

# Calamitics, Cubics, and Columnars—Liquid-Crystalline Complexes of Silver(I)

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## ABSTRACT

The study of metallomesogens has added several new dimensions to the wider field of liquid crystals. In this Account, just one family of complexes is considered, namely alkoxystilbazole complexes of various silver(I) salts. These complexes show an incredibly rich and diverse mesomorphism ranging from nematic and smectic to columnar phases; in particular, many complexes show the still rare thermotropic cubic phase. Through systematic structural variations, it has been possible to gain a good understanding of the factors influencing the behavior of these fascinating systems.

## Introduction

By the mid 1970s, liquid crystals had really taken off following the realization by Gray and co-workers of materials with suitable chemical and physical properties for proper commercial exploitation in displays. Liquid crystals represent the fourth state of matter, existing between the highly ordered solid state and the highly disordered liquid state, and the liquid-crystal *mesophases* are stabilized by the anisotropic dispersion forces which exist between the anisotropic molecules that give rise to them. Liquid crystals are first classified according to the way in which the order of the solid state is destroyed to give the mesophase, and this Account will concentrate on *thermotropic* liquid crystals where phase transitions are caused by a temperature change at a given pressure. Thermotropics are further classified according to the shape of the molecule giving rise to the mesophase, and while other classifications are additionally useful, this does provide a helpful starting point. The most common molecular motif is that of a rod (*calamitic* liquid crystal) and rod-shaped liquid crystals form two main classes of mesophase, the nematic phase and the smectic phases.

Duncan Watson Bruce was born in Carlisle, UK, on 31 May 1960. He obtained his B.Sc. in 1981 from the University of Liverpool, where he also obtained his Ph.D. under the supervision of David Cole-Hamilton. In 1984, he was appointed to a Temporary Lectureship in Inorganic Chemistry at the University of Sheffield, and in 1986 he was awarded a Royal Society Warren Research Fellowship, which he also held in Sheffield until 1991. He was then appointed Lecturer in Chemistry and was promoted Senior Lecturer in 1994, in which year he became co-director of the Sheffield Centre for Molecular Materials. In 1995, he was appointed Professor of Inorganic Chemistry at the University of Exeter and became Head of School in 1997. He is Secretary of the British Liquid Crystal Society, which awarded him their first Young Scientist prize in 1990. He was awarded the Royal Society of Chemistry's Sir Edward Frankland Fellowship in 1994/95 and the 1996 Corday-Morgan Medal and Prize. He is UK Editor of *Molecular Crystals and Liquid Crystals* and is a member of the Advisory Editorial Board for *Chemical Communications*. The second edition of *Inorganic Materials*, co-edited with Dermot O'Hare, was published in 1996.

The other common shape is that of the disk (so-called *discotic* liquid crystals), and these form either the nematic phase or columnar phases.

The nematic phase (abbreviated N) is the most disordered mesophase, and in it, molecules possess only one-dimensional orientational order and no positional order. A schematic (Figure 1) shows the nematic phase of both rodlike and disklike molecules—note that in each case it is the unique molecular axis which is correlated; the nematic phase of calamitic molecules is used in commercial displays. There exists a whole family of smectic mesophases which are, in addition, characterized by the presence of partial translational ordering. Where both exist in a compound, the smectic phase(s) are found at lower temperatures than the nematic phase. The phases are distinguished by letters of the alphabet (smectic A, S<sub>A</sub>; smectic B, S<sub>B</sub>); this Account concerns only the S<sub>A</sub> and S<sub>C</sub> phases. Thus, the S<sub>A</sub> phase is the most disordered type of smectic phase, and, in addition to the one-dimensional orientational order of the nematic phase, it possesses partial translational ordering which is caricatured as ordering into layers (Figure 2). Evidence for this arrangement comes from X-ray diffraction, which can “see” the layers, and while Figure 2 will suffice for our discussion, in reality the layers are not so well defined as this; a more accurate description is found elsewhere.<sup>1</sup> The S<sub>C</sub> is similar to the S<sub>A</sub> phase except that the molecules are now tilted within the “layers” (Figure 2).

Columnar phases of disklike molecules are composed of stacks of molecules with the phase symmetry being described by the arrangement of the columns (Figure 3). We would note that in the liquid-crystal literature, the crystal phase is abbreviated “Crys”, while the (normal) liquid state is abbreviated “I” (for isotropic).

Liquid-crystal phases are normally identified using a combination of three techniques: polarized optical microscopy, differential scanning calorimetry, and X-ray diffraction. The first two are used in a complementary fashion, with phases being identified initially by the defect textures of the birefringent mesophases, the enthalpy changes on phase transitions being evaluated by the calorimetry. Although fluid in nature, liquid-crystal mesophases are periodic on the scale of angstroms, and so X-ray diffraction can often give definitive structural information, especially if performed on a macroscopically aligned sample.

## The Story Begins

Although the history of metallomesogens can be traced back as far as the history of liquid crystals themselves, when our work began in 1984, interest was beginning to grow in the subject following studies by Giroud-Godquin, Ghedini, Ohta, Simon, and Galyametdinov in the previous six years.<sup>2</sup> The field of metallomesogens has since grown

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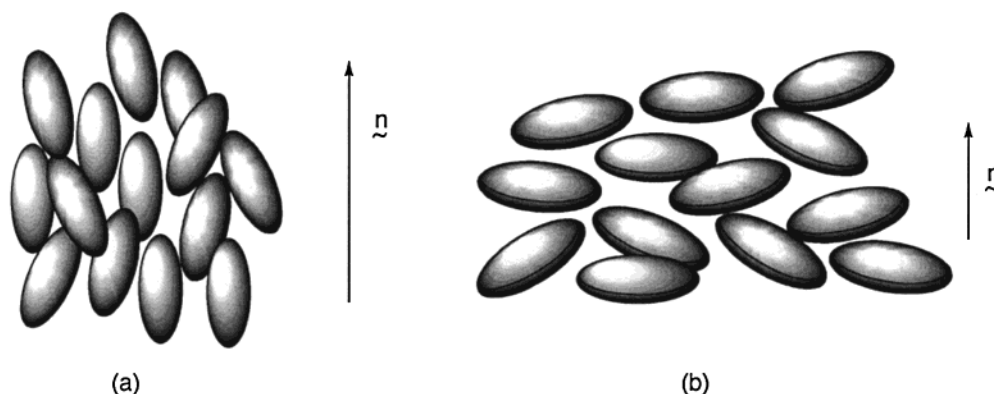


FIGURE 1. Schematic to show a liquid-crystal nematic phase of (a) rodlike and (b) disklike molecules.

