

行政院國家科學委員會補助專題研究計畫成果報告

新型態盤狀液晶之設計，開發合成，物性及應用研究

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計畫主持人：徐秀福

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行政院國家科學委員會專題研究計畫成果報告

新型態盤狀液晶之設計，開發合成，物性及應用研究

Design, Synthesis, Properties and Application of New Chiral Columnar Liquid Crystals

計畫編號：NSC 89-2113-M-032-027

執行期限：89年8月1日至90年7月31日

主持人：徐秀福 執行機構及單位名稱：淡江大學化學系

I. 中文摘要

由兩個帶有乙炔的芳香環化合物偶合而成的1,3-丁二炔衍生物具有向列型液晶相，另外，在部分化合物中亦有層列液晶相的生成。此1,3-丁二炔衍生物經以鈷催化劑進行三分子環化反應則可以成功合成出一中心苯環在1,3,5-位置接芳香環而2,4,6-接乙炔芳香環之對稱衍生物，而且具有預期的筒狀液晶相。

關鍵詞：筒狀液晶相、向列型液晶相、層列液晶相

Abstract

The coupling of two alkoxy phenyl acetylene molecules yielded the biaryl-1,3-butadiyne compounds which exhibited nematic and/or smectic liquid crystal phases. With a cobalt catalyst, the cyclotrimerization of 1,3-butadiyne derivatives lead to the formation of the symmetrical 1,3,5-triaryl-2,4,6-tri(arylethynyl)-benzene compounds which showed the targeted columnar mesophases.

Keywords: Nematic, Smectic, Columnar, Liquid Crystal

II. Background and Objectives

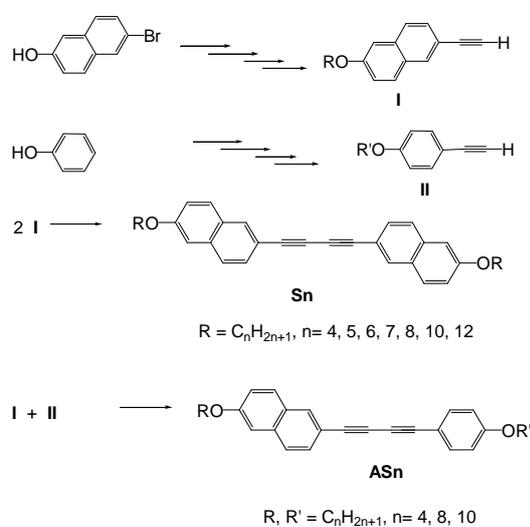
The development of columnar liquid crystals has been important for the preparation of photoelectric devices.^{[1], [2], [3], [4]} However, compared with nematic and smectic mesophases, the study of columnar phases is still new but fast growing. Up to date, only a few skeletons of the organic mesogens show columnar liquid crystal behavior.^[5] Hence, designing of new mesogenic cores for columnar phases are of interests for material scientists both for better understanding of the relatively new liquid crystal phases and for their potential as photoelectric materials especially conducting materials. The most studied mesogenic organic core with columnar phases is triphenylene in which six side chains are attached to show the most ordered mesophases.^[6] When the side chains are replaced with alkynyl derivatives, a discotic nematic instead of columnar phase was observed.^[7] In this project, columnar liquid crystals with a new core that steric factors may play an important role for the

formation of chiral mesophases were prepared and studied.

III. Results and Discussions

A series of 1,3-butadiyne compounds, **Sn**, were successfully prepared by coupling of two ethynylaryl compounds. These compounds with a rod-shape core were liquid crystals themselves and resemble to those used in liquid crystal displays. Their mesophase behavior were studied by the use of polarizing optical microscopy and differential scanning calorimetry. Compounds with shorter side chains exhibited a schlieren texture indicating a nematic liquid crystal phase. Longer side chains tend to induce a second mesophase, smectic phase, in addition to the nematic phase.

Large mesophase temperature range was found for all the compounds. For the symmetric series, the temperature range peaked at $n = 6$ of almost 100 and sloping down to both ends. When one of the naphthalene is replaced by phenyl ring to break the symmetry, the temperature range decreased with increasing chain length. For the smectic phase, the temperature range increased with chain length for the asymmetric series although the overall mesophase temperature range decreased. For **ASn**, when one more alkoxy chain was attached to the phenyl ring, the mesophase behavior disappeared.

