$\lambda = 0.71073$ Å]. $Z = 4$, $\rho_{calcd} = 2.531$ g cm^{-3}, $F(000) = 2944$, $T = 220$ K, $\mu(Mo_{K\alpha}) = 6.692$ mm^{-1}. Dark red block, $0.27 \times 0.27 \times 0.19$ mm^3. Absorption correction based on ψ-scans ($T_{min} = 0.051$, $T_{max} = 0.103$). Data collection and processing: The unit cell was obtained by using the program DIRAX[19] for 19 out of 25 reflections located during a random search. The two crystallographically unique macrocycles were restrained to be geometrically similar, while the displacement parameters of the C and O atoms were subject to rigid bond and body restraints. The refinement converged to a conventional R value of 0.069 with difference map extrema of $+2.61$ and -1.66 e Å^{-3} and a large number of poorly agreeing data with $l = 8n$. The matrix (-1 0 -0.75/0 -1 0/0 0 1) converts the cell into an equivalent cell. Reciprocal lattice points from these two cells will coincide only when l is a multiple of 4 and the sum of the transformed indices h and k is even (because of the lattice centering). Splitting the reflections in this way and proceeding with refinement with a scale factor relating the two twin components [0.147(4)] gave a final conventional R value of 0.0624 (based on F and 3839 data with $F > 4\sigma(F)$) and $wR2 = 0.1633$ (based on F^2 and all 4690 data used during refinement) for 362 parameters. The final difference map extrema were 1.44 and -1.46 e Å^{-3}; the Flack absolute structure parameter was 0.16(13). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100768. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(44)1223336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Breaking the Mold of Discotic Liquid Crystals**

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Organic Chemistry is currently living its "supramolecular epoch". Innovative and fascinating research has been focused on the synthesis and study of "living" molecules in an interdisciplinary field.[1] Development of the chemistry of complex molecules such as crown ethers, cryptands, phthalocyanines, dendrimers, catenanes, rotaxanes, and a variety of related compounds could seem, at first sight, interesting only from an exotic or theoretical point of view. However, possibilities have turned into reality for many of these systems.[1] Researchers in Chemistry, Biology, Materials Science, and even Physics are looking at these supramolecules as unique tools for achieving the ultimate aim of miniaturization. Alternatively, chemists are also becoming increasingly interested in investigating chemistry beyond the covalent bond; a concept expressed by J. M. Lehn as "the chemistry beyond the molecule".[1b] In this case, the active supramolecular structures are obtained by simple interactions between suitable functional units.

Liquid crystals are well-known examples of supramolecular assemblies.[1, 2] Based on self-organization, they combine the properties of order and mobility, a combination which allows the broad range of applications already exploited for these systems. Calamitic liquid crystalline compounds have been known since the end of the last century. However, in 1977 a new type of liquid crystal emerged, the discotic liquid crystals (DLCs).[3] These compounds have enriched the research and the possibilities of the so-called fourth state of matter.

Discotic liquid crystals are characterized by their ability to self-organize into columns, giving rise to two-dimensional superlattices of different types.[1c, 2b, 4] Consequently, one of the main issues in relation to columnar liquid crystals is the possibility of generating one-dimensional molecular "pathways" for electron, photon, energy or ion migration.[5]

Many molecules, either of low molecular mass or polymeric, have been reported to arrange in columnar mesomorphic states.[2b, 4, 5b, 6] However, most of these systems follow common structural guidelines. In general, DLCs consist of a rigid central core (planar, conical, pyramidal, or other such geometry) surrounded by four or more flexible groups, which make up the "soft" region. In certain cases, individual molecules do not match these criteria, but they are capable of aggregating into units which do fulfill them.[6] Scarce variations to this general structure are the "carbonaceous" group of compounds,[7] which are large, disc-shaped, polycondensed aromatic molecules with high molecular mass or, in the field of the lyotropic mesophases, the chromonic liquid crystals. These latter compounds with no flexible hydrocarbon chains in their structure exhibit columnar phases in the presence of a solvent.[8] The role of the soft region is played by water or another suitable liquid.

