行政院國家科學委員會補助專題研究計畫成果報告

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※ 液晶材料研究 ※

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Banana Mesogens Derived from Thiodiphenol

Abstract

Non-conventional banana mesogens are obtained by esterification of thiodiphenol with 4-(4-alkyloxy-benzoyloxy) benzoic acids and the analogous acids in a dry solution of THD/DCC/DMAP. All the mesogens obtained consist of six phenyl rings. B1 phases are obtained for the shorter chain homologues, B2 and B7-like phases are obtained for the longer chain homologues. This study shows that thiodiphenol can be employed as the bent unit, instead of the conventional 1,3-phenylene and 2,7-naphthalene, for constructing the banana mesogens.

Key words: banana mesogen, banana mesophase, thiodiphenol

摘要

本實驗證實香蕉形液晶分子可以用二苯酚硫與不同長度的苯酸經酯化反應得到 長度較短生成 B1 相 長度較短生成 B2 與類 B7 相 二苯酚硫是可以用來當彎曲液晶分子的骨架 本實驗中的蕉形液晶分子皆含六個苯環 低於六個苯環則無液晶相生成

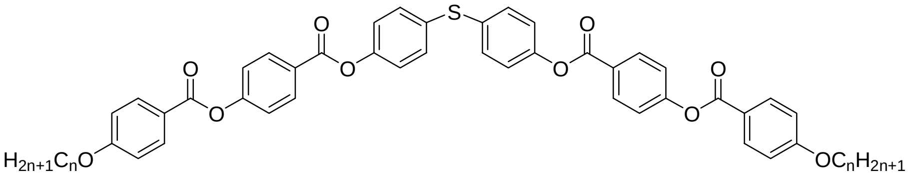
關鍵詞: 香蕉形液晶分子 香蕉形液晶相 二苯酚硫

Banana Mesogens Derived from Thiodiphenol

Banana mesophases formed by banana-shaped molecules have attracted intensive studies for their great potential of application and academic interests since the confirmation of ferroelectric switching behaviors for the B2 phase by Niori et al.[1] The polarization is in the molecular layer and in the direction perpendicular to the tilt-plane of molecular axis and layer normal. This polar liquid is different from the well-known chiral tilted smectics[2] in that the constituting molecules do not possess chiral centers. The general structure of the banana-shaped molecule consists of a bending unit (BU) connected with two rigid cores (usually equivalent) as two arms (A), and ended with a flexible chain on each arm.[3] For most of the banana-shaped mesogens reported thus far, the 1, 3-disubstituted benzene serves as the bending unit. The rigid cores employed normally possess two, or more, phenyl rings linked by the imino and/or ester functional groups. Having five or more phenyl rings as the skeleton, and associated with the symmetrically substituted BU, the banana mesogens inevitably exhibit relatively high mesophase temperatures, although these tempera- tures have been lowered slightly by the inherent bent skeleton. It is observed that the higher the number of phenyl rings the higher the mesophase temperatures, and the minimum number of rings required for the formation of banana mesophase seems to be five. The Schiff-bases have been well known for their photo- and chemical activities. It is therefore highly desirable to have more stable compounds with these mesophase temperatures lowered for the purpose of applications.

Molecular structure-mesophase properties relationship is of primary importance in the design of new mesogens. Instead of the 1,3-phenylene, the most commonly employed bent unit, a bent unit other than the phenyl ring is employed. In the present study, it is shown that banana mesophases B1, B2 and B7-like are observed for the mesogens obtained by connecting the thiodiphenol with 4-(4-alkyloxy-benzoyloxy) benzoic acid of various alkyl chain length. Compounds 4-hydroxy benzoic acid having 3-chloro and 3-methoxy substituents were also used to replace the terminal benzoic acid unit. The esterifications were carried out with the aid of DCC/DMAP in dry solvent. The final banana mesogens obtained consisted of six phenyl rings. The characterizations of mesophases were carried out by optical polarzing microscopy, differential canning calorimetry, powder X-ray diffraction and electric field effects.