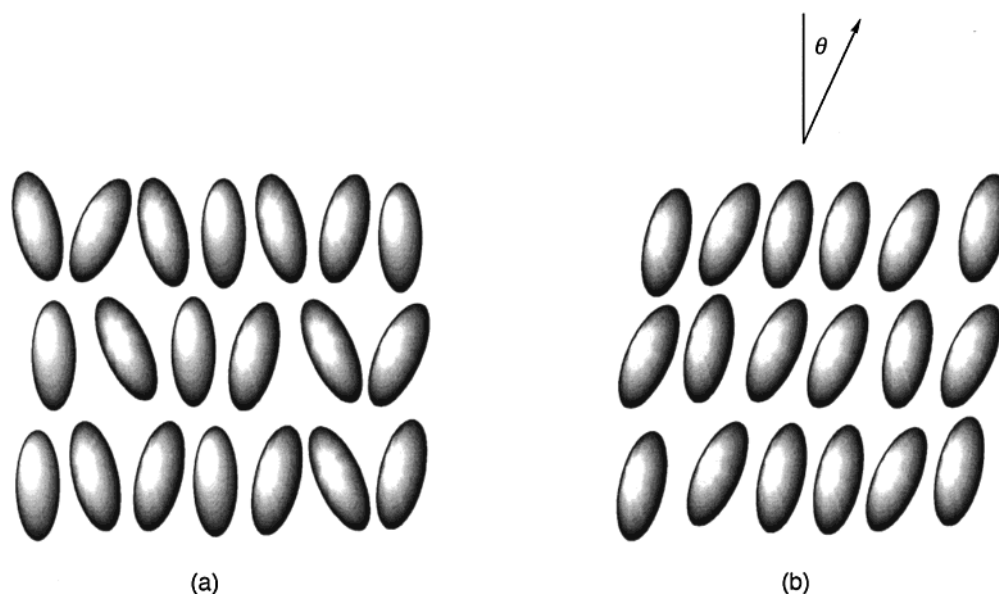


FIGURE 2. Schematic to show (a) a smectic A ( $S_A$ ) phase and (b) a smectic C ( $S_C$ ) phase.

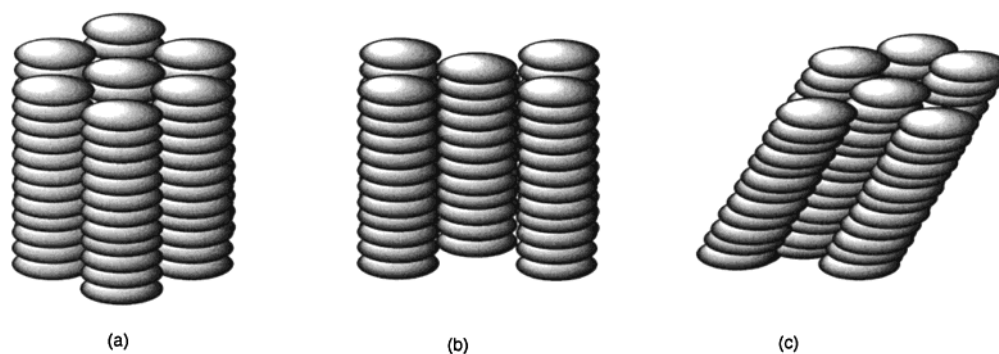


FIGURE 3. Schematic of the (a) columnar hexagonal ( $Col_h$ ), (b) columnar rectangular ( $Col_r$ ), and (c) columnar oblique ( $Col_{ob}$ ) phases.

rapidly, both because it represents a challenge to coordination chemists and liquid-crystal scientists, and because the mesogenic complexes on offer will have properties which depend on the inclusion of the metal. Thus, the metal can have a purely structural role, can act (perhaps in combination with the ligand) as a chromophore, can be paramagnetic, can be a source of reactivity, and so on. In addition, it is possible to realize coordination numbers from 1 to 12, and so there will be geometries and modifications available which would otherwise not

be the case. Therefore, while much of what we find with metallomesogens will parallel that found in purely organic systems, there will be aspects of the physical properties and the mesomorphism which are different and new.

Among the first systems we examined were complexes of alkoxystilbazoles<sup>3</sup>—simple, substituted pyridines. While we have worked extensively with these materials and their complexes in hydrogen bonding,<sup>4</sup> L–B films,<sup>5</sup> nonlinear optics,<sup>6</sup> and other metallomesogenic systems,<sup>7</sup> this Account will concentrate on complexes of silver(I). Alkoxy-

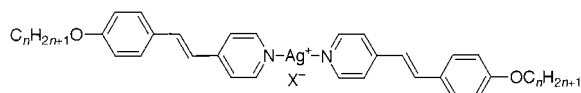


FIGURE 4. General structure of the linear bis(4-alkoxystilbazole)-silver(I) complexes.

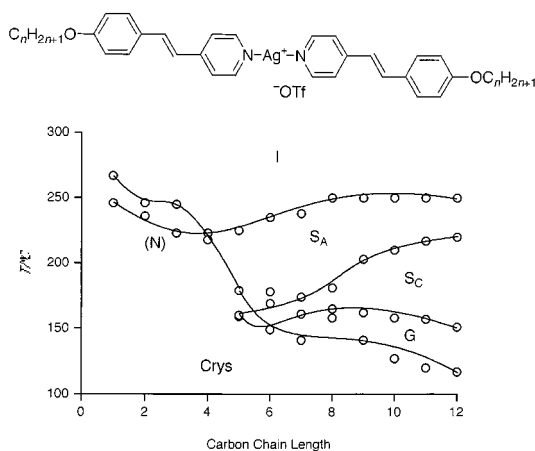


FIGURE 5. Phase diagram depicting the mesomorphism of silver triflate complexes of 4-alkoxystilbazoles (G refers to the crystal smectic G phase; see ref 1).

stilbazoles can be reacted with a variety of silver salts, AgX, to yield the two-coordinate, linear complexes shown in Figure 4. The liquid-crystalline behavior of these systems depends strongly on the anion, the alkoxy chain length, and other substituents which may be present on the stilbazole.

