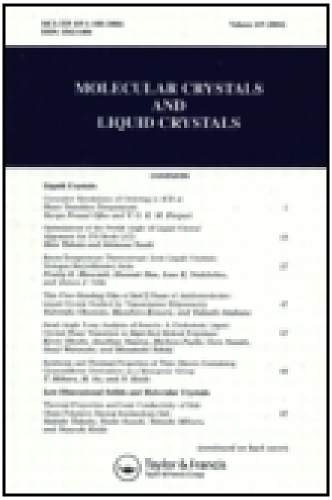

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New Mesogenic Compounds Exhibiting a Thermotropic Optically Isotropic Phase

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New Mesogenic Compounds Exhibiting a Thermotropic Optically Isotropic Phase

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The only two series of carboxylic acids, 3-nitro- or 3-cyano-4-alkoxybiphenyl-4'-carboxylic acid, are known to exhibit the optically isotropic phase (S_D). Now we synthesised 4-(branched alkoxy)-anilinebenzylidene-4'-carboxylic acid series, all being racemic, and investigated their mesophase properties by means of DSC, optical microscopy and X-ray measurement. As a result, some branched azomethine derivatives were found to form a S_D phase. We also synthesised cinnamic acid derivatives with branched alkoxy tail that were turned out to exhibit either S_D phase or hexagonal columnar phase. We tried biphenyl or azobenzene core analogues which were found to produce a highly ordered smectic phase or no mesophase, respectively. At this stage, we suppose it plays an important role that the branch is introduced into the terminal chain and a certain dipole moment is located within the mesogenic core. These factors may allow the peculiar molecular packing that causes an optically isotropic property.

Keywords: optically isotropic phase; carboxylic acid; branched tail; hexagonal columnar phase

Introduction

There are several materials which exhibit a thermotropic smectic D phase [1-5]. In spite of the liquid crystal state, this phase has no optical anisotropy and therefore there is no microscopic texture observed under the polarised optical microscope. The first compound exhibiting such a strange phase is 3-substituted-4-n-alkoxy-biphenyl-4'-carboxylic acid derivatives reported by

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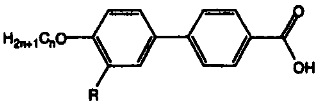
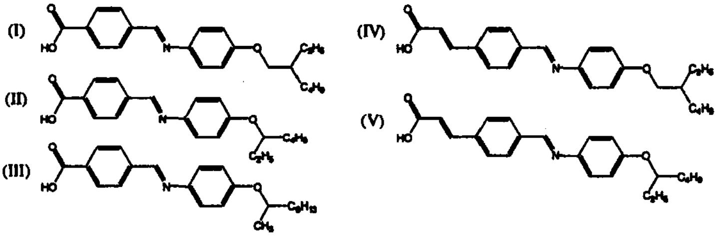


$R = NO_2, CN$

Gray *et al.* in 1957 [1]. Since then, another samples have been discovered and the vigorous efforts on the structural investigation have been made [6-9]. On the other hand, it is also well known that in the lyotropic system which is composed of the mixture of hydrophilic and hydrophobic, a cubic phase appears in the region between the hexagonal columnar and the lamella phase, depending on the concentration of the constituents [10]. In both systems, cubic space group is believed to be formed. However the origin of the occurrence seems to be different between both systems and in the thermotropic system the origin of this unique phase has seldom been discussed. Now we will report the new series of compounds which show a thermotropic optically isotropic phase and propose the structural factors for a cubic phase, from the chemical point of view.