Structure and phase behaviors of CnS



	K_1		K_2		B_1		X		Iso.
n=8	•	169.19	—		•	191.33	—		•
		【24.8】				【24.9】			
n=10	•	151.45	•	153.61	•	175.87	—		•
		【15.8】		【0.7】		【25.4】			
n=12	•	149.53	—		•	165.98	—		•
		【20.9】				【24.8】			
n=14	•	151.98	—		—		•	157.99	•
		【20.8】						【25.5】	
n=16	•	151.46	—		—		•	157.73	•
		【21.4】						【25.8】	
n=18	•	138.29	•	146.82	—		•	155.42	•
		【21.0】		【23.8】				【28.1】	

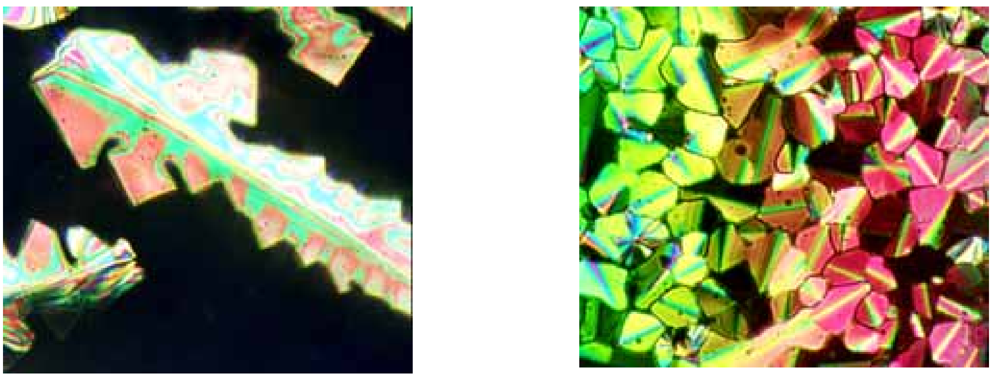


Figure 1. Textures of B1 phase for $C_{10}S$

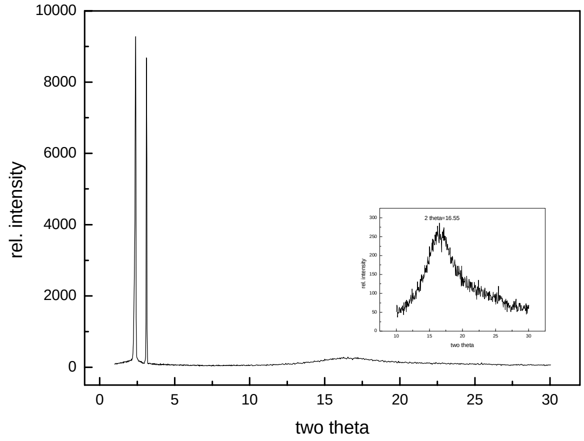


Figure 2. X-ray diffraction pattern for B1 phase of $C_{10}S$

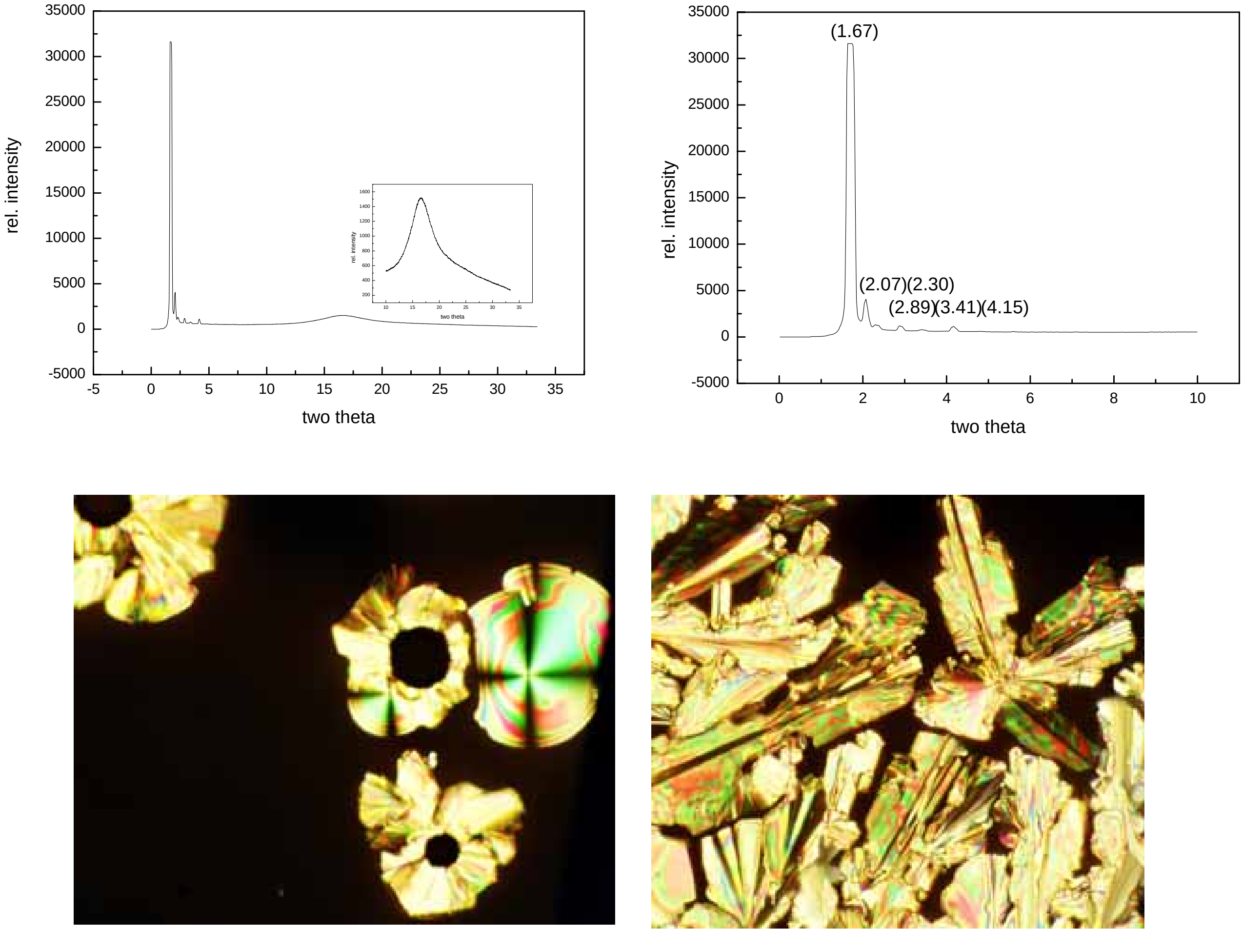