For example, tetrafluoroborate salts show S<sub>A</sub> and S<sub>C</sub> phases but are none too stable, and further, their transition temperatures are very high (in the range 200–300 °C). However, two things immediately stand out. First, while the ligand showed a S<sub>B</sub> and a crystal smectic E phase,<sup>8</sup> the complexes had S<sub>A</sub> and S<sub>C</sub> phases; thus, complexation had changed the mesomorphism. Second, at this time they were almost unique examples of formally ionic compounds showing a mesophase other than S<sub>A</sub>.<sup>9</sup> This latter point is important, and we will return to it later. Related complexes were made with nitrate and triflate anions,<sup>10</sup> and while for the former, broadly similar behavior was found (S<sub>A</sub> and S<sub>C</sub> phases at high temperature), the phase diagram (Figure 5) for the triflates showed a remarkable additional feature: the presence of a nematic phase.<sup>11</sup> Why remarkable? Well, when we consider nematic phases of liquid crystals, we attribute the stabilization of the phase to weak, anisotropic dispersion forces, while when we consider ionic materials, we think of rather strong, isotropic, Coulombic forces.

One of the problems in studying these complexes, and one which can affect the study of some metallomesogenic systems, was the very high transition temperatures at which the phases existed and the fact that decomposition was often observed in the upper reaches of the S<sub>A</sub> phases. In what was, at the time, a rather naïve attempt to reduce these temperatures, we simply changed the small anions for dodecyl sulfate (DOS) by reacting the stilbazoles with AgDOS, reasoning that this rather “floppy” anion would

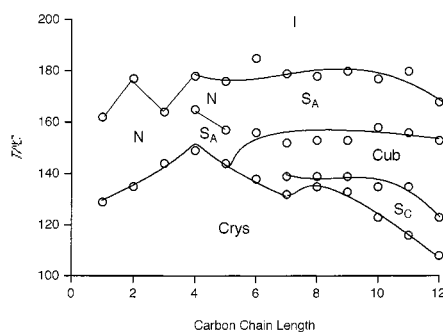
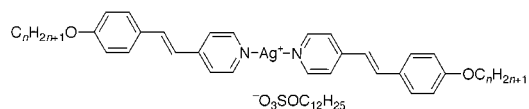


FIGURE 6. Phase diagram depicting the mesomorphism of silver dodecyl sulfate complexes of 4-alkoxystilbazoles.

destabilize both the crystal phase and the liquid-crystal phases. It was this change which really opened up this area for us as is now described.

First, the DOS anion *did* do the job of reducing temperatures, and whereas transitions to isotropic had been observed around 250 °C with the small anions, with DOS they were around 170–180 °C (phase diagram, Figure 6). Second, there were more materials which exhibited nematic, S<sub>C</sub> and S<sub>A</sub> phases. Third, there was another phase which we could not initially understand which appeared between the S<sub>C</sub> and S<sub>A</sub> phases, gave no optical texture,<sup>12</sup> and appeared very viscous (note that the S<sub>A</sub> and S<sub>C</sub> phases are not viscous). Eventually, we worked out that the viscous phase was almost certainly a cubic phase (or “S<sub>D</sub>” as it was then called<sup>13</sup>) which was rather exciting, as at that time, there were only some half-dozen or so compounds known with this phase; we had effectively doubled that number. More about the cubic phase later.

Chronologically, the next development was that, having made the series of materials with the DOS anion, we proceeded to make the equivalent series with octyl sulfate (OS). Two interesting results came out of this study.<sup>14</sup> First, we were able to grow single crystals of one complex; the structure is displayed in Figure 7. Second, we found that the phase diagrams of the DOS and OS salts were largely superimposable *except* that the cubic phase was absent in the OS salts, its position in the phase diagram being taken by an extended S<sub>A</sub> range.

The crystal structure is interesting on several counts, but we will consider only two for now. The structure is dimeric, with two silver cations being “supported” by bridging sulfate groups with Ag–O distances (2.7–2.9 Å) indicative of predominantly ionic interactions; the Ag–Ag distance was 3.21 Å. Further, it is interesting, and we believe crucial, to note that the octyl sulfate chain does not extend past the rigid core of the cation.

Now, before we begin an initial interpretation of the mesomorphism in detail, we need to consider another set of materials, this time formed by lateral fluorination of the stilbazole ligands. Lateral fluorination, the subject of a recent excellent review,<sup>15</sup> is a common and highly effective tool used in liquid-crystal chemistry to exert

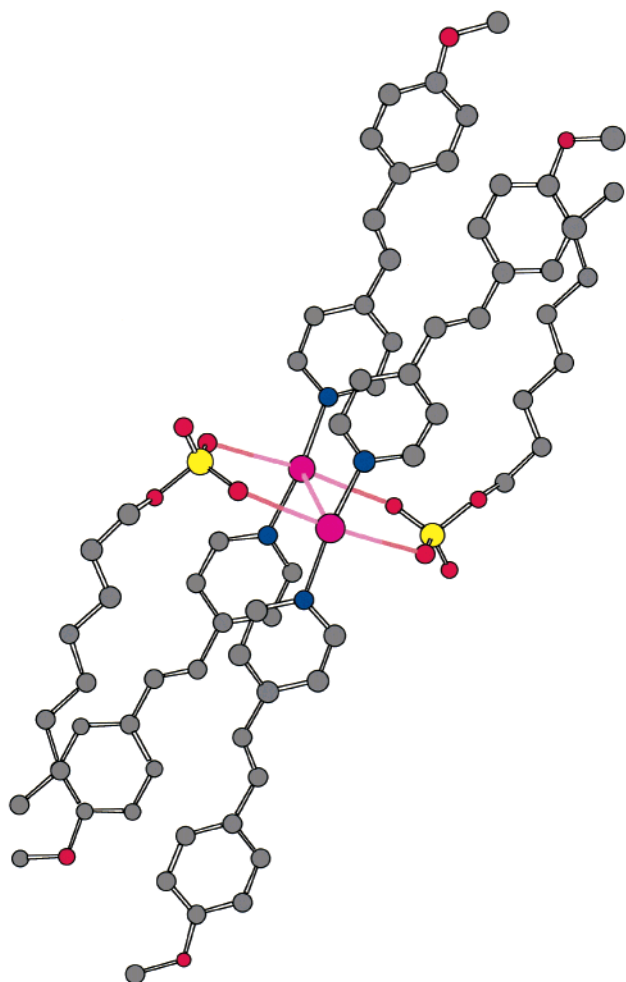


FIGURE 7. Molecular structure of the silver octyl sulfate salt of 4-methoxystilbazole.

