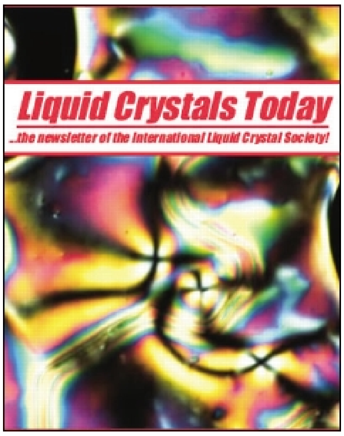

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Materials Highlights

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Materials Highlights

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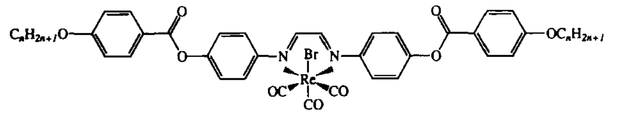
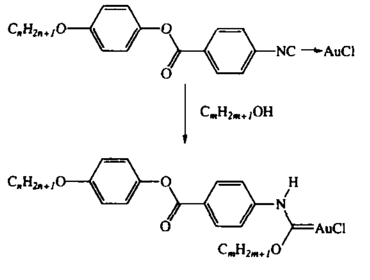
An aim of chemists in recent years has been to develop synthetic routes for the preparation of thermotropic, calamitic metallomesogens with high coordination numbers. Bruce and his colleagues (*Adv. Mater.* 1995, 7, 665) have now reported a methodology for the synthesis of mesogenic complexes formed by the coordination of the $[ReBr(CO)_3]$ fragment to 1,4-diaza-1,3-butadienes, 1. The parent ligands exhibit smectic C and nematic phases while the octahedral complexes are exclusively nematogenic. The destruction of smectic behaviour on complexation is attributed to the bulky $[ReBr(CO)_3]$ fragment disrupting molecular packing. The nematic-isotropic transition temperatures of the complexes are higher than those of the parent ligands. The authors speculate that this surprising observation may be related to a decrease in the flexibility of the -N=CH-CH=N- segment of the ligand on complexation. It is anticipated that diazabutadienes will become an important synthetic building block for the preparation of new metallomesogens incorporating high coordination number centres.



1

Metallomesogens, i.e. liquid crystals incorporating complexed transition metals, continue to be the focus of considerable research activity. By contrast, organometallic liquid crystals have received much less attention. In an attempt to remedy this, Takahashi and co-workers (*J. Chem. Soc., Chem. Commun.* 1995, 1215) have reported the synthesis and mesogenic properties of gold (I)-(alkoxy)(amino)carbenes, **2**; these are the first examples of liquid crystalline transition metal-carbene complexes. These were prepared by the nucleophilic addition of an alcohol to gold-isonitrile complexes (see Scheme1). The partial double bond character of the C-N bond gives rise to the existence of two geometric isomers. These can be separated by fractional crystallization and differing melting points are observed for the isomers. On melting, however, an isomerization occurs and a thermodynamic mixture of the two isomers is obtained. The gold(I)-carbenes, **2**, are exclusively smectic with clearing temperatures lower than the corresponding gold-isonitrile complex. The authors attribute this decrease to the introduction of the lateral alkyl chains which weaken the lateral intermolecular interactions.

Scheme 1



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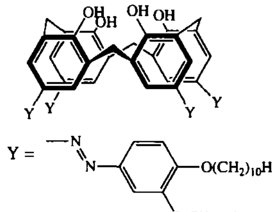
The principles of supramolecular chemistry are finding widespread application in the design of new liquid crystalline materials. Xu and Swager (*J. Am. Chem. Soc.* 1995, **117**, 5011) have shown how specific host-guest associations can be used to produce a bowlic hexagonal columnar mesophase. In these experiments, the host, a calix[4]arene derivative **3**, is mixed with the guest molecule, **4**, which contains two formamides linked by a flexible spacer. The guest was designed in order to enforce a cone conformation to be adopted by the host and also to disrupt the head-to-tail association of **3** resulting from intermolecular hydrogen bonding; hence the need for two formamide groups per guest molecule. Contact preparations of the two compounds revealed the formation of a mesophase and the authors speculate that one amide of the guest binds in the cavity producing the cone conformation while the other interacts with a second host molecule via hydrogen bonding (see figure 1). Surprisingly only small amounts of **4** are required to induce liquid crystallinity and the stability of the mesophase is independent of the host:guest ratio. Thus this implies that the guest needs to force only a fraction of the host molecules into cone conformations and head-to-tail arrangements. The authors propose, therefore, that the guest induced transition to a liquid crystal phase must be co-operative in nature.



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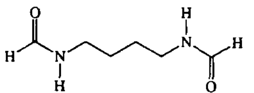

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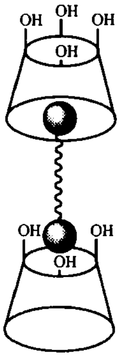
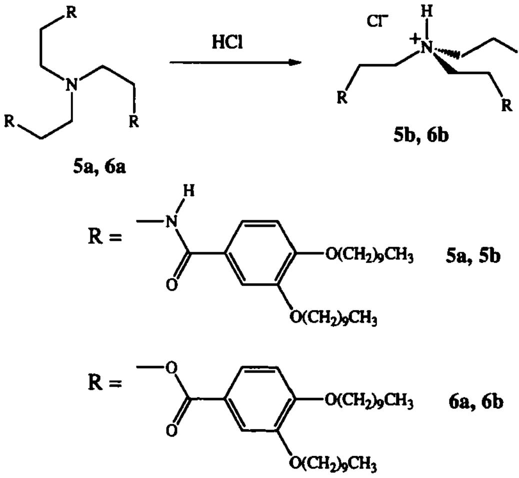
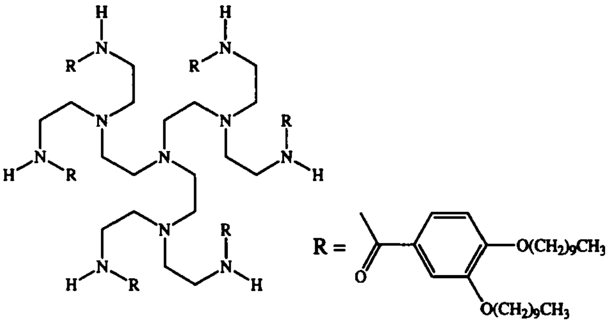