Experiment

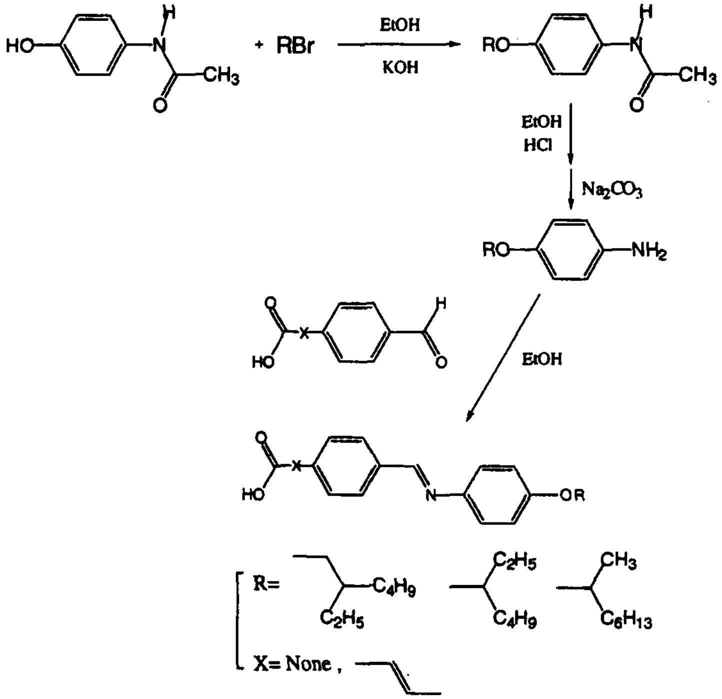
The series of materials used in this study are listed below and all



compounds were synthesised according to the following scheme and synthesis of compound (I) is described below as an example.

To the mixture of 4-Hydroxyacetanilide (30mmol) and Potassium hydroxide (30mmol) in 200ml of Ethanol, 1-Bromo-2-ethylhexane (31mmol) in 30ml of Ethanol was added dropwise. Then this solution was heated under reflux for 24hrs. The precipitated KBr was filtered off and the solvent was removed. The residue was purified by column chromatography (Silica gel, chloroform as eluent). The acetanilide derivative was dissolved in

100ml of Ethanol in the presence of 20ml of conc. HCl and the solution was refluxed for 24hrs. The resulting mixture was cooled down and the solvent was evaporated under reduced pressure. The remaining solid was dissolved in Chloroform and washed with aqueous Sodium carbonate and brine successively. Then organic layer was removed and the residue was purified



by the same method as mentioned above. The target compound was prepared by condensation of this aniline derivative (10mmol) with Terephthalaldehydic acid (10mmol) by heating under reflux in Ethanol for 6hrs. After cooling, the precipitates were collected and recrystallised at least twice from Ethanol (some compounds were from the mixture of Ethanol and Hexane).

The transition temperatures and transition enthalpies of compounds (I) – (V) are listed in the **Table 1**.

Table 1. Phase transition temperatures and enthalpies of this series.

Compound	Phase Transition / °C (Transition enthalpies / kJ mol^{-1}) Iso. ——— Mesophase ——— K		Mesophase
(I)	205.4 (7.84)	181.2 (7.21)	SD
(II)	165 (1.44)	141.4 (9.76)	SD
(III)	195.9 (4.71)	146.6 (10.7)	SC
(IV)	233.2 (11.9)	113.5 (10.3)	SD
(V)	203.7 (7.56)	123.2 (12.0)	Hexagonal columnar

Results and discussion

Figure 1 shows the DSC cooling scans of this series at the rate of 10°C/min. As can be seen this figure, two peaks are observable except for compound (I) which exhibits crystal – crystal transition at the lowest peak. Between two peaks (highest and middle peak for compound (I)), the typical textures can be observed for each mesophase under polarised microscope.

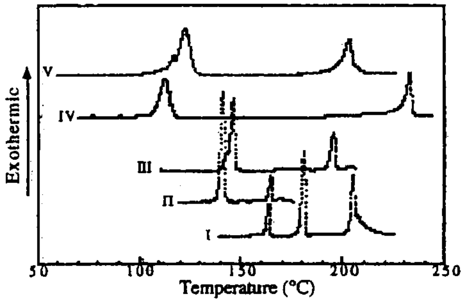


Figure 1. The DSC cooling scans of compound (I) – (V) at the scanning rate of 10°C/min.