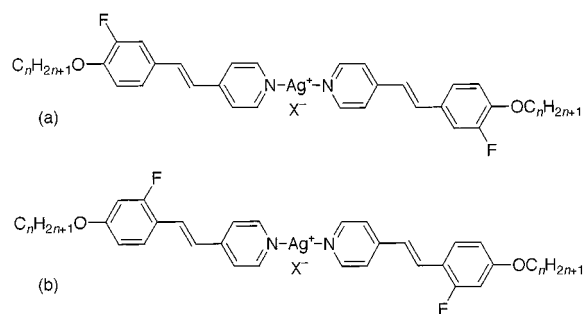
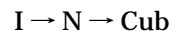


FIGURE 8. Structure of the fluorinated stilbazoles.

control over mesomorphism, crystal phase stability, and physical properties. We synthesized 4-alkoxy-2-fluorostilbazoles and 4-alkoxy-3-fluorostilbazoles and made their silver triflate and DOS salts (Figure 8).<sup>16</sup> The effect on the mesomorphism was governed by dipolar effects, but suffice to say that 3-fluoro substitution led to the promotion of the  $S_A$  phase, destabilization of the nematic phase, and total destabilization of the cubic phase in the DOS salts, while 2-fluoro substitution had the opposite effect, with the cubic phase being retained and the nematic promoted at the expense of the  $S_A$ . This retention of the cubic phase and promotion of the nematic turned out to be fortuitous as now they coincided in one complex in

the phase diagram, giving a phase sequence on cooling of

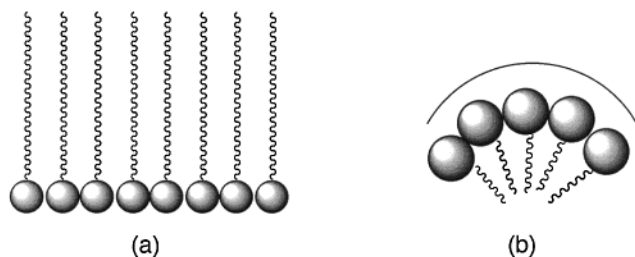


At the time, only one other material with such a phase sequence was known.<sup>17</sup> The advantage of this phase sequence is that, due to the fluid nature of the nematic phase and the diamagnetic anisotropy of liquid-crystal mesophases, it is rather easy to align a nematic phase with a moderate applied field (ca. 0.5 T), giving the possibility of obtaining a monodomain cubic phase and, thus, allowing the space group to be determined by X-ray diffraction.

### Taking Stock—1

Now we have some explaining to do; indeed, it turned out that there were more things to explain than ever we imagined! Let us start with the nematic phase. For all of the reasons outlined above, it would seem counterintuitive to have a nematic phase exist in the presence of strong, Coulombic forces. However, while the complexes are formally ionic, when the conductivity is measured in the mesophase<sup>18</sup> it is found to be nonexistent, leading to the conclusion that the silver cation and alkyl sulfate anion are very closely paired. Thus, the relative dispositions of the cation and anion found in the crystal structure of the octyl sulfate salt (Figure 7) must remain broadly true in the mesophase. Nevertheless, nematic phases of formally ionic materials remain rare.<sup>19</sup> Let us next turn our attention to the existence of the  $S_C$  and  $S_A$  phases in these materials and, in particular, the complexes with alkyl sulfate anions. Thus, when purely organic liquid crystals are considered, it is found to be true that when a lateral alkyl chain is added to a mesogen, the *only* phase formed is a nematic phase.<sup>20</sup> This observation is readily understood by considering that the flexible alkyl chain serves simply to disrupt the packing into the layers which characterize the smectic phase. However, the silver alkyl sulfates are mesogens with a lateral chain (the alkyl sulfate), and yet they show *two* smectic phases. How can these observations be explained?

We have already discussed the fact that the complexes must exist as tightly bound ion pairs due to the lack of conductivity found in the mesophase, which locates the sulfate group in close proximity to the silver cation. Let us now consider the phase diagram of the dodecyl sulfate salts as we move from left to right. Considered in relation to the points above, that we find a nematic phase at short chain length is now not surprising because of the presence of the lateral chain and because nematic phases are most commonly found at the shortest chain lengths in an homologous series. Moving across the phase diagram, in general, smectic phase formation is more favored as the chains become longer, as there is a microphase separation between the aromatic part of the molecule and the aliphatic chains, promoting layering. However, in the presence of a lateral alkyl chain, this is suppressed, so there must be another factor stabilizing the  $S_A$  and  $S_C$



**FIGURE 9.** Schematic diagram to show the interfacial curvature generated as a function of the headgroup size in an amphiphile: (a) no curvature (e.g.,  $L_\alpha$  phase); (b) curvature (e.g.,  $H_1$  phase).

mesophases. This factor is, we believe, the presence of intermolecular ionic interactions between the silver cation and the alkyl sulfate anion. That the complexes show a nematic phase indicates that these interactions are not too strong; otherwise, a smectic phase would be seen across the phase diagram. However, the combination of the ionic interactions, coupled with the lengthening terminal chains, is clearly sufficient to stabilize the smectic phases.

Next, we turn to the cubic phase, beginning by discussing those formed in surfactant systems. There is a class of liquid crystals where the mesophase is formed when the order of the solid state is destroyed by a solvent (usually water). These are known as *lyotropic* liquid crystals,<sup>21</sup> with the largest family being formed of amphiphilic molecules. Here, cubic phases are common,<sup>22</sup> and their formation is rather well understood. Thus, when amphiphiles are dissolved in water, micelles form above the critical micelle concentration, and the shape of these micelles is largely determined, at least to a good first approximation, by the relative volumes of the chain and the headgroup.<sup>23</sup> Thus, where there is a mismatch between headgroup size and chain volume, a curvature is established at the interface between the hydrophilic headgroup and the hydrophobic chain. Simply stated, larger headgroups lead to micelles with significant curvature (rod or spherical micelles), while much smaller headgroups generate no curvature, leading to disk micelles (Figure 9). Eventually, the concentration of micelles becomes so high that the micelles must order—such ordered phases of micelles are known as *lyotropic* liquid-crystal phases, whose structures can be explained in terms of interfacial curvature. Cubic phases of lyotropic liquid crystals are of two types: cubic arrays of micelles (I phases) and more elaborate bicontinuous phases (V phases), whose structures rely for their description on interconnecting rod, and minimal surface, models as described below.

Cubic phases are exactly what their name says—mesophases of cubic symmetry—and, having such high symmetry, their physical properties are no longer anisotropic. Thus, under the polarizing microscope, no optical texture is seen, and the phase is very viscous, its kinetics of formation often being very slow. In thermotropic systems, cubic phases normally form above an  $S_C$  phase and below an  $S_A$  or  $N$  phase (where it is present) in calamitic systems, while in lyotropic systems, a cubic phase is possible, in principle, between any pair of phases.