This paper deals with a type of compound which constitutes the first exception to the above trends in the field of thermotropics. We report here the first examples of thermotropic DLCs which do not contain flexible groups, namely indenes **1**–**4** and pseudoazulene **5**.

Our interest in these organic compounds is twofold. Their synthesis has recently been reported[9] to proceed by a unified mechanism based on the initial abnormal Beckmann rearrangement of oximes to cyanides, followed by cyclization and/or exhaustive chlorination and dehydrochlorination. Furthermore, and surprisingly, when these small molecules were treated thermally and studied under polarized light, the

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[**] This work was supported by the Comisión Interministerial de Ciencia y Tecnología (project MAT96-1073-CO2-02) and the Dirección General de Investigación Científica y Técnica (projects PB93-0414 and SAB94-0169) of Spain, and the Conserjería de Educación de la Junta de Extremadura y Fondo Social Europeo (ref. EIA94-93).

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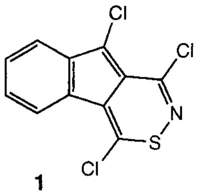

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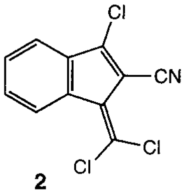

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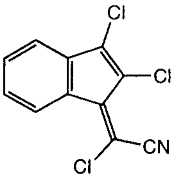

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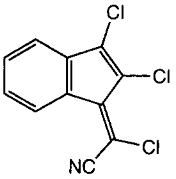

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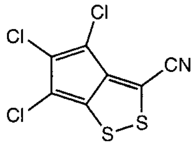

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fluid samples exhibited birefringence. Such behavior suggested thermotropic transitions to a liquid crystalline state. Therefore we investigated the liquid crystal behavior of these compounds by polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction. The most important data obtained from these three techniques are summarized in Table 1 and Table 2.

Table 1. Optical and thermal properties of the compounds **1**–**5**.

Compound	Mesomorphic properties (T [ΔH])[a]
1	K (205.1 [12.2]) Col_h (230.0 [11.9]) I
2	K (183.9 [13.9]) Col_h (196.4 [12.0]) I
3	K (131.6 [9.9]) Col_h (152.3 [6.04]) I
4	K (97.3 [9.8]) M[b] (159.5 [1.1]) Col_h (184.8 [10.0]) I
5	K (144.0[c] [13.4]) I I (144.0 [0.81]) Col_h[d] (120)[e] K

[a] K = crystal, Col_h = hexagonal columnar phase, I = isotropic phase, T = temperature in °C; ΔH = transition enthalpy in kJ mol^{-1}. The temperatures given are for the onset of the first scan transitions. Heating and cooling scans at 10 K min^{-1}. [b] Unidentified phase. [c] Transition observed after successive cooling and heating scans. [d] Monotropic mesophase. [e] Optical data.

On examination by optical microscopy (OM) with polarized light (Figure 1) all the compounds display pseudo-focal-conic or mosaic textures on heating and form leaflike domains on cooling from the isotropic liquid (in most cases, the dendritic formations are seen more clearly without crossed polarizers). These textures strongly suggest columnar mesophases of hexagonal symmetry.[4b, 10] Likewise, on cooling some of the samples, large black areas lacking birefringence were observed. This indicates that the optical axis readily aligns normal to the glass microscope slides.

Analysis by DSC revealed melting and clearing endotherms of similar enthalpy in the range of 6–14 kJ mol^{-1}, which indicates a high degree of order within the mesophase (Figure 2). With the exception of **4**, all compounds exhibit a

Table 2. X-ray diffraction data for the mesophase of compounds **1**–**5**.