The SD phase of compound (I), (II) and (IV) appears as the maple-like mosaic domain from the isotropic melt (see **Figure 2**) and then this birefringence disappears immediately (see **Figures 3**).

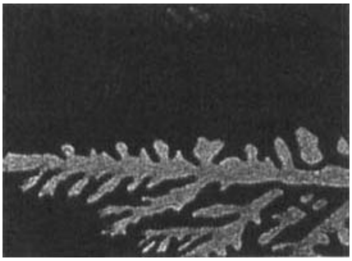


Figure 2. The maple-like mosaic texture taken at 165°C for compound (II).

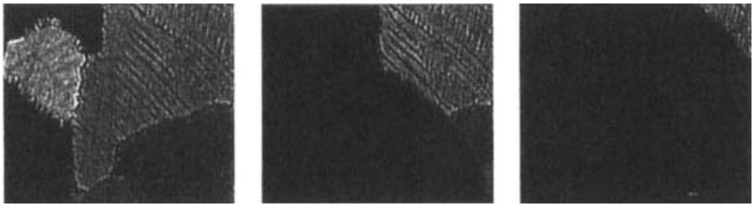


Figure 3. The disappearance of the birefringence, which begins at the bottom left of the photograph, taken at 165°C for compound (II).

As can be seen **Table 1**, compounds (III) and (V) exhibit Sc and hexagonal columnar phase, respectively, instead of SD phase. Each mesophase could be easily identified by the microscopic texture and the X-ray investigation. The X-ray measurement was performed for all compounds prepared and the result is shown in **Figure 4**. As can be seen this figure, there is no temperature variation of the layer spacings and the values of them are quite reasonable if the molecules are dimerising in the liquid crystalline state. On the basis of this assumption, the tilt angle of compound (III) of Sc phase can be estimated as 42° (molecular length L = 21.7Å). On the other hand, the layer reflection profile along the 2θ observed for compound (V) of hexagonal columnar phase is shown in **Figure 5** in which the inset is the expansion of the range between $2\theta = 1°$ and 6°. The arrow indicates the (100) reflection ($2\theta = 2.40°$) and the lines reveal the (110) and the (200) reflections, respectively (see **Table 2**). Therefore the hexagonal unit cell can be easily estimated as a = 43.5Å that is just twice as long as the calculated molecular length L = 21.5Å.

Table 2. The indices of reflections and the layer spacings observed for compound (V).

(100)	(110)	(200)
37.6Å	21.7Å	18.2Å

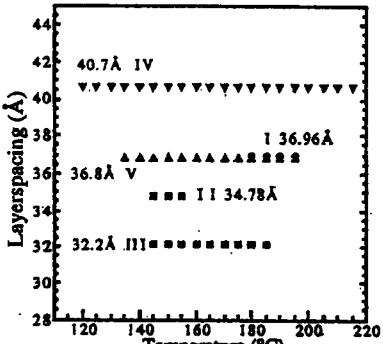


Figure 4. The temperature variation of the layer reflections observed for this series.

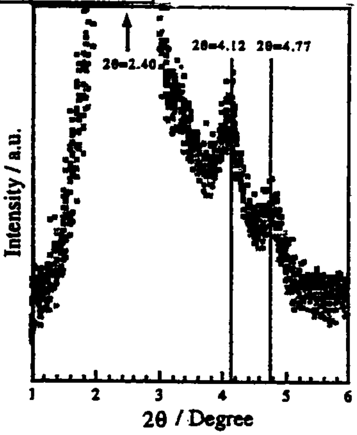


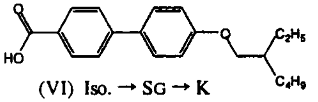
Figure 5. The layer reflection profiles observed for compound (V) of hexagonal columnar phase.