While it is not too difficult to identify a cubic phase from optical microscopy, determining the exact symmetry of the phase requires X-ray diffraction studies on monodomain samples, which are not always easy to obtain, particularly in thermotropic systems. In our silver salts, we were able to obtain such a monodomain in the fluorinated complex which had the nematic phase above the cubic phase and in two derivatives of the DOS salts; this led us to identify the phase (at least in these materials) as possessing  $Ia\bar{3}d$  symmetry.<sup>24</sup> So, how are the molecules arranged in these phases?

The structure of cubic phases has been described by three models, namely the micellar model, the interconnecting rod model,<sup>25</sup> and the infinite periodic minimal surface model (IPMS).<sup>26</sup> The first describes well the micellar cubic phases in lyotropic systems, while the latter two are more applicable to the so-called bicontinuous lyotropic cubic phases<sup>22</sup> and the cubic phases of most thermotropic systems. The rod model is illustrated for  $Ia\bar{3}d$  and  $Im\bar{3}m$  and the IPMS model for  $Im\bar{3}m$  in Figure 10. In the rod model of lyotropic systems, the rods are held to consist of the polar headgroups, with the chains filling the space between. Extending this idea to thermotropic systems suggests that the rods consist of the central, rigid part of the molecule, with the chains extending to fill the space between. The arrangement of the rods is related to the minimal surfaces as the minimal surfaces divide space into parts; so, for example, the Schwartz P surface (Figure 10c) contains the symmetry elements of the  $Im\bar{3}m$  space group and gives rise to two, non-interconnected rod networks (Figure 10b). Thus, one can consider that the molecular cores form the rods and the chains extend out to describe the minimal surfaces, illustrating the role of curvature in the structure of these phases.

But why do these cubic phases form, and how can we develop a structure/organization relationship? A clue comes from the observation above that, while the dodecyl sulfate salts do show the cubic phase, the octyl sulfate salts do not. Recall also that the crystal structure of a derivative of the latter (Figure 7) shows that the alkyl sulfate chain does not extend past the cation core. It is also noteworthy that we have shown that the cubic phase is absent from the related silver decyl sulfate salts (where the anion chain again does not extend past the cation core), while it is retained in the tetradecyl sulfate salts (where it does).<sup>27</sup> Thus, qualitatively, we can advance that it is necessary in these systems for the anion chain to extend past the cation core in order for a cubic phase to be observed. In such a situation, the alkyl sulfate chain is beginning to contribute to the space occupied by the terminal chains of the cation. Further, as the volume occupied by the terminal alkyl chains gets larger, remembering that the cation volume is constant, there then exists the possibility for a mismatch between the chain and core volumes which will generate curvature at the interface between the two. This idea is developed in more detail below.

However, let us also not lose sight of the fact that the role of the ionic interactions must also still be significant, as above and below the cubic phases there exists a

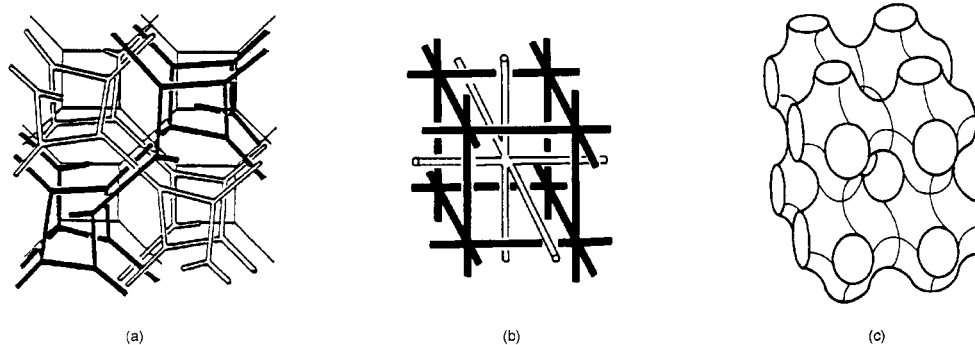


FIGURE 10. Interconnecting rod model for the (a)  $Ia\bar{3}d$  and (b)  $Im\bar{3}m$  space group and (c) the infinite periodic minimal surface representations for  $Im\bar{3}m$ .

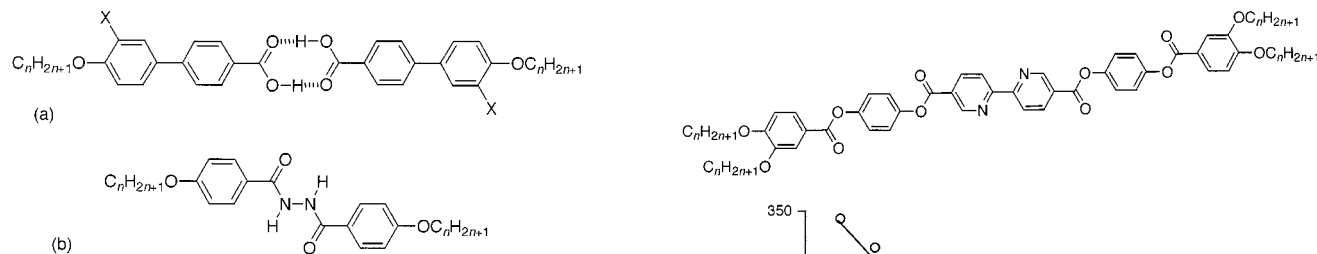


FIGURE 11. The two earliest calamitic mesogens showing a thermotropic cubic phase.

lamellar phase. The importance of these ionic interactions takes on a greater significance when we look at the two examples of thermotropic cubic materials known when we first carried out this work, namely the laterally substituted biphenylcarboxylic acids reported by Gray<sup>28,29</sup> (the first calamitic materials to be identified as possessing a cubic phase) and some hydrazines reported by Demus<sup>30</sup> (Figure 11). In both materials, the possibility exists for lateral interactions through hydrogen bonding. Considering other rodlike mesogens which form cubic phases also leads to the view that all have some possibility for specific, lateral intermolecular interactions which we<sup>31</sup> and others<sup>32</sup> now believe to be significant.

## Polycatenar Systems

So far, we have concentrated on rodlike silver complexes and the mesophases they form. Recall also that, in the Introduction, disklike systems were introduced that form mesophases of the nematic and columnar types. Thus, in rods and disks we can recognize two extremes of form, and so we are not surprised that the phases they form result from different types of organization. However, there exists a family of molecules, known as *polycatenar* mesogens,<sup>33</sup> which can “bridge the gap” between the phases formed by rods and those formed by disks.