Compound	T [°C]	hkl	d_{obs} [Å]	d_{calcd} [Å]	Hexagonal lattice constants [Å]
1	210	100	8.49	8.52	$a = 9.84$
		110	4.93	4.92	
		200	4.27	4.26	
2	187	100	8.29	8.28	$a = 9.56$
		110	4.77	4.78	$c = 3.6$
		001	3.63		
3	145	100	8.36	8.37	$a = 9.66$
		110	4.81	4.83	$c = 3.6$
		200	4.20	4.18	
		001	3.60		
		210	3.17	3.16	
4	165	100	8.36	8.35	$a = 9.64$
		110	4.81	4.82	$c = 3.6$
		200	4.17	4.17	
		001	3.63		
		210	3.16	3.16	
5	135[a]	100	7.57	7.53	$a = 8.69$
		200	3.74	3.76	$c = 3.5$
		001	3.48		

[a] Monotropic mesophase obtained by cooling the isotropic liquid

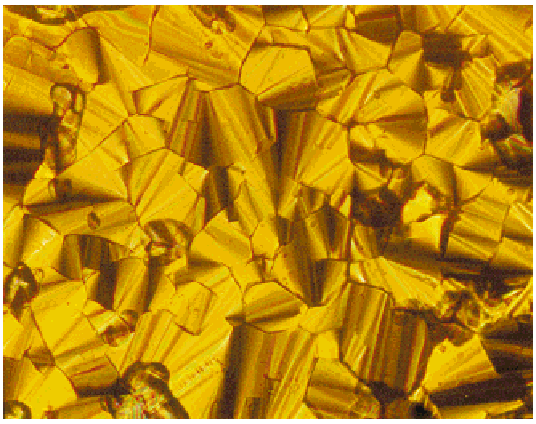


Figure 1. Pseudo-focal-conic texture of the Col$_h$ phase of compound **2** viewed by optical microscopy through between crossed polarizers.

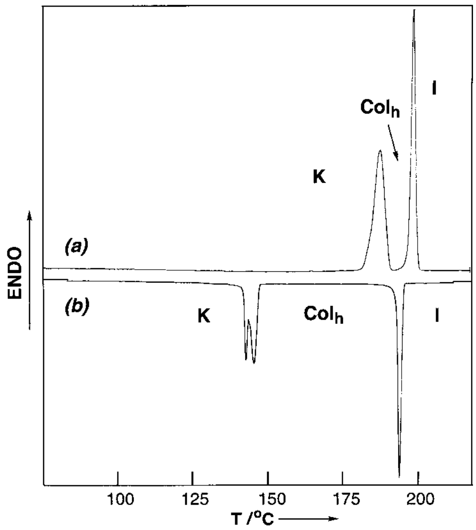


Figure 2. DSC traces corresponding to the first heating (a) and cooling (b) runs of compound **2** (scan rate = 10 K min^{-1}).

single mesophase that is either enantiotropic (**1**, **2**, and **3**) or monotropic (**5**) in nature. The *Z* isomer **4** displays one intermediate peak before the clearing endotherm, which can also be detected by OM as a smoothing of the broken pseudofocal-conic texture. On cooling, an exotherm corresponding to the liquid–mesophase transition is observed for all the compounds. However, although a clear crystallization is observed by OM and DSC for indenes **1** and **2**, no such peak is observed in the thermograms of **3**, **4**, and **5**. This fact is consistent with the subtle texture changes detected for the latter compounds on cooling to room temperature.

To confirm the observations discussed above and to obtain more information on the structures of the liquid-crystalline arrangement exhibited by these compounds, their mesophases were studied by powder X-ray diffraction with a pinhole camera equipped with a high-temperature device. Typical of crystalline structures, the patterns taken at room temperature are, in all cases, characterized by the presence of numerous diffraction rings across the whole angular region, which can only be assigned to a three-dimensional arrangement. When the samples are heated above their melting temperature, the diffraction patterns contain fewer rings, which indicates a loss of order relative to the crystalline solid. The spacings measured experimentally for compounds **1**–**5** are collected in Table 2 together with the proposed indexation and the calculated spacings.