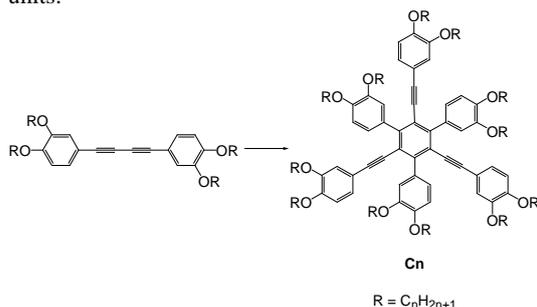


Single crystal X-ray analysis of compound **S4** has been carried out to elucidate the intermolecular correlation in the condense phase. The molecular structure of **S4** has the same features as that of a similar compound with no alkoxy chains reported by Prasad et al.^[8] However, the molecular packing for these two are quite different. The two naphthalene units are coplanar and can be interchanged by an inversion center and a C2 rotation axis. In the packing diagram, the molecules align along the molecular axis and appear to show lamellar arrangement with apparent overlap between layers. On the other hand, the solid state packing motif of the nonalkoxy analog, 1,4-bis(1-naphthyl)-buta1,3-diyne, showed apparent layers without any overlap between layers.

The polymerization of these butadiyne compounds in liquid crystal state was also of interests in this project. Thermal polymerization was found for the shortest analog, **S4**. Upon polymerization, the birefringence disappeared and the material changed to orange. For the intermediate chain lengths, little or none thermal polymerization was detected up to 250 . However, when the chain length is longer than ten, difficulties were encountered even at the purification stage of the compounds. Blue particles obtained during recrystallization indicating highly polymerization were obtained for these long side chain compounds.

Packing diagrams of S4

With a di-cobalt catalyst,^[9] the 1,3,5-triaryl-2,4,6-triethynylaryl benzene compounds, **Cn**, were obtained through cyclotrimerization of three ethynyl units.



Thermal Behavior of Cn

n	compound	observed transitions T(°C)(H(kJ/mol))
6	C6	K $\xrightarrow[54.7 (-21.60)]{67.4 (12.12)}$ M $\xrightarrow[82.9 (11.18)]{131.7 (5.08)}$ Col _{hd} $\xrightarrow[131.2 (-5.09)]{131.7 (5.08)}$ I
10	C10	K $\xrightarrow[58.7 (-17.24)]{68.3 (26.31)}$ Col _{hd} $\xrightarrow[128.7 (-4.15)]{129.3 (4.16)}$ I
14	C14	K $\xrightarrow[63.2 (-77.78)]{75.2 (70.53)}$ Col _{hd} $\xrightarrow[115.0 (-6.46)]{115.3 (6.68)}$ I

Interestingly, these compounds also showed mesogenic behavior. However, the calamitic phases

of the butadiyne compounds disappeared, and instead, a columnar phase showed up. From thermal behavior and optical texture, a disordered phase was assigned and the powder X-ray diffraction study further elucidated the existence of a hexagonal columnar mesophase in these compounds. Both the melting and clearing temperatures increased with longer chain length, however, a slight depress was found for their mesophase range with increasing chain length.

Compounds **Cn** can be viewed as a hybrid of multi-arene and multi-yne compounds. Usually, multiarene derivatives exhibited higher order mesophases, e.g. columnar, and the discotic nematic phase could be found for the multi-yne compounds. The hybrid compound **Cn** showed exclusively a columnar mesophase, which was somewhat surprising. Since simple simulation showed a very crowded core in which all dangling rings are not coplanar with the central benzene ring and are sterically affecting each other. Good match among molecules for proper stacking is needed in order for columnar packing. Therefore, it may be possible to manipulate the optical sense of the dangling rings by means of introducing chiral side chains to bias the preferred formation of enantio-pure mesophases.

IV. Self-Evaluation

In this project, we have finished the preparation and property study of the calamitic liquid crystals **Sn** and **ASn**. Moreover, the columnar mesophase with a novel new core of symmetrical triyne-triaryl benzene has been successfully achieved. Currently, we are trying to expand the investigation of other possible variations on the core structure for the formation of mesophases. The study of its macroscopic optical sense expressed by the introduction of chiral side chains will be pursued.

V. References

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