Figure 1

The theme of novel mesogenic materials is continued with the report by Stebani and Lattermann (*Adv. Mater.* 1995, **7**, 578) describing the thermal behaviour of two new classes of liquid crystals. The first of these comprises of an amine core, attached to which are three anisometric moieties, **5a** and **6a**. The compound possessing amide moieties, **5a**, has a relatively high melting point precluding the observation of liquid crystallinity; the authors attribute this to the possibility of forming three hydrogen bonds per molecule. Replacing the amide link by an ester group, **6a**,



reduces the melting point but does not reveal liquid crystallinity. The authors speculate that the highly flexible amine core prevents the formation of a liquid crystal phase. To test this view, the authors protonated **5a** and **6a** using hydrochloric acid. The resulting ammonium salts, **5b** and **6b**, in which the molecular flexibility has been reduced, are indeed mesogenic and form a smectic phase. The authors pursue this design approach further and report the properties of a substituted hyperbranched polyamine, **7**; this exhibits a monotropic columnar phase. Protonation of **7**, in which only three of the four tertiary nitrogen atoms are protonated, yields and enantiotropic smectogen with a high clearing temperature. Thus, **7** and its protonated analogue represent the first examples of new class of non-ionic and ionic liquid crystalline dendrimers, respectively.



7

Re-entrant nematic and cholesteric phases have been known for many years. Vill and Tunger (*J. Chem. Soc., Chem. Commun.* 1995, 1047) have now discovered a re-entrant TGB_A phase in a pure carbohydrate-based compound, **8**. The authors also describe mixtures of other members from the same homologous series with CCH7 which also exhibit re-entrant TGB_A behaviour. These studies also revealed what the authors believe to be the first observation of smectic C* phase formed by mixing mesogens exhibiting only smectic A and cholesteric phases. Light driven erasable direct read write (EDRAW) memory devices offer many advantages over conventional devices based on magnetic materials. Suarez and Schuster (*J. Am. Chem. Soc.* 1995, **117**, 6732) describe the use of a number of axially chiral bicyclic ketones, see figure 2, as potential triggers for a liquid crystal-based optical switch in which a reversible nematic to cholesteric transition is induced photolytically. Irradiation of the optically active ketones with unpolarized light results in photoracemization by isomerization about the carbon–carbon double bond. Subsequent irradiation of the racemic mixture with circularly polarized light, however, results in partial photoresolution. On irradiation, therefore, cholesteric mixtures of the ketone in a nematic solvent undergo a transition to a nematic. The reverse transition, however, i.e. from a nematic to a cholesteric mixture, could not be observed optically because the calculated pitch for the cholesteric mixture was too large. The authors speculate, however, that by modifying the structures of the ketones so that they resemble more closely that of the nematic solvent, the transfer of chirality from the solute to the bulk will be enhanced. These chemical modifications, it is hoped, may result in useful triggers for chiro-optical liquid crystal-based switches.

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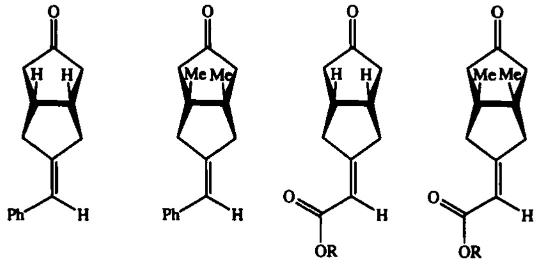

Figure 2

People in the News

We reported in the last issue of *Liquid Crystals Today* the award of the prestigious 1995 Kyoto Prize for Advanced Technology to Professor George Gray. This Award along with others for Basic Sciences and Creative Arts and Moral Sciences was marked by a series of events in Japan in November, culminating in the presentation of the Laureates to the Emperor and Empress at the Imperial Palace Tokyo. The Prize Presentation Ceremony took place in Kyoto on 10 November, and was presided over by the President of the Inamori Foundation, Kazuo Inamori, who instituted the Kyoto Prizes in 1984. Each prize carries with it a Certificate of Recognition, a Gold Medal and a prize of 50 000 000 Yen. In his prize lecture entitled 'My Life Working with Liquid Crystals – and How They Work for Us', Professor Gray paid tribute to the early influence of his father, a pharmacist, and went on to describe the timely coincidence of the discovery of the Twisted Nematic Display and his own discovery of the first stable room temperature nematic liquid crystals, which were ideally suited to the TN Display. To mark the Kyoto Prize Award to Professor Gray, a Symposium on 'New Developments and Applications of Liquid Crystals' was held on 12 November in which a series of speakers presented aspects of current research on liquid crystals. Professor Gray delivered a Commemorative Lecture on 'Four Decades of Liquid Crystal Research – A Look at the Past and Tomorrow's Possibilities'. Many will take pleasure from this recognition of the work of Professor Gray, and in particular the recognition of a synthetic organic chemist for his contributions to Advanced Technology.

Thanks are due to Drs H Kagawa, and L Farrand, Hitachi Research Laboratory for providing details of the Prize Award Ceremonies.