The high temperature patterns of all the compounds considered are qualitatively very similar, although the number of diffraction rings observed depends on the particular compound. The patterns of compounds **3** and **4** taken at 145°C and 165°C, respectively, have in common the existence of a set of four sharp maxima with a reciprocal spacing ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ (Figure 3). This is characteristic of a hexagonal lattice, and the four maxima can be assigned to the (100), (110), (200), and (210) reflections. The additional sharp ring observed at 3.6 Å is assigned to the (001) reflection and corresponds to the *c* parameter of the hexagonal network. The absence of reflections with Miller indices *h*, *k*, and *l* simultaneously different from zero, even on overexposed photographs, indicates that there is no three-dimensional order. All these features are characteristic of a columnar hexagonal mesophase. Moreover, when treated mechanically at the mesophase temperature range, a sample of compound **3** yielded an aligned pattern with the column axes oriented along the stretch direction. This confirms the columnar liquid-crystalline nature of the phase. The sharpness of all the diffraction rings indicates that there is long-range order not only in the plane of the hexagonal lattice, but also in the stacking direction, and thus the hexagonal columnar mesophase can be described as *ordered* (Col_{ho} mesophase). The X-ray patterns suggest that the phase exhibited by compound **4** between 97°C and 159°C (see Table 1) could be either a disordered solid or a very organized mesophase. However, we have not been able to assign its structure unequivocally.

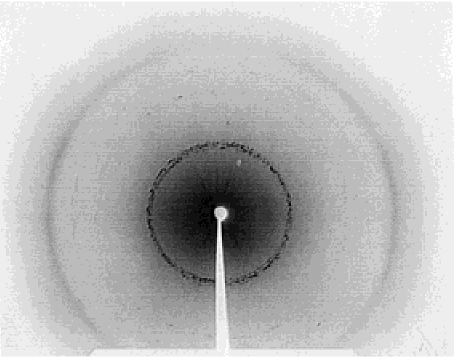


Figure 3. X-ray diffractogram of compound **4** at 165°C (Col_h mesophase).

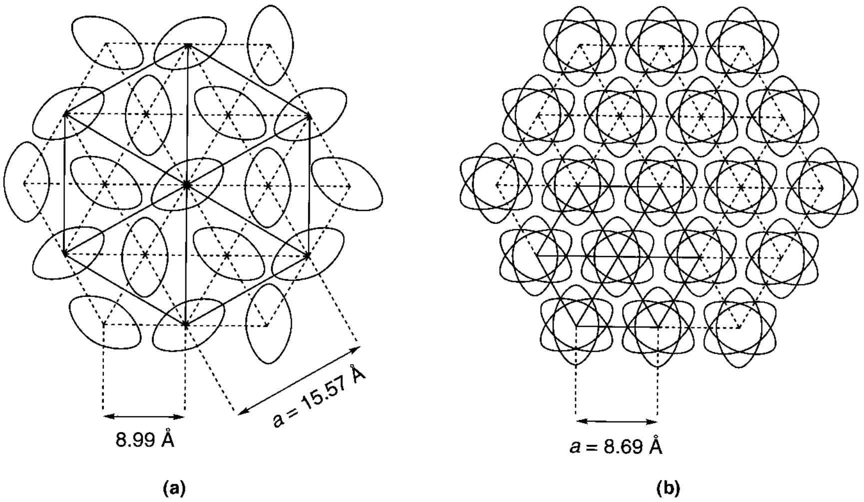
As compounds **1** and **2** exhibit the mesomorphic state at very high temperatures, decomposition was detected after long exposure times. Furthermore, the mesophase of compound **5** is monotropic, that is, it is thermodynamically unstable and has a strong tendency to crystallize. Consequently, it was not possible to obtain long-exposure photographs for compounds **1**, **2**, and **5**, and therefore fewer maxima are observed on their X-ray photographs. Nevertheless, in spite of the absence of some reflections that were observed for compounds **3** and **4**, all the patterns are consistent with a columnar hexagonal mesophase (see Table 2).

