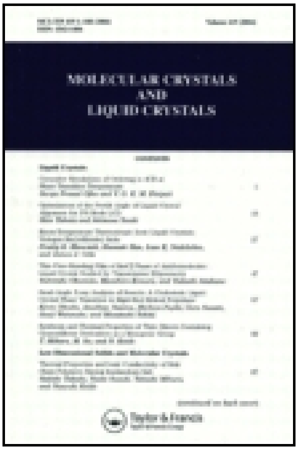

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Mesomorphic Properties and Hydrogen Bonding Formation of Asymmetrical Triphenylene Discotic Liquid Crystals

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To cite this article: Wen Wan, Hirosato Monobe, Takushi Sugino, Yuko Tanaka & Yo Shimizu (2001): Mesomorphic Properties and Hydrogen Bonding Formation of Asymmetrical Triphenylene Discotic Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 597-603

To link to this article: http://dx.doi.org/10.1080/10587250108025029

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 597-603
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Mesomorphic Properties and Hydrogen Bonding Formation of Asymmetrical Triphenylene Discotic Liquid Crystals

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Asymmetrical triphenylene derivatives containing ester or carboxylic acids as terminal substituents were synthesized and characterized by DSC, optical microscopy and X-ray diffraction. It was found that in the ester homologues, only one compound exhibits a monotropic nematic (N_D) mesophase, while most of the carboxylic acid derivatives show a hexagonal columnar (Col_h) mesophase. Temperature dependent infrared spectra of the carboxylic acid derivatives indicate the existence of strong hydrogen bonding interactions in the isotropic, mesomorphic and solid phases.

Keywords: hydrogen bond; discotic; liquid crystal; triphenylene

INTRODUCTION

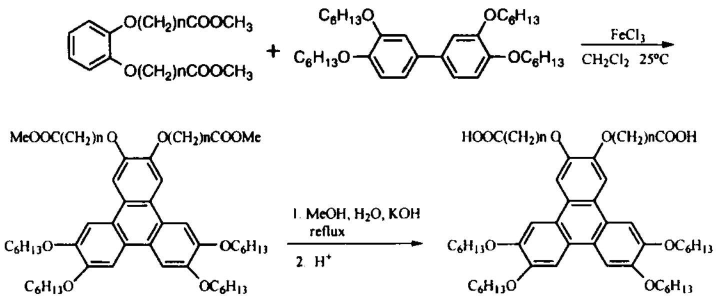
The supramolecular assemblies of disc-shaped molecules have much potential uses in opto-electronic application such as high-resolution xerography, sensors and information storage[1~3]. Discotic liquid crystal possessing triphenylene cores were reported to give fast charge carrier mobility, which exceeds the values of the photoconducting polymers presently used by two to three orders of magnitude[4, 5]. In recent years, a lot of asymmetrically-functionalized triphenylene have been reported on the study of relationship between discotic structure and mesomorphic property[6~8]. However, most of the functional groups are hydroxy, and its acrylate. No asymmetrical triphenylene derivative containing carboxylic acid functional group has been reported.

In this work, we report the mesomorphic properties of long-chain triphenylene derivatives possessing terminal functional groups such as ester and carboxylic acid. The temperature dependence of infrared spectra for the hydrogen-bonding interaction has also been investigated so as to study the effect of intermolecular hydrogen-bonding interaction on mesomorphism.

EXPERIMENTAL

Synthesis

The triphenylene derivatives were prepared according to Scheme as shown below.



1a~1f **2a~2f**

n	3	4	5	6	7	10
	a	**b**	**c**	**d**	**e**	**f**

Scheme

The ester derivatives (**1a~1f**) were prepared using ferric chloride mediated oxidative coupling of tetrahexyloxy biphenyl with 6-(1,2-phenyloxyl) dihexanoate, followed by termination using methanol[9, 10]. The corresponding carboxylic acid derivatives (**2a~2f**) were obtained by hydrolysis of the ester compounds in NaOH aqueous solution.