Polycatenar mesogens are characterized by having a rather extended core (normally at least four rings) and three to six terminal chains. Those with four chains are termed *tetracatenar*, those with six chains *hexacatenar*, and so on; the other variable is the position of attachment of these terminal chains.

In general, hexacatenar systems (and, to an extent, pentacatenar systems) show almost exclusively columnar phases, while tricatena systems show mainly  $S_C$  and N

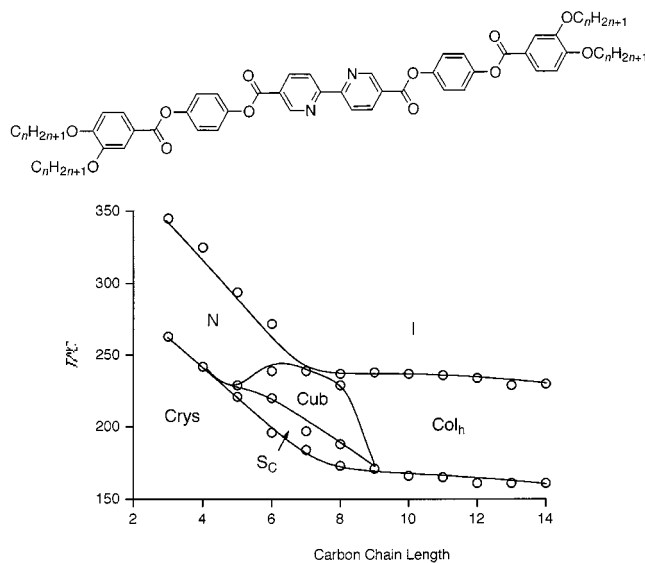


FIGURE 12. Phase diagram for tetracatenar bipyridine mesogens.

phases. However, for tetracatenar systems in which the terminal chains are in the 3,4-positions, the situation is much more interesting. At short chain lengths such materials show N and  $S_C$  phases, while at much longer chain lengths columnar phases are seen; cubic phases can be a feature of intermediate chain lengths. An illustrative phase diagram is shown in Figure 12. So, here we have materials which can show, in one homologous series, the mesomorphism characteristic of rods and that characteristic of disks.

We therefore synthesized some di- and trialkoxystilbazoles in order to realize related polycatenar silver complexes. The first series we made were silver dodecyl sulfate complexes of 3,4-dialkoxystilbazoles, which produced the phase diagram shown in Figure 13.<sup>34</sup> As expected, we found columnar phases at long chain lengths and cubic phases (identified as belonging to the  $Ia\bar{3}d$  space group by freeze–fracture electron microscopy) at shorter chain lengths, but there was no evidence of an  $S_C$  phase. Thus, we had some of the characteristics of polycatenar systems, but not all. It is interesting to note in these systems that the presence of the extra two chains in the 3-positions of the ligand does destabilize the crystal phase, with all homologues melting at lower temperatures than the 4-alkoxystilbazole complexes. However, once in

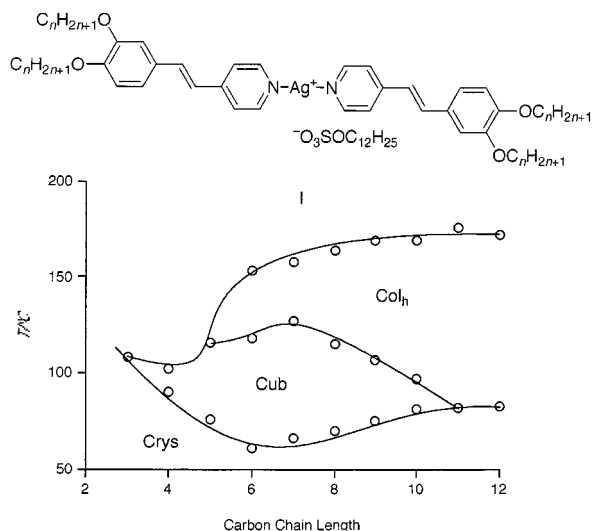


FIGURE 13. Phase diagram for silver dodecyl sulfate complexes of 3,4-dialkoxy stilbazoles.

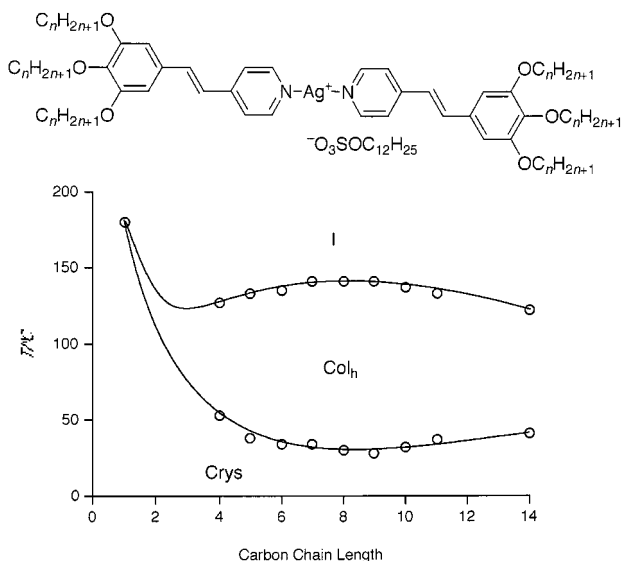


FIGURE 14. Phase diagram of the silver dodecyl sulfate complexes of 3,4,5-trialkoxy stilbazoles.

the columnar phase, the columnar-to-isotropic transition is not much lower than the  $S_A$ -I transition in the 4-alkoxy stilbazole complexes, although the cubic phase is not so stable, becoming isotropic or columnar between 100 and 125 °C.

We then proceeded to make silver dodecyl sulfate complexes of 3,5-dialkoxy stilbazoles and 3,4,5-trialkoxy stilbazoles.<sup>35</sup> In the latter case, the mesomorphism was as might have been predicted with the formation of columnar phases close to room temperature (Figure 14), although we would note that, in polycatenar systems, it is not common to form a mesophase from a compound having six terminal chains and only four rings. In the case of the 3,5-disubstituted systems, however, the results were slightly more surprising, as we saw columnar mesomorphism across a good part of the phase diagram (Figure 15). It is not at all common to find extensive mesomorphism in series of 3,5-disubstituted systems, especially with such a short rigid core. Note here that the different