For all the compounds except **1**, for which the extent of decomposition precludes the appearance of the corresponding reflection, the stacking distance (*c* axis of the hexagonal network) is 3.5–3.6 Å. In contrast, the hexagonal lattice constant (*a* axis) depends on the particular compound (see Table 2). On comparison of the experimental values for *a* (column diameter) with the molecular sizes estimated from Dreiding stereomodels, it can be deduced that the columns contain single molecules as stacking entities. This deduction leads to reasonable density values for the mesophases.

Discotic mesomorphism is the result of the balance between interactions of the central core and the peripheral flexible structure (soft part). The hard central core is responsible for the columnar stacking, while the flexible part acts as a lubricant and plays an active role in reducing correlation between neighboring columns. This role is usually played by conformationally disordered aliphatic chains, although in some short-chain ionic discotic materials, mesophase formation has been explained in terms of rotation of tetrafluoroborate anions which reduce correlation between the cationic columns.[11] In the compounds described in this paper, the aromatic structures constitute the hard part, while the polarizable chlorine and sulfur atoms, as well as the polar and polarizable cyano groups, behave as *unusual* soft parts through weaker molecular interactions.[12] In the solid these atoms and groups give rise to strong intermolecular attractions,[9] which become weaker as the temperature increases due to increasing thermal disorder. On melting, the weakening of the polar attractions relaxes the molecular packing, and thus the transition from the crystal to the mesophase is associated with the onset of molecular rotation.

It is worth noting the similar enthalpy changes measured for both the melting and the clearing processes for these compounds. Typical ordered hexagonal discotic liquid crystals exhibit Col_h-I enthalpies in the same range as those reported in this paper.[4, 10, 13] However, the transitions from the solid to the Col$_h$ state, which are attributed to the melting of the flexible chains, involve energies two to three times higher than the ones reported here.

The crystal structure of pseudoazulene **5** is hexagonal with cell constants $a = 15.57$ Å and $c = 6.815$ Å, and six molecules per unit cell.[9] The molecular packing corresponds to a pseudo-hexagonal arrangement in which the centers of close-neighboring molecules lie at $15.57/{:}\sqrt{3} = 8.99$ Å (Figure 4a). In the solid the molecules are kept in a fixed orientation by strong intermolecular attractions. However, upon transition to the mesophase these attractions become weaker, thus allowing rotation of the molecular planes around the c axis (Figure 4b) in such a way that the molecules project an averaged circular shape along the columnar axis (c axis). The transition to the liquid-crystalline state implies that neighboring columns become discorrelated, and a hexagonal columnar structure is obtained in which the interdisc interactions inside the columns are still maintained. In accordance with this, the intercolumnar parameter in the mesophase of 8.69 Å is similar to the intermolecular distance in the hexagonal crystal (8.99 Å).



(a) (b)

Figure 4. Schematic drawing of the structure of the crystalline phase (a), and of the Col$_h$ mesophase (b) of compound **5** viewed along the c axis. The transition from the crystal to the mesophase is associated with the onset of molecular rotation: neighboring columns become less correlated.

In summary, we have described the first examples of thermotropic DLCs without long terminal substituents, which opens new and interesting possibilities for the study and the design of this type of material. Synthesis of other suitable compounds for the study of the relationship between structure and liquid crystal activity is currently in progress. The new scope for novel soft units within disclike systems, along with the study of the influence of their position and number on mesomorphic behavior and other physical properties (electrical, optical, etc.), provides a very promising direction for new areas of research.

Received: July 9, 1997 [Z10664IE]
German version: *Angew. Chem.* **1998**, *110*, 308–312

Keywords: liquid crystals • materials science • mesophases • supramolecular chemistry

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