The detailed synthetic procedures were described elsewhere[11].

Measurements

The phase transitions were detected by a Differential Scanning Calorimeter (TA Instrument, 2920 MDSC) and the texture of mesophase was observed by a polarizing microscope (Olympus, BH-2) equipped with a hot stage (Mettler, FP80HT). The temperature dependent FT-IR spectra was measured using a FT-IR sepectrometer (Bio-Rad FTS 6000) with a hot stage (Mettler, FP90HT). The sample was sandwiched by two KBr crystal plates for the measurement. The thickness of sample was adjusted by silica beads (2μm diameter).

Results and dissusion

Mesophase behavior

The optical, thermodynamic data for the homologues containing carboxylic acid (**2a~2f**) are summarized in Table I.

Table I. Transition temperatures and enthalpies of the carboxylic acid derivatives

Compound	Phase transition	Temperature	$\Delta H/kJmol^{-1}$
2a	Cr--- (Col_h)--- I	130 (117)	55.8 (4.77)
2b	Cr---Cr'	91.3	35.8
	Cr'--- Col_{sh}^a	94.0	7.74
	Col_{sh}---Col_h	102	6.7
	Col_h---I	105.3	0.87
2c	Cr--- (Col_h)--- I	103.8 (78)	67.17 (2.87)
2d	Cr--- (Col_h)--- I	106.1 (68)	87.5 ^{b}
2e	Cr--- I	95.4	71.0
2f	Cr--- I	69.1	53.4

a, birefringent columnar mesophase b, crystallization while mesophase forms

The DSC measurements for compounds **2a**, **2c**, **2d** showed one peak on heating and two peaks on cooling, which support the monotropic mesophase transition as observed by a cross polarizing microscope. Typical textures of columnar mesophase could be seen and further assigned to hexagonal columnar arrangement by the X-ray diffraction measurements. Compound **2b** gave a complex phase transition on the DSC data. The observation of **2b** under the optical microscopy showed a crystal-to-crystal transition at 92°C. Further heating the sample gave a mosaic texture (Fig.1). When temperature was increased to 105°C, a typical texture similar to that of other hexagonal mesomorphic homologues appeared.

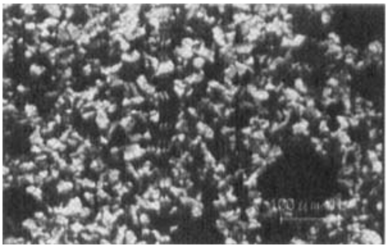


FIGURE 1 The texture of **2b** at 95°C on heating.

A X-ray diffraction measurement was performed on **2b** at 100°C. The lattice constant α_{hex}, indices and d-spacing for the X-ray reflections in the mesophase are summarized in Table II.

Table II The lattice constant α_{hex}, indices and d-spacing (in Å) for the X-ray reflections.

α_{hex}	(010)	(020, 100)	(030)	(110)	(200, 040)	210	300	001
21.69	37.41	18.74	12.47	10.75	9.28	7.08	6.01	3.73

The X-ray pattern in wide angle region exhibits a broad halo centered around $2\theta=20°$ which corresponds to a Bragg spacing of molten alkyl chains. The Small-angle region shows several reflection peaks. Considering the possible structure of dimeric molecules formed by carboxylic acids, birefringent mesophases could exist in this phase. If the sharp reflection at $2\theta=4.7°$ is indexed as d_{100}, the reflections characteristic for two-dimensional hexagonal lattices can be assigned as $d_{100}:d_{110}:d_{200}:d_{210}:d_{300} = 1:(1/\sqrt{3}):(1/2):(1/\sqrt{7}):(1/3)$[12, 13]. Other reflections could be responsible for the layered-structure, which is caused by an arrangement of dimeric discogens. The ratio of the layered-spacing is $d_{010}:d_{020}:d_{030}:d_{040} = 1: 1/2 :1/3:1/4$, among which d_{020} and d_{040} are overlapped by reflection d_{100} and d_{200}. The hypnosis of layered superstructure which is induced by hydrogen-bonded dimeric discogens can also be proved by X-ray diffraction in the small angle scattering of **2a**, **2c**. A possible model for this supermolecular arrangement is depicted in Fig.2. At present, we tentatively assign this birefringent mesophase as super hexagonal columnar mesophase Col_{sh}.

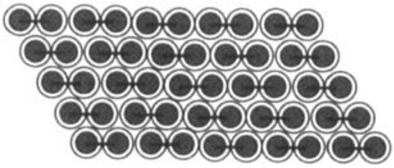


FIGURE 2 A possible model for the superstructure for the carboxylic acids.

Temperature dependent Infrared spectra

In order to study the formation of dimeric molecules in mesophase, temperature dependent Infrared spectra were performed on carboxylic acid derivative. Fig.3 gives the IR spectra of C=O stretching band of carboxylic acid derivative **2c** in the isotropic, mesomorphic and solid phase. The strong carbonyl stretching vibration band around 1708 cm^{-1} is characteristic for the dimeric carboxylic acids[14,15]. The weak carbonyl band at 1741 cm^{-1} due to the monomeric **2c** appears only in the isotropic and mesomorphic phase. Fig.4 shows the intensity of free C=O stretching band (1741cm^{-1}) dependent on temperature. It is suggested that the free carboxylic acids gradually associate as the phase becomes more and more ordered. In the crystal phase, no free carboxylic acids can be detectable in the spectrum. These results indicate that there is a significant amount of hydrogen-bonded pairing of acid groups in the crystal, mesomorphic and isotropic phases.

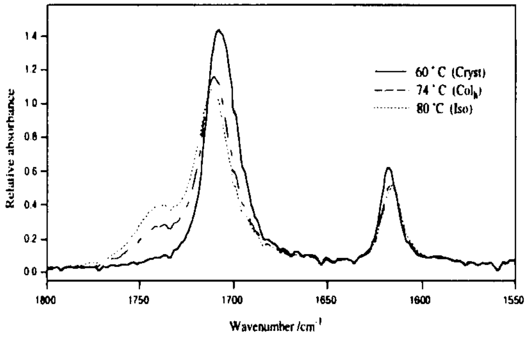


FIGURE 3 IR spectra of C=O stretching band of **2c** in the isotropic, mesomorphic and crystal phase.

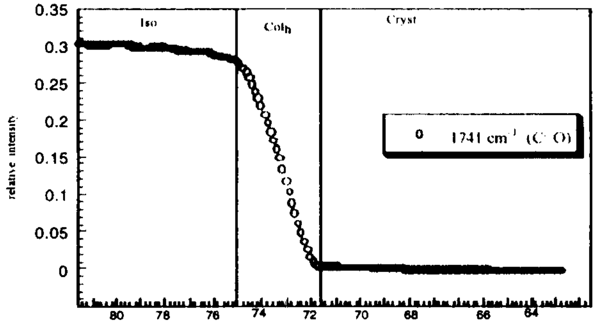


FIGURE 4 Temperature dependent relative intensity of the carbonyl stretching band.

CONCLUSION

Two new series of asymmetrically substituted triphenylene derivatives possessing two terminal ester and two carboxylic acids were obtained.

DSC, X-ray diffraction and optical microscopic studies show that the carboxylic acid homologues possessing the shorter spacer of functionallized chains have mesomorphic properties. Temperature dependent Infrared spectra indicate that dimeric discotic cores formed by hydrogen-bonding interactions among carboxylic acids could account for the XRD results, in which a hexagonal columnar arrangement and a layered structure co-exist in the mesophase.

ACKNOWLEDGEMENT

This work is financially supported by NEDO for a R&D project of novel cryogenic polymers. W. WAN thanks NEDO for providing NEDO fellowship. The authors also acknowledge AIST-MITI for their financial support in part based on a national R&D project " Harmonized Molecular Materials" operated by Industrial Science and Technology frontier Program.

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