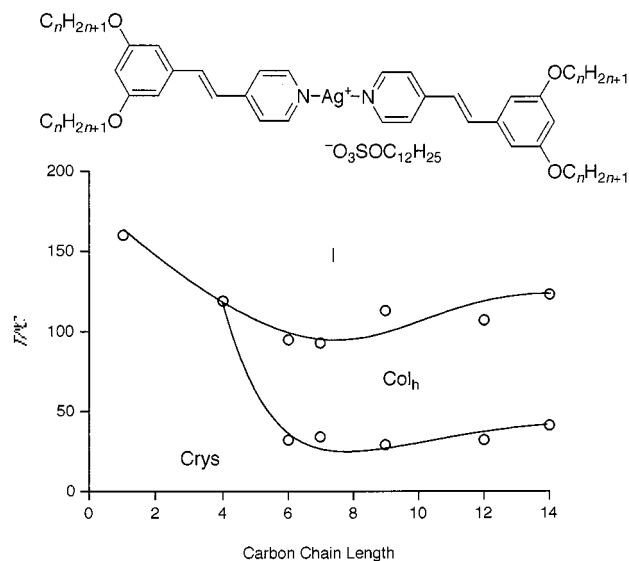


FIGURE 15. Phase diagram of the silver dodecyl sulfate complexes of 3,5-dialkoxy stilbazoles.

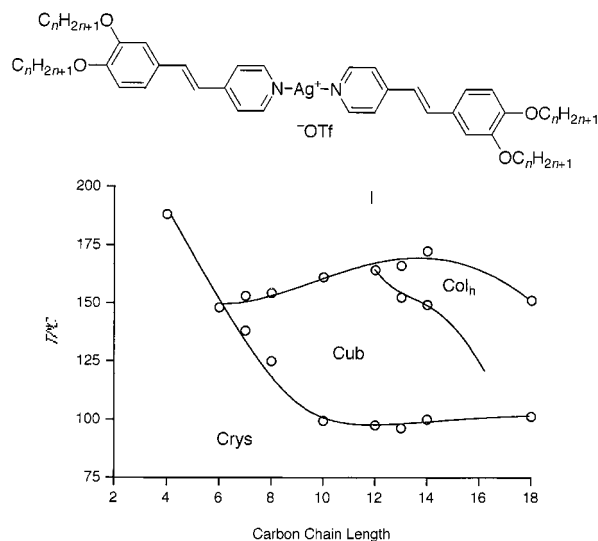


FIGURE 16. Phase diagram of the silver triflate complexes of 3,4-dialkoxy stilbazoles.

substitution pattern leads to much lower melting and clearing points and a less diverse mesomorphism.

The final modification to be discussed is that, for the 3,4- and 3,5-dialkoxy stilbazole and 3,4,5-trialkoxy stilbazole complexes, we varied the anion used so that for all three ligands we made the silver triflate complexes, while for the 3,4-dialkoxy stilbazole system we also made a series of complexes using alkyl sulfate anions of different chain length.<sup>36</sup> For the triflate systems, we found that the mesomorphism of the complexes of 3,5-dialkoxy stilbazoles had all but disappeared, while it was retained in the 3,4-dialkoxy- and 3,4,5-trialkoxy stilbazole systems (Figures 16 and 17), albeit with increased melting points.

For the silver complexes of the 3,4-dialkoxy stilbazoles with silver alkyl sulfate ligands, we found only cubic and columnar phases which appeared as a function of the ligand and alkyl sulfate chain lengths (Figure 18). Here we can see that, for the didodecyloxy stilbazole ligands, only a columnar phase is formed whatever the alkyl sulfate

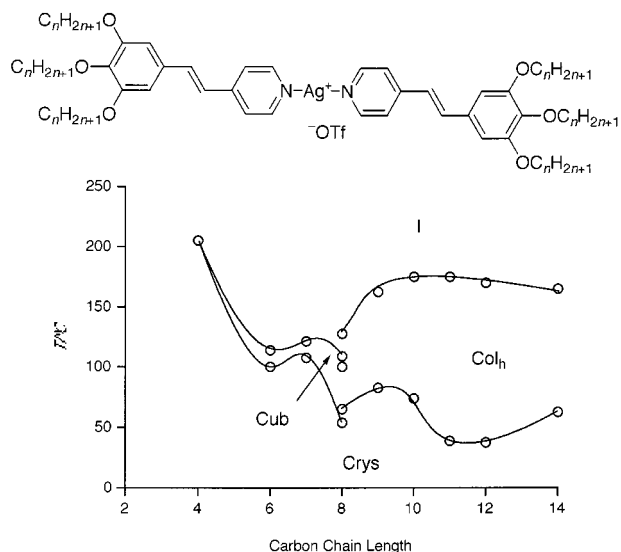


FIGURE 17. Phase diagram of the silver triflate complexes of 3,4,5-trialkoxystilbazoles.

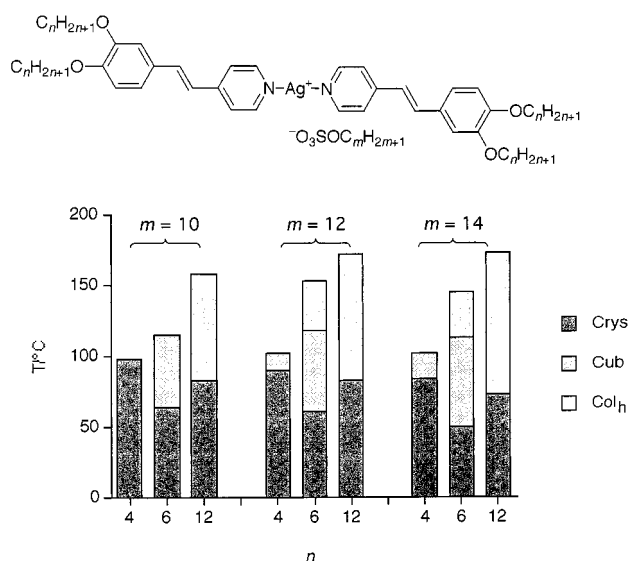


FIGURE 18. Bar chart to show the mesomorphism of 3,4-dialkoxystilbazoles complexed to a range of alkyl sulfates.

chain length, whereas for the dihexyloxystilbazole ligands, a cubic phase is seen, too, with the columnar phase being absent with the decyl sulfate anion; dibutyloxystilbazole gave either a cubic phase or no mesophase at all. Note here that as the ligand chain length increases, the stability of the phases also increases.