Let's return attention to the SD phase here, we also tried the X-ray investigation on the SD phases of compound (I), (II) and (IV) and in the small angle region two layer reflections were observable. These appear as several spots along the two rings which correspond with 2θ = 2.39° and 2θ = 2.79°for compound (I). In addition, there are at least three more reflections observed around 2θ = 3°- 4°. However, these are too weak to index them. The detailed investigation is now in progress. At this stage, it is reasonable that the former two reflections are indexed as (200) and (210), respectively. This assumption gives a cubic lattice constant a = 74Å for compound (I) and this value is 4.2 times as long as the calculated molecular length L = 17.5Å. It may suggest that the dimerised pair molecules constitute a rod or a micell and such microstructure form a gyroidal macrostructure in which overall structure has cubic symmetry. The layer reflections (2θ and d) of compound (I), (II) and (IV) and the lattice constants (a) of them are listed in the **Table 3** together with the other parameters such as the molecular length (L) and a / L ratio.

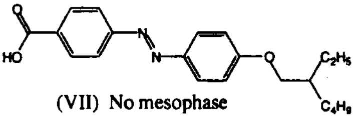
Table 3. The layerspacing (d), the lattice constant (a), molecular length (L) and a / L ratio.

	2θ / degree		d / Å		a / Å	L / Å	a / L
(I)	2.39	2.79	36.96	31.67	73.92	17.5	4.2
(II)	2.54	2.95	34.78	29.95	69.56	18.9	3.7
(IV)	2.17	2.45	40.7	36.06	81.4	20.4	4.0

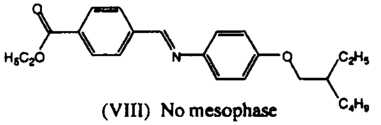
Next let's turn attention to the chemical structure of the molecule. In order to investigate the effect of the chemical structure on the mesophase properties, we synthesised the other series of carboxylic acids described below.



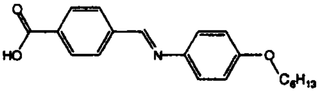
(VI) Iso. → SG → K
183°C 145°C



(VII) No mesophase



(VIII) No mesophase



(IX) Iso. → N → SC → K
263°C 254°C 180°C

Comparing the mesophase behaviour of compound (I) with that of (VI) and (VII), the –C=N- double bond in the mesogenic core is very important for SD phase to form. It means some kind of strong dipole moment is needed to make up the peculiar structure. Then comparing compound (I) with (VIII), the carboxylate has no ability to form a mesophase as well as SD phase. It suggests that dimerising is also needed to show not only SD phase but liquid crystal. Finally let's consider the introduction of the branch into the terminal chain. Compound (IX) shows a bimorphism, nematic phase at higher temperature and SC phase at lower and wider temperature region, but no SD phase. It can safely lead us to the conclusion that introducing the branched terminal chain plays an important role to form the cubic packing.

Branching out of the terminal chain induces both the steric hindrance and the conformational change of the molecular shape (see **Figure 6**).

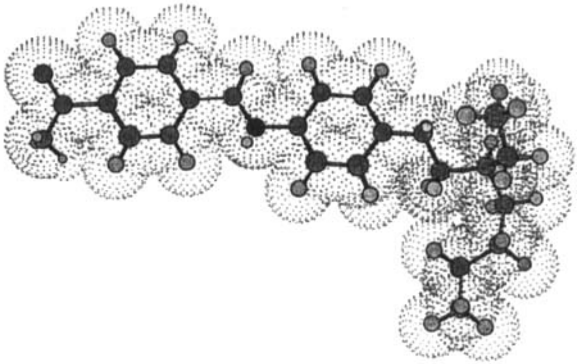


Figure 6. The molecular structure of compound (I).

Summary

We synthesised the series of carboxylic acid derivatives of which the branched terminal chain was attached at the one end. Some of these materials show the optically isotropic phase (SD) and the others exhibit a hexagonal columnar, SG, SC or no mesophase, depending on the chemical structure. We suppose it is important factors for the formation of the cubic structure both to introduce the branch into the terminal part and to arrange a certain dipole moment within the mesogenic core. The structure of SD phase has a cubic symmetry and the detailed structural investigation is now in progress.

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