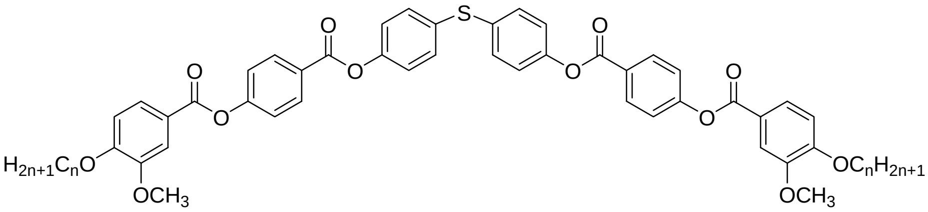


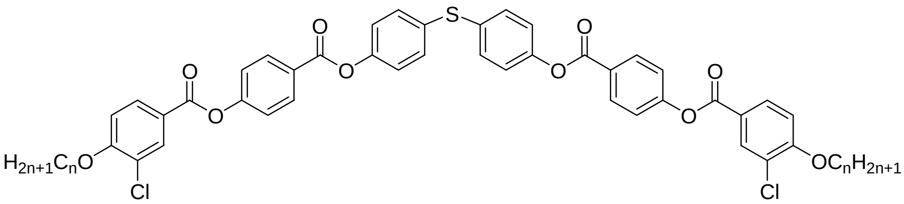
Figure 3. X-ray diffraction patterns and textures for the X phase of $C_{18}S$.

Structure and the phase behaviors for CnMS series



	K		Iso.
C_{12}MS	•	126.51	•
		【65.03】	

Structure and the phase behaviors for CnClS series



	K.		B_1'		B_1		B_7-like		Iso.
n=8	•	115.54	•	121.60[a]	•	177.34	—		•
		【10.3】		【0.47】[a]		【21.9】			
n=10	•	108.11	—		•	170.82	—		•
		【4.31】				【21.7】			
n=12	•	111.47	—		—		•	167.02	•
		【3.09】						【22.9】	
n=14	•	110.81	—		—		•	166.46	•
		【2.70】						【24.5】	
n=16	•	108.15	—		—		•	165.41	•
		【4.25】						【27.9】	