## Taking Stock—2

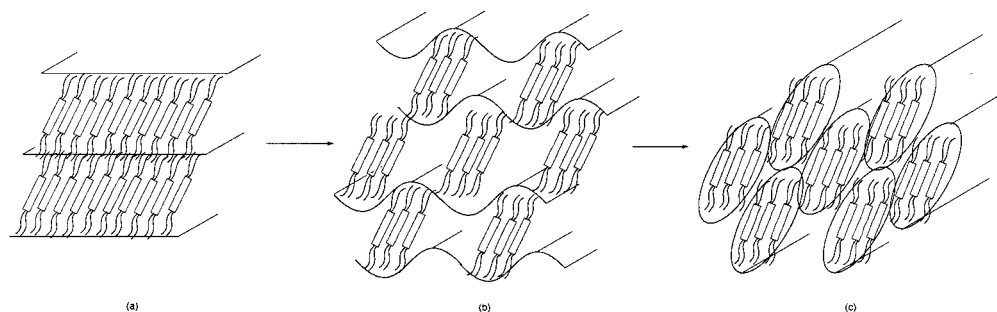
The way in which we can describe the mesomorphism of polycatenar mesogens bears a number of similarities to the way in which we discussed the mesomorphism of lyotropic liquid crystals, invoking ideas of interfacial curvature. In polycatenar mesogens, the interface we are considering is that between the (normally) aromatic core and the paraffinic chains. Thus, when there are short chains attached to the core, there is no great mismatch between the volume required by the core and that required by the chains, there is no curvature at the

interface, and a lamellar phase results, in this case  $S_C$ . However, as the chain length increases, so the volume occupied by the chains increases, and there develops a mismatch between the volumes that chains and core require. This generates a curved interface as indicated in Figure 19. At the extreme, this leads to a break-up of the lamellar structure to form columnar phases as proposed by Guillon<sup>37</sup> and by analogy with work by Kékicheff<sup>38</sup> with lyotropic systems and also by analogy with the arguments above which relate molecular structure to micelle morphology. This same model of behavior would then explain that cubic phases arise at curvatures which are intermediate between those required for columnar phase formation and the zero curvature of the lamellar phase; i.e., we are looking at analogues of the bicontinuous cubic phases. This model also gives a pictorial view of the way it is envisaged that the molecules arrange themselves in the columnar phase, as now we are not dealing with a simple stacking of disks. Figure 19<sup>37</sup> shows that as the lamellae break up, columns form with the columnar axis perpendicular to the tilt direction and each "slice" of column containing molecules arranged roughly parallel with the chains helping to fill space. One of the important things to take from this discussion is that the mesomorphism therefore depends on the relative volumes of the core and the chains. Now, considering the polycatenar silver complexes described above, we can begin to understand some of the patterns of mesomorphism in terms of the immediately preceding discussion and in terms of the mesomorphism of the simple, calamitic systems described above.

Starting with the 3,4-dialkoxystilbazole complexes of silver dodecyl sulfate, we see that two phases dominate the phase diagram, namely cubic and columnar, both of which are typical of polycatenar systems. Note, however, that it is not a straightforward matter to classify these complexes as tetracatenar due to the presence of the lateral alkyl sulfate chain, and so it is not entirely clear whether we should be surprised that no  $S_C$  phase is seen. Nevertheless, the trend in mesomorphism from cubic to columnar phase with increasing terminal chain length is typical of a polycatenar mesogen. We were also able to study the cubic–columnar transition in some detail by using a combination of X-ray diffraction and dilatometry, which allowed us to propose a mechanism for the transition.<sup>35</sup>

Consideration of the phase diagram (Figure 16) for the triflates shows that, once more, the cubic and columnar phases are seen but now the cubic phase appears at longer chain length (heptyloxy), as does the columnar phase (tridecyloxy). This is consistent with the idea that the dodecyl sulfate anion extends beyond the core of the silver cation and contributes to the interfacial curvature, so that in the absence of this anion, a longer ligand chain length would be needed to generate the same curvature. This is also entirely consistent with the results of the study of various alkyl sulfate counteranions with silver cations bound to 3,4-dialkoxystilbazoles. Here, a short alkyl sulfate and short ligand chain can, at best, give rise to a cubic





**FIGURE 19.** Diagram to show the curvature of the lamellar phase interface in polycatenar systems: (a) no curvature; (b) curvature leading to undulating structure; (c) sufficient curvature to lead to columnar phase.

phase, suggesting small but finite curvature, but as either chain length is increased, the columnar phase begins to appear and at the longest ligand chain lengths it totally replaces the cubic phase, consistent with the increased curvature.

The case of the 3,5-dialkoxystilbazoles requires more careful explanation, and we still await more definitive information from in-mesophase X-ray diffraction studies to develop the argument further. Thus, we see in the phase diagram that all homologues from hexyloxy to tetradecyloxy show a columnar phase which exists from close to room temperature to around 100 °C. Mesomorphic polycatenar materials with this substitution pattern and only four rings are extremely rare, and so we believe that, once more, there is a special role for the dodecyl sulfate anion related to the fact that it extends beyond the cation core, influencing space-filling and curvature thereby. This view is supported by the observation that, for the triflate salts, mesomorphism is almost totally absent.

Finally, we can consider the mesomorphism of the 3,4,5-trialkoxystilbazole complexes. For the DOS salts, the columnar phase extends from around room temperature to 140 °C for ligand chain lengths from butyloxy onward, showing only a small dependence on ligand chain length. However, while columnar phases are typical of hexacatenar mesogens, they are not common when the molecular core is as short as it is here. The fact that the columnar phase also dominates the behavior of the triflates implies that it may well be intermolecular ionic interactions which act to stabilize the “aggregates” that form the columnar repeat unit. However, we were very surprised to see that for the triflate salts there was a cubic phase present at shorter chain lengths which we would not have predicted. It may well be here that arguments concerning interfacial curvature are important, as clearly, the triflate anion will increase the volume of the molecular core and so reduce the effective surface curvature, leading to the formation of the cubic phase. However, we still feel that ionic interactions play their part, too.

## Bringing It All Together

What is clear from this study is that there are subtle combinations of factors which determine mesomorphism. Thus, we have been able to invoke arguments of surface curvature to explain the behavior of the polycatenar systems, and we have hinted that similar effects contribute

to the formation of the cubic phases in the calamitic materials. However, perhaps the most important theme developed follows from a suggestion in an article we published with Levelut<sup>26</sup> on the role of specific intermolecular ionic interactions in determining the mesomorphism in these systems. This is clearly also a very subtle effect, as within the same homologous series it permits the formation of a nematic phase and yet also allows smectic phases to form where otherwise they should not. It clearly also plays a role in cubic phase formation and in the mesomorphism of the polycatenar systems, although less overtly so in the latter case. The rich and diverse mesomorphism in these materials has been a constant source of surprise and joy and has clearly contributed to the demonstration of how the structural possibilities offered by using metal centers has broadened and enriched the subject of liquid crystals.

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