by thermotropic discoid mesogens, for example compounds **1h**–**1j**



5, $X = CH_2(OCH_2CH_2)_2OCH_3$



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(figure 2) [40]. These mesogens form corresponding columnar and nematic (N_D) phases, but there are surprisingly few examples of the latter. Columnar to N_D transitions have been observed [41] for the hexa-*n*-alkoxybenzoates of triphenylene **1j**. The lower members of the series, $n = 4$ and 5, show only the N_D phase. The next few members show both columnar and N_D phases, the temperature range of the N_D phase decreasing with chain length until at $n = 12$ the columnar phase transforms directly to the isotropic liquid. This behaviour is quite analogous to that of the TP6EO2M/water system if the identity between side-chain length and volume fraction of micelles is made. The strength of the interaction driving the nematic to columnar transition increases with side-chain length in the thermotropic series but with the volume fraction of micelles in the lyotropic system. The mechanism of these interactions is quite different in the two systems. In the thermotropics the interaction has its origins in the mutual attraction of the aromatic cores for each other, whilst in the lyotropics it arises from the mutual repulsion of the micelles. Thus, in the latter case, the micelles are the fundamental mesogenic particle and the transition is to be viewed as a simple disorder–order transition of these particles. In thermotropics the molecule is considered to be the mesogenic particle, but there is no *a priori* reason why it should not be possible in some instances for the molecules to stack into columnar aggregates in the nematic phase, i.e. to form N_C phases. In this case there would be a direct correspondence in the mechanisms of the nematic to hexagonal transitions. Conversely, there is no *a priori* reason why lyotropic amphiphilic discoid mesogens should not form thermotropic N_D and columnar mesophases. Thus, the distinction between the thermotropic and lyotropic amphiphilic classes of liquid crystals is much less dramatic than generally considered. Indeed, we have recently proposed [14] that it should be possible to modify the traditional thermotropic mesogen molecules into amphiphiles which will form mesophases on dissolution in water. Thus, introducing hydrophilic groups into the side-chains of thermotropic discoid mesogens will give amphiphiles which will form columnar and N_C phases in water, whilst similar modification of lath-shaped mesogen molecules will give amphiphiles which will form lamellar and N_D phases†. Clearly, there is also no reason why it should not be possible to design mesogens that will form both thermotropic and lyotropic mesophases.

Finally, it is important to note that, despite these similarities, the ordering at the molecular level in aggregates of TP6EO2M in water is the result of a balance between strong hydrophobic and hydrophilic interactions. This contrasts with the case of the thermotropic discoid mesogens where the ordering into columns arises from rather weaker dispersion forces. We have termed this ordering imposed by the hydrophobic–hydrophilic interactions, solvent driven aggregation [14]. It is the principle which underlies the self-assembly and ordering of many biomolecules and we believe that its application to a wide variety of organic structures should lead to important new materials.

For consistency with the general thesis of the paper we have compared the behaviour of TP6EO2M with that of other amphiphiles with similar topology. These could, if one wished to invent terminology, be referred to as 'polypodands'. Nevertheless, it is not inappropriate to refer here to the similar phase behaviour exhibited by a wide variety of polycyclic amphiphilic compounds. These include bromophenanthrene sulphonic acids [42], naphthylamine disulphonic acids [43], dyes [44], and certain drugs such as the anti-asthmatic drug disodium chromoglycate [45]. It has recently been proposed that these substances be collectively referred to as 'chromonics' [46]. These amphiphiles are generally quite irregular in shape and their arrangement in the columnar aggregates which they seem to form in aqueous solution have yet to be established.

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† *Note added in proof.*—Since our paper was submitted for publication an interesting example of this type has been described by Lühmann, B., and Finkelmann, H., 1986, *Colloid Polym. Sci.*, **264**, 189.

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