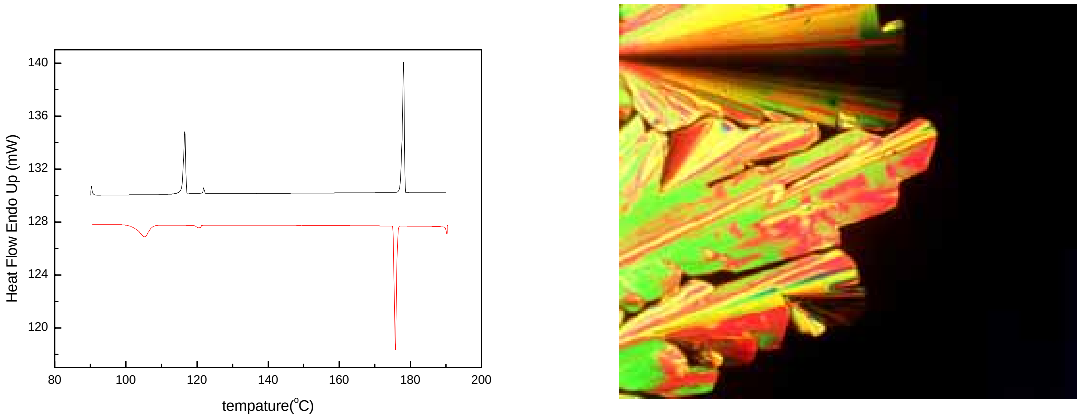


Figure 4. DSC thermogram and texture for the B1 phase of C_8ClS.

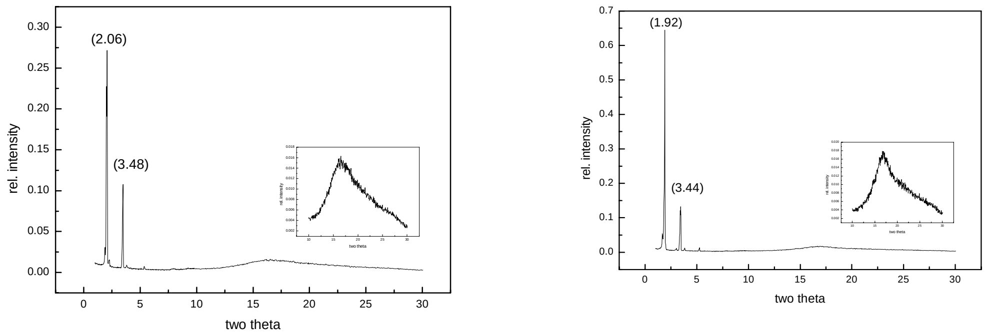


Figure 5. The X-ray patterns for C_8ClS at 160 and 118 ℃.

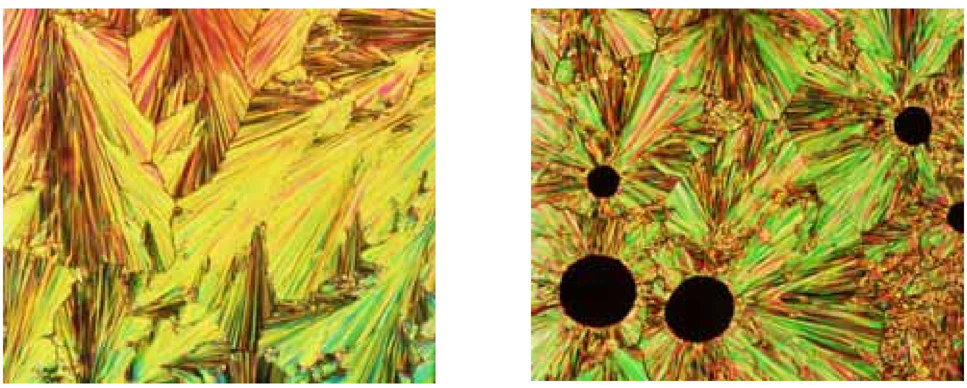


Figure 6. The textures of B7-like phase of $C_{16}ClS$.

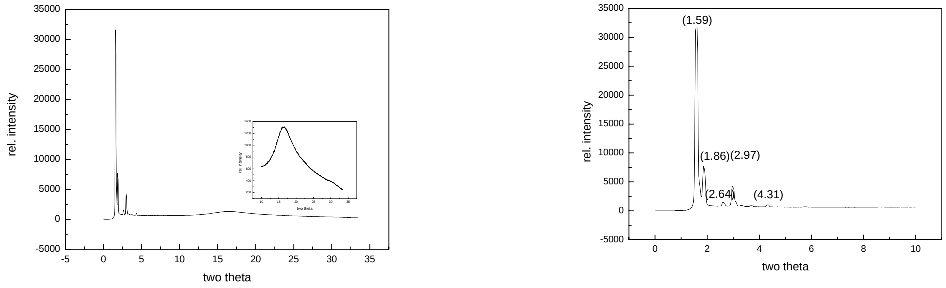


Figure 7. The X-ray diffraction patterns for the B7-like phase of $C_{16}ClS$.

References:

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(3) Pelzl, G.; Diele, S.; Weissflog, W. Adv. Mater.1999